STUDIES OF SOME COORDINATION COMPLEXES OF INDIUM (I) AND (III).

by

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ABSTRACT

Complexes of indium with halides, acetylacetone, bipyridyl, phenanthroline, pyridine and d_5-pyridine, as well as some cyclopentadienyl derivatives, have been prepared and studied by means of analytical and spectroscopic techniques to determine their coordination and structure. The full X-ray crystal and molecular structure of $In(acac)bipyCl_2$ is also reported.

I. Anionic Complexes Derived from the Lower Halides of Indium

The halide salts of the dipositive N,N'-dimethyl-4,4'-bipyridinium cation (Me_2bipyX_2; X = Cl, Br or I) react with indium monohalides to give salts of the trihalogenoindate(I) anions $Me_2bipy \cdot InX_3$, in which the anion is isoelectronic with SnX_3^- and SbX_3. With indium trihalides the products are either $Me_2bipy \cdot InCl_5$ or $Me_2bipy^{2+} + InX_4^- + X^-$ (X = Br or I); the $InCl_5^{2-}$ anion has C_{4v} symmetry in the salt prepared, and this result is discussed in terms of earlier studies of this anion. The indium dihalides yield a mixture of In(I) and In(III) anions. The Raman spectra are recorded for the anionic complexes prepared, for the indium monohalides and for indium dibromide and diodide.

II. Force Constant Calculations for Anionic Indium(I) and (III) Halide Complexes

A simplified generalized quadratic valence force field has been used to calculate force constants for the anionic indium(I) species InX_3^{2-} (X = Cl,Br or I) and for the anionic indium(III) halide complexes InX_4^-,$InCl_5^{2-}$ and $InCl_6^{3-}$. The primary stretching force constants for the indium(III) chloro-anions decrease linearly with the increasing coordination number. The results for the indium(I) complexes are compared with those in the literature for isoelectronic tin(II) and antimony(III) species.

III. Some Reactions of Cyclopentadienylindium(I)

(a) Cyclopentadienylindium(I) (CpIn) in chloroform reacts with gaseous BX_3 (X = F,Cl,Br or CH_3) to yield solid $CpIn \cdot BX_3$ species,whose structures have been investigated. Vibrational spectroscopy shows that the BX_3 group has the expected trigonal pyramidal structure. The cyclopentadienyl ligand is in the monohapto (σ-bonded diene) form in the adducts,in marked contrast to the stereochemistry of the parent CpIn. Reactions of CpIn and $CpIn \cdot BCl_3$ with maleic anhydride showed that Diels-Alder addition occurs in both cases.

(b) Cyclopentadienylindium(I) reacts with iodine to yield the polymeric $CpInI_2$ species. Adducts of this species with some nitrogen-donor ligands have been prepared and studied by means of vibrational and mass spectroscopies. The reaction products of $CpInI_2$ with Cp_3In and $(propyl)_4NI$ have also been studied.

IV. Monoacetylacetonatoindium(III) Complexes

The reaction of 2,2'-bipyridyl,1,10-phenanthroline, pyridine and d_5-pyridine with the brown pasty solid obtained from the dissolution of indium(I) halides in acetylacetone, yields solids of the type $In(acac)LX_2 \cdot C_2H_5OH$ (X = Cl,Br,I) whose vibrational spectra have been studied in the range 600-100 cm^{-1}. Vibrational spectroscopy does not allow a clear distinction of a cis or trans arrangement of the halide ligands. Evidence for a possible mechanism for the dissolution process of the indium monohalides in acetylacetone is given.

V. The Crystal and Molecular Structure of Acetylacetonato-2,2'-bipyridyldichloroindium(III)

The crystal and molecular structure of $In(acac)bipyCl_2$ has been determined by means of X-ray structural methods. $In(acac)bipyCl_2$ belongs to the monoclinic $P2_1/c$ space group, a = 11.340(3), b = 12.198(3), c = 14.330(3) Å and $\beta = 120.25(2)^{\circ}$. The structure consists of six coordinate indium atom whereby the indium atom is surrounded by two cis chlorine atoms,a bidentate bipyridyl and a bidentate acetylacetonato anion. The $InO_2N_2Cl_2$ group has a distorted octahedral configuration. The indium-chlorine bond lengths are 2.443(1) and 2.394(1) Å, the indium-oxygen bond distances are 2.124(3) and 2.164(3) Å and the indium-nitrogen bond lengths 2.276(4) and 2.299(4) Å .

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CHAPTER I

LITERATURE SURVEY

1.1 The Chemistry of Indium

Indium belongs to the group III of the periodic system. First discovered in 1863 by Reich and Ritcher[1] from its emission spectrum,it was isolated from a zinc-iron mineral,sphatrite. Indium,like gallium,can be obtained by the electrolysis of aqueous solutions of its salts as a soft,silvery-white metal with a melting point of 157° C and a boiling point of about 2,700° C.

Group III of the periodic table begins with the non-metal boron and ends with thallium,a metal. Table 1 gives some properties of the elements of the group III. Despite the large amount of energy required to remove three electrons from the gaseous atom,the tripositive state dominates most of the chemistry of the elements of this group. Although boron is formally in the +3 oxidation state in its compounds,there is no chemistry of the free B^{3+} ion.

The monopositive state is known for aluminium,gallium, indium and thallium,becoming increasingly more stable as the atomic number increases. For thallium,both the +1 and +3 oxidation states are well known.

From boron to thallium there is a change in the non-metallic to metallic properties. Thus, it is found that boron oxide is an acidic oxide, whereas Al_2O_3 is amphoteric and gallium, indium and thallium oxides are definitely basic.

Going down the group III one finds that the bonding in the halide compounds changes from a distinctly covalent bonding in BX_3 (X = Cl, Br or I) to a nearly ionic in the corresponding thallium halides. With regards to the redox properties, from table 1 it is seen that the reducing power decreases strongly from aluminium to indium. Thallium in its +3 oxidation state has a considerable oxidizing power as it is shown in the half reaction given below

$$Tl^{3+}(aq) + 2e^- = Tl^+(aq) \qquad E^o = 1.25 \text{ volts}$$

Indium forms compounds in the +1, +2 and +3 oxidation states. Since the chemistry of the +3 oxidation state has been throughly reviewed[2-7], the following review will deal mainly with the chemistry of indium in its lower oxidation states; the chemistry of indium(III) will be surveyed only briefly.

1.2 Compounds of Indium(I)

Compounds in which indium has the formal oxidation state +1 have been known for a long time. Indium oxide[8,9], sulphide[10], selenide, telluride[8], chloride[11], bromide[10] and iodide[11] are known.

Crystal structure determinations of the halides reveal that in the bromide[12] and iodide[13], each indium atom is surrounded by five halide ions located at the corners of a regular

TABLE 1

Properties of the elements in Group III

	B	Al	Ga	In	Tl
Atomic Number	5	13	31	49	81
Electronic Configuration	[He]$2s^2 2p^1$	[Ne]$3s^2 3p^1$	[Ar]$3d^{10} 4s^2 4p^1$	[Kr]$4d^{10} 5s^2 5p^1$	[Xe]$4f^{14} 4d^{10} 6s^2 6p^1$
Ionization Potential (e.v.)					
First I.P.	8.30	5.98	6.00	5.79	6.11
Second I.P.	25.15	18.82	20.43	18.79	20.32
Third I.P.	37.92	28.44	30.6	27.9	29.7
Fourth I.P.	259.30	119.96	63.8	57.8	50.5
Standard Potential (volts)					
$M \rightleftarrows M^{3+} + 3e^-$		1.67	0.52	0.34	-0.719
$M \rightleftarrows M^{1+} + e^-$				0.147	+0.34
Covalent radius, Å	0.80	1.248	1.245	1.497	1.549
Crystal radius M^{3+}, Å	0.20	0.50	0.62	0.81	0.95

square-based pyramid, with the axial indium-halide distance somewhat greater than the other four in the base of the pyramid. The chloride[14] has a different structure, each indium(I) ion being surrounded by twelve other indium(I) ions and twelve chloride ions in a distorted NaCl type structure.

Indium(I) has been obtained in low concentration in solution by anodization of indium metal in perchloric acid[15,16]. Indium(I) is rapidly oxidized by both H^+ and air according to the reaction

$$In^+(aq) + 2H^+ = In^{3+}(aq) + H_2(g) \qquad \log K = 14.7$$

It follows that indium(I) is a very strong reducing agent; it is also thermodynamically unstable with respect to indium(III) and indium(0).

$$3In^+ = In^{3+} + 2In^0 \qquad \log K = 8.4$$

The product of the reaction of indium(III) chloride with sodium cyclopentadienyl in ether, followed by sublimation under vacuum, is an indium(I) compound, cyclopentadienylindium(I)[17], the first organometallic compound of indium(I) to be prepared. More recently methylcyclopentadienylindium(I) has also been prepared[18].

1.3 Complexes of Indium(I)

The action of dry ammonia at 2 to 2.5 atmospheres and 0° C on indium(I) halides yields compounds of the type $InX{\cdot}NH_3$ (X = Cl, Br or I). At 3 to 4 atmospheres of ammonia, the product is $InX \cdot 2NH_3$[19]. The products are black solids, insoluble in water and dilute acids, and disproportionate rapidly on contact with water. The diammines lose ammonia when heated. Unfortunately there are no structural or spectroscopic data available for these complexes and hence there is some difficulty in distinguishing between bonded ammonia and ammonia trapped in the monohalide lattice. At 6 to 8 atmospheres of ammonia the products are undoubtedly indium(III) complexes, $InX_3 \cdot 6NH_3$.

In studies of the reaction of morpholine and aniline with indium(I) halides, Goggins and McColm[20] found that the halides dissolve slightly in these basic solvents; solids of the type $In(morph)_2X$ (morph = morpholine) and $In(anil)_4X$ (anil = aniline)(X = Cl, Br or I) were obtained after addition of ether. The complexes (which were analysed for indium and halides only) were formulated as 1:1 electrolytes on the basis of conductivity measurements in nitrobenzene ($\Lambda_M \approx 28$ ohm^{-1} cm^2).

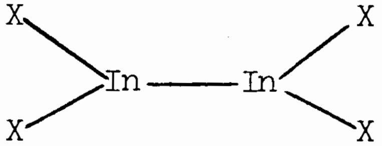
Oxidative insertion of indium(I) bromide into Co-Co bond has been observed in the reaction of InBr and $Co_2(CO)_8$ in tetrahydrofuran at room temperature[21]. When the reaction is carried out in benzene, the stoichiometry of the product is $Br_3In_3Co_4(CO)_{15}$[22], rather than $BrIn(Co(CO)_4)_2$ obtained in tetrahydrofuran. Indium(I) bromide also inserts into the Mn-Mn bond of $Mn_2(CO)_{10}$. Drastic conditions (heating the reaction mixture at 180° C for 22 hours in a sealed tube) were required[23], but Hsieh and Mays[24] showed that this oxidative insertion occurs smoothly in refluxing dioxane (boiling point 100-102° C). Similar conditions allow the insertion of InBr into the metal-metal bond in (π-$C_5H_5M(CO)_3)_2$ where M = W or Mo. Similarly indium(I) bromide reacts with (π-$C_5H_5Fe(CO)_2)_2$ to form BrIn(π-$C_5H_5Fe(CO)_2)_2$[25]. Indium(I) chloride was reported to insert into a metal-halogen bond to form $MnInX_2$ species[24].

Recently[26], it has been found that indium bromide inserts into the carbon-bromine bond of methyl bromide to give a product of stoichiometry CH_3InBr_2. Oxidative insertion of this type were also found to occur for indium(I) iodide into the carbon-iodine bond of a variety of alkyl iodides[27]. The products have the stoichiometry $RInI_2$ where R = methyl, ethyl or n-butyl.

1.4 Compounds of Indium(II)

Earlier studies reported the preparation of InF_2[28], $InCl_2$[29], $InBr_2$[30] and InI_2[31].

Magnetic studies of the $InCl_2$[32] and $InBr_2$[33] have shown that they are diamagnetic rather than paramagnetic as one would predict for a monomeric indium(II) species. To explain the observed diamagnetism, Puzako et al[34] suggested a dimeric structure of the type shown below



(X = Cl or Br)

where the diamagnetism would be due to a spin-pairing process as a result of the metal-metal bond. An alternative structure[39] could be an ionic dimer similar to that found for gallium dihalides, $Ga(I)[Ga(III)X_4]$ (X = Cl,Br or I)[35-38].

The mixed oxidation state structure has received support from the Raman spectrum of molten $InCl_2$,which shows unequivocally the presence of the $InCl_4^-$ ion[40]. Brinkman and Gerding[41] reported the X-ray powder diagrams of the solids $InCl_2$, In_4Cl_7 and In_5Cl_9[42]. The d spacing as well as the intensities quoted indicate that all three lattices are made up of the same species,presumably $InCl_6^{3-}$. On the other hand Atkinson et al[43] suggested a mixed valence structure for the solid In_5Cl_9 which could be formulated as $In_3[In_2Cl_9]$ on the basis of structural relationship between this solid and $Cs_3Tl_2Cl_9$ whose crystal structure[44] revealed that the $Tl_2Cl_9^{3-}$ anion is built up of two regular octahedra sharing a face.

Phase studies of the indium-chlorine system[43] have also shown the presence of In_2Cl_3 whose Raman spectrum resembles closely the spectrum of a molten 1:3 mixture of $InCl_3$ and KCl which is expected to have the structure $3K^+[InCl_6]^{3-}$[40]. In_2Cl_3 has been formulated as $In_3[InCl_6]$. On the other hand the Raman spectrum of this melt also shows a band at 311 cm^{-1}, assigned to the symmetric In-Cl stretching mode of the $InCl_4^-$ ion;any $InCl_4^-$ would come from dissociation of the $InCl_6^{3-}$ species.

Despite of the number of vibrational and phase studies on the indium-halide systems, conclusive evidence is so far not available and at present the nature of these solids is unsettled and confusing.

Support for the existence of an indium(II) state comes from the experimental fact that InI_2 and $InBr_2$ can be ammoniated to yield compounds of the type $In_2X_4 \cdot 6NH_3$ and $In_2X_4 \cdot 8NH_3$. Since complexes with no more than two molecules of ammonia could be prepared from the monohalides, Kochetkova et al[45] concluded that the indium dihalides could not form the observed ammoniates if they were mixed oxidation state compounds. The results are dubious because of the high pressure of ammonia used and the experimental fact that the ammoniates decompose even in the presence of ammonia at 3 to 4 atmospheres to yield $InX \cdot 2NH_3$ and $InX_3 \cdot 6NH_3$, i.e., the indium(I) and indium(III) derivatived.

Indium dihalides were found to dissolve slightly in morpholine and aniline to yield, after ether addition, compounds of the type $InX(morph)_2$ and $InX_2(anil)_2$ respectively[20]. Conductivity measurements in nitrobenzene showed that these compounds are 1:1 electrolytes being best formulated as $[In(morph)_2][InX_4]$ and $[In(anil)_4][InX_4]$ favouring the mixed valence structure formulation for the dihalides of indium.

Sutton[46] reported that indium dihalides react with ethylenediammine (en) with disproportionation according to the equation:

$$3InX_2 + 6en \; = \; 2In(en)_3X_3 + In$$

The action of hydrogen and hydrocyanic acid on indium metal yields a solid of stoichiometry $In(CN)_2$ which has been formulated as $In(I)[In(III)(CN)_4]$[47].

1.5 Compounds of Indium(III)

Compounds in which indium is in its +3 oxidation state are well known and many simple and complex compounds have been prepared.

In the +3 oxidation state indium displays coordination numbers four,five and six.The coordination number three is reported to exist only in the planar trigonal structure of InX_3 (X = Cl,Br or I) monomers in the gas phase,whereas coordination numbers greater than six have not so far been reported. It is believed that the complex anion $In(NO_3)_4^-$ [48] would involve a formally eight coordinate indium(III),but at present no structural information is available.

1.6 Complexes of Indium(III)

The indium(III) complexes can be classified into three groups:(a) neutral complexes,(b) cationic complexes and (c) anionic complexes.

(a) Neutral Complexes of Indium(III)

Indium(III) halides react as Lewis acids with a variety of donor molecules to give neutral complexes. The stoichiometries InX_3L_3, $InX_3L_{2.5}$, InX_3L_2, $InX_3L_{1.5}$ and InX_3L (X = Cl, Br or I) have been reported. The stoichiometry InX_3L_3 where L = diethylammine,pyridine,aniline[49],morpholine[50] and dimethylsulphoxide[51] involving six coordinate indium have been characterized by means of vibrational spectroscopy,conductivity measurements and in some cases unambiguously by X-ray structural methods.

The $InX_3L_{2.5}$ type complexes where L = N,N'-dimethylacetamide[52] exhibit molar conductities between a neutral and a 1:1 electrolyte. No definitive structure can be inferred,but probably they could be ionic or dimeric with halogen and or ligand bridges.

Complexes of the type InX_3L_2 involving a variety of monodentate ligands such as PPh_3,Ph_3PO,pyridine,ammines and dimethylsulphoxide[53,54] have been prepared. The structural possibilities for these five coordinate indium(III) complexes are trigonal bipyramidal (D_{3h}) or square-based pyramidal (C_{4v}). The X-ray molecular structure determination[55] on the triphenylphosphine adduct revealed that $InCl_3(Ph_3P)_2$ possesses D_{3h} symmetry. Five coordination is not involved in $InI_3(dmso)_2$, for which X-ray crystal structure determination showed the ionic structure $[InI_2(dmso)_4][InI_4]$[56].

The products of the reaction of indium(III) halides and pseudohalides with bidentate ligands such as 1,10-phenanthroline (phen) and 2,2'-bipyridyl (bipy),are solids of stoichiometry $InX_3L_{1.5}$[57,58]. Unfortunately no structural data are available for these species.

The complexes InX_3L are formed from indium(III) halides and phosphine ligands[52,53,59]. They probably involve four coordinate indium species.

Neutral tris chelate InL_3 complexes derived from acetylacetone[48],8-hydroxyquinoline[60],dithiobenzoate anion,dithiophenylacetate anion[61] and 0,0'-dimethyldiselenophosphate anion[62] have been reported. The crystal structure determination of $In(acac)_3$[63] (acac = acetylacetonate anion) showed that this complex is isostructural with the iron(III) analog. $In(dtp)_3$ (dtp = dithiophosphate anion) has a distorted octahedral $In\text{-}S_6$ kernel;although all six In-S bond distances are approximately equal,each ligand has two different P-S bond lengths[64].

(b) Cationic Complexes of Indium(III)

Both four and six coordinate indium(III) cationic complexes have been prepared[48,60]. Indium(III) halides and pseudohalides react with mono and bidentate ligands such as phen,bipy, en,dmso,urea,dimethylacetamide,N-methyl-γ-butyrolactam[65] and antipyrine[66] to yield cationic complexes of the type $In(AA)_3{}^{3+}$ or $InA_6{}^{3-}$. Four coordinate indium(III) complexes of the type $[InL_4]^{3+}$ were obtained with phosphine and arsines.

The indium(III) cation $[InL(dmso)_4]^+$ (L = 1,2-bis(trifluoromethyl dithiolate anion) was identified in the product of the reaction of this ligand with indium(I) halides in dimethylsulphoxide[67].

Finally a number of cationic complexes of the type $[InX_2L_2]^+$ where the balancing ion is perchlorate or hexafluorophosphate and L is bipy or phen[58],have been prepared.

(c) Anionic Complexes of Indium(III)

A considerable number of anionic halide complexes of indium(III) have been reported. Coordination numbers four,five and six have been found. Ekeley and Potratz[68] have prepared a series of anionic complexes of the type InX_4^-,InX_5^{2-} and InX_6^{3-}. X-ray crystal structure determinations of $InCl_4^-$ [69]and InI_4^- [70] and $InCl_5^{2-}$ [71] anions have revealed a tetrahedral structure for the four coordinate complexes and a C_{4v} square-based pyramidal structure for $InCl_5^{2-}$.

Maleonitrile-dithiolate,iso-maleonitrile-dithiolate and toluene-3,4-dithiolate from a series of four,five and six coordinate anionic complexes[2,72]. The X-ray crystal structure determination of $[(C_2H_5)_4N]_3[In(MNT)_3]$ (MNT = maleonitrile-dithiolate)[73] confirmed the distorted octahedral arrangement of the In-S_6 kernel. Maleonitrile-dithiolate anionic complexes of the type $[R_4N][In(MNT)_2Cl]$ (R = methyl or ethyl) have also been reported[74].

1.7 Organometallic Compounds of Indium

Organic derivatives of indium have not been extensively studied, but an increasing amount of attention has recently been given to this important field.

As the atomic weight of the elements of group III increases, low oxidation states become relatively more stable. Thus, organometallic derivatives of gallium(I) are so far unknown, whereas cyclopentadienylindium(I)[17] and methylcyclopentadienylindium(I)[18] have been prepared.

A number of alkyl indium(III) derivatives, Me_3In[75], Et_3In[76,77], $(i\text{-}Bu)_3In$[78] (Me = methyl, Et = ethyl, i-Bu = i-Butyl) are known. The aryl derivative Ph_3In has also been prepared[79].

Fischer and Hofmann[17] found that tris(cyclopentadienyl) indium(III) is obtained as a side product in the preparation of cyclopentadienylindium(I). $(C_5H_5)_3In$ can be obtained in good yield if lithium cyclopentadienide is used in place of the sodium salt[18]. An X-ray molecular structure determination of $(C_5H_5)_3In$[80] showed that the structure consists of infinite polymeric chains with each chain unit comprised of an indium atom linked to two terminal and two bridging cyclopentadienyl groups giving rise to an almost tetrahedral $In\text{-}C_4$ arrangement around the indium atom.

Halogeno derivatives of Me_3In of the type Me_2InX (X = F, Cl, Br or I) have been prepared[75,81]. Dimethylindium halides as well as trimethylindium react with donor molecules such as pyridine, Ph_3P, Ph_3PO, bipy, en[81] to yield complexes of the type

Me_2InXL or Me_2InL depending whether L is a mono- or bidentate ligand.

Finally, the cation $[Me_2In]^+$ identified in aquous solution[82] is believed to be in methylindium diodide, which has been formulated as $[Me_2In][InI_4]$[27].

1.8 Contents of the Present Thesis

The work reported in the following chapters is related with the study of indium(I), indium(II) and indium(III) complexes with halides, oxygen donor and nitrogen donor ligands as well as some organometallic derivatives.

The second chapter of this thesis deals with the preparation, characterization and vibrational spectra of some halide complexes derived from indium(I), (II) and (III).

The third chapter is devoted to the theoretical calculation of the vibrational spectra of those complexes prepared in the second chapter. Although this work is closely related with that in the second chapter, it is presented separately in order to identify the nature of the calculations carried out.

Chapter four refers to some reactions of cyclopentadienylindium(I) with boron trihalides as well as with iodine. The preparation, characterization and vibrational spectra of the resulting addition compounds are reported.

Chapter five deals with the preparation, chemical characterization and vibrational spectra of some complexes of the type In(acac)LX_2,where acac = acetylacetonate anion, L = bipy, phen,pyridine or its deutero derivative,and X = Cl,Br or I.

Finally,the sixth chapter refers to the X-ray crystal and molecular structure determination of In(acac)(bipy)Cl_2.

CHAPTER II

ANIONIC COMPLEXES DERIVED FROM THE LOWER HALIDES OF INDIUM

2.1 Introduction

The general chemical behaviour of the elements of group III has been discused in chapter I. Although there is now a good understanding of the chemistry of indium in its +3 oxidation state,very little is known about the lower oxidation states of this element. Thus,very few coordination compounds of indium(I) and indium(II) have been prepared,although the +1 oxidation state is an important feature of the two lower members of the group III.

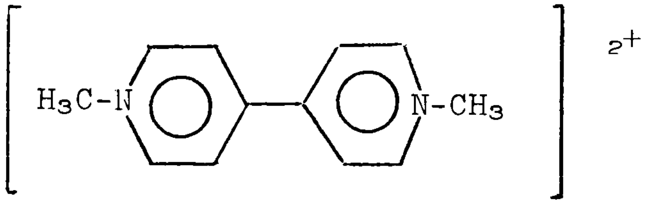
Indium(II) compounds have been the subject of curiosity for some time,but only recently has any structural information been forthcoming. Unstable indium(II) species have been detected in gamma irradiated glasses formed by freezing 5.4 M sulphuric acid containing indium(III) sulphate[83].

The investigation of indium(II) halides in the solid state has been restricted to vibrational spectroscopy,phase studies and X-ray powder methods. The mixed valence structure proposed for the indium(II) halides is strongly supported by vibrational spectroscopy in some cases,but clearly fails in others. For indium-chloride system,on the other hand, the literature is extensive and rather confusing.

Molten $InCl_2$ is shown by Raman spectroscopy to contain $InCl_4^-$ anions[40], but the spectrum of the solid state is variously claimed to show the presence[40] or the absence[41,43] of this species.

Much less attention have received indium dibromide and indium diodide. One phase study on the indium-bromide system has been published[30] and none for the indium-iodide system.

It was therefore decided to explore the possibility of preparing some complexes of indium(I), and to attempt to obtain some chemical evidence on the structure of the indium dihalides. It was thought that probably a large dipositive cation could be able to break up the indium monohalide lattice and bring indium(I) into solution. For that purpose a large organic cation, namely, N,N'-dimethyl-4,4'-bipyridinium was used.



The cation used in this work is one of the few readly available dipositive organic cations. The preparation of its salts was first described by Michaelis and Hill[84] who studied these species in terms of its use as redox indicator.

On the other hand, if the dihalides are really mixed oxidation state compounds of the type In(I)[In(III)X_4] they might give a mixture of halide complexes of indium(I) and indium(III). In this context, and in order to compare the resulting products, indium(III) halide complexes with the same cation were also prepared.

2.2 The Trihalogenoindate(I) Anions

Anionic complexes of tin(II) of the type SnX_3^- (X = Cl, Br or I) have been reported[85]. As indium(I) is isoelectronic with tin(II), it seemed likely that the InX_3^{2-} species could be also stabilized in some suitable lattice. Since the obvious starting materials, the indium(I) halides, are insoluble in all the solvents so far tested, their dissolution was taken as a visual test for complexation. Since indium monohalides do not dissolve in molten tetraethylammonium halides, this route to the trihalogenoindate(I) anions was nct available.

Indium(I) halides react smoothly with the appropriate salt of the cation N,N'-dimethyl-4,4'-bipyridinium ($\doteq$ Me_2bipy) in dry methanol to yield solids of stoichiometry [Me_2bipy][InX_3] where X = Cl, Br or I.

2.3 Reactions Involving Indium Dihalides

The structure of the indium dihalides has been the subject of considerable discussions. The compounds are not simple M^{2+} salts, as they are diamagnetic. Formulae involving either a metal-metal bonded dimer of the type X_2M-MX_2, or a ionic dimer involving a mixed oxidation state such as $M(I)[M(III)X_4]$ have been proposed. Both spectroscopic and chemical evidence have been advanced in support of each of these formulations.

It was found that the indium dihalides react smoothly with the appropriate salt of the Me_2bipy^{2+} cation in methanol to give compounds of the type $Me_2bipy \cdot InX_4$ (X = Cl,Br or I). As in the case of the reaction of the monohalides with the same cation,the dissolution of the indium salt required stirring of the reaction mixture for 2 to 3 hours under nitrogen to prevent oxidation of the indium(I) species formed.

2.4 Reactions Involving Indium Trihalides

In order to elucidate the nature of the products of the reaction of Me_2bipyX_2 with the corresponding indium dihalide, it was necessary to investigate the reaction of these organic salts with the neutral indium(III) halides. The results are interesting in terms of the comparison with earlier studies of anionic indium(III) halide complexes[86].

In each case the reaction product is a solid of stoichiometry $Me_2bipy \cdot InX_5$ (X = Cl,Br or I).

2.5 Reactions of $Me_2bipy \cdot InX_3$ with Indium Trihalides

The electron pair donor properties of the $Sn(II)X_3^-$ species are now well established. Since the trihalogenoindate(I) anions are isoelectronic with their tin(II) analogs, it seemed worthwhile to investigate the donor properties of the indium(I) species. For this purpose reactions of the trihalogenoindate(I) anions with the electrophilic InX_3 species as well as boron trihalides (see chapter four) were carried out.

$Me_2bipy \cdot InX_3$ compounds react with the corresponding neutral indium(III) halide on refluxing in methanol under nitrogen for several hours to yield compounds of the type $Me_2bipy \cdot In_2X_6$ (X = Cl,Br or I). The complexes are colourless (Cl,Br) or orange (I) solids.

2.6 Experimental

(a) General

Indium(I) compounds are rather light-sensitive and readily disproportionate in the air (moisture) or in the presence of protic solvents. No extreme precautions were taken to avoid photo-decomposition,except by avoiding unnecessary exposure to light.

Since indium(I) compounds disproportionate on contact with water,all solvents were dried over either activated molecular sieves or freshly pressed sodium wire to remove any traces of water and then distilled.

In order to avoid the contact of indium(I) compounds and their complexes with the atmosphere,all reactions and operations were performed under a stream of dry nitrogen,or in a nitrogen dry-box.

(b) Preparative Chemistry

Preparation of Indium(I) Halides

Indium(I) halides were prepared by reacting the corresponding indium(III) halide with the calculated quantity of indium metal.

$$InX_3 + 2In = 3InX \qquad (X = Cl, Br \text{ or } I)$$

Both reactants were placed in a sealed tube and heated to 250° C for 4 hours, after which the tube was opened under nitrogen and a small excess of indium metal added. The tube was resealed and heated (to 350°C for the chloride and bromide and to 450°C for the iodide) for a further 24 hours. In each case the resulting solid was finely ground, the nodule of excess of indium metal removed and the product washed with ether, dried and stored in the dark under nitrogen. The yield was better than 95% in all cases.

In view of the problems encountered by some authors in the identification of the lower halides of indium, the composition of all these substances were confirmed analytically (see table 3).

Preparation of Indium Dihalides

Indium dihalides were prepared by reacting the corresponding indium trihalide with indium metal in the mole ratio 2:1 in a sealed tube. The tube was maintained at 400°C for 24 hours with occasional shaking; the dihalide was quenched by cooling the tube rapidly. The dihalides were crystalline solids. The yield was quantitative in each case. Analyses for the indium dihalides are given in table 3.

Preparation of Indium Trihalides

(a) Preparation of Indium(III) Chloride

Dry chlorine gas was slowly passed over molten indium metal. The indium(III) chloride formed as a fine white solid, sublimes on the cooler parts of the flask;excess of chlorine was removed with a stream of nitrogen at reduced pressure. The trichloride was stored under nitrogen.

(b) Preparation of Indium(III) Bromide

Nitrogen,saturated with bromine was slowly passed over molten indium metal. The white solid formed sublimes on the cooler parts of the apparatus. The product was stored under nitrogen.

(c) Preparation of Indium(III) Iodide

Indium metal and resublimed iodine were heated in an evacuated sealed tube to 180°C for 24 hours. The tube was opened under nitrogen and the indium(III) iodide formed purified by vacuum sublimation at 120-130°C.

Preparation of N,N'-Dimethyl-4,4'-Bipyridinium Halides

The N,N'-dimethyl-4,4'-bipyridinium cation was prepared by refluxing 4,4'-bipyridyl and dimethyl sulphate together for 6 hours. The resulting solution was cooled,treated with water and further stirred for 30 minutes. The aqueous layer was extracted several times with 20 ml. portions of ether to remove any dimethyl sulphate,and then treated with an excess of an aqueous solution of picric acid.

The yellow precipitate was filtered off and washed with acetone until the filtrate was clear (viz,free of picric acid). This solid was then suspended in acetone and treated with an excess of the corresponding concentrated hydrohalic acid,filtered,washed with acetone and dried. Recrystallization from aqueous solutions followed by drying at 85°C gave yields better than 75%,calculated on the basis of the initial 4,4'-bipyridyl.

Preparations of Indium(I) Complexes

To prepare the indium(I) halide complexes,a methanolic solution of Me_2bipyX_2 (X = Cl,Br or I) was stirred with a suspension of the indium monohalide under nitrogen. After 4 to 5 minutes the solution became blue,because of the indicator properties of the cation. The mixture was stirred for 2 to 3 hours;removal of solvent in vacuo gave solids of stoichiometry $Me_2bipy \cdot InX_3$ in quantitative yield.

Unless a trace of halogen was added to the final reaction mixture,the products were dark blue. The "bleached" compounds were colourless (Cl),pale yellow(Br) or orange (I). In all cases the product melts at over 350°C.

Analyses are shown in table 2.

Reaction of Me_2bipyX_2 with Indium Dihalides

A solution of the corresponding halide salt of Me_2bipy cation in methanol was stirred with a suspension of the corresponding indium dihalide under nitrogen. After 2 to 3 hours with stirring,the solvent was removed. In all cases the residual product analysed as $Me_2bipy \cdot InX_4$ (see table 2).

Reaction of Me_2bipyX_2 with Indium Trihalides

Indium trihalide and the corresponding salt of the Me_2bipy cation in a mole ratio 1:1,were dissolved in methanol; the resulting solution was left with stirring for one hour and then the solvent partially taken off. The resulting solids were filtered off,washed with ether and dried. The solids are colourless (Cl),light yellow (Br) or orange (I) and analyse as $Me_2bipy \cdot InX_5$. Analyses are given in table 2.

Reaction of $Me_2bipy \cdot InX_3$ with Indium Trihalides

Indium(III) halides dissolved in dry methanol were added to the corresponding $Me_2bipy \cdot InX_3$ compound under nitrogen. The resulting solutions were refluxed for 10 hours. Colourless (Cl,Br) or orange (I) solids were obtained,filtered off,washed with methanol and dried.

(c) Physical Measurements

Raman Spectra

The Raman emission from powdered solids was recorded at room temperature with a Cary 81 spectrometer,using He/Ne laser excitation.

Melting Point Determination

Melting point determinations were carried out in sealed tubes under nitrogen,using a Gallenkamp melting point apparatus.

Conductivity Measurements

Conductivity measurements were performed with 10^{-3}M solutions in nitrobenzene or acetonitrile as dictated by the solubility of the compounds. A conductivity meter type CDM-2d (Radiometer Ltd.,Copenhagen) with a commercial platinum black electrode were used;the cell constant was determined as 0.1065.

The solvent nitrobenzene was purified by fractional distillation. Acetonitrile was purified by shaking it with a cold saturated aqueous solutions of potassium hydroxide,followed of a preliminary drying over anhydrous Na_2CO_3;two final distillations at 81°C from phosphorus pentoxide gave the necessary purity.

The molar conductivity for the compounds reported in this chapter are given in table 4.

Magnetic Susceptibility Measurements

Magnetic susceptibility measurements were carried out by the Faraday method on powdered solids at room temperature. A Cahn RG electrobalance attatched to a electromagnet from Varian Associates was used. $Hg[Co(NCS)_4]$ was used as calibrant.

Analytical Techniques

Microanalyses

Elemental analyses for carbon,hydrogen and nitrogen were determined by M.K.Yang of Simon Fraser University.

Indium Analyses

Indium analyses were determined from atomic absorption spectroscopy,using a Perkin Elmer atomic absorption spectrophotometer. The apparatus was calibrated with indium standard solutions containing 75, 50, 25 and 10 μg/ml.

Halogen Analyses

Halogen analyses were performed gravimetrically. The halides were weighed as silver halides.

TABLE 2

Analytical Results for Anionic Indium Complexes

Compound[(a)]	Found %					Required %				
	C	H	N	X[(b)]	In	C	H	N	X	In
C $InCl_3$	36.7	3.7	7.0	26.4	28.4	35.4	3.4	6.9	26.2	28.2
C $InBr_3$	26.8	2.7	5.1	44.3	21.3	26.6	2.6	5.2	44.4	21.2
C InI_3	21.3	2.2	3.9	55.2	16.2	21.1	2.1	4.1	55.9	16.8
C $InCl_4$	32.8	3.2	5.6	32.1	25.8	32.5	3.2	6.3	32.1	25.9
C $InBr_4$	23.0	2.4	4.4	51.5	18.5	23.2	2.3	4.5	51.5	18.5
C InI_4	17.7	1.7	3.2	62.6	14.7	17.8	1.7	3.5	62.8	14.2
C $InCl_5$	30.5	2.9	5.5	37.4	24.2	30.1	2.9	5.9	37.1	24.0
C $InBr_5$	20.6	2.0	3.7	56.7	16.7	20.6	2.0	4.0	57.1	16.4
C InI_5	15.4	1.5	3.1	67.5	12.3	15.4	1.5	3.0	67.9	12.3
C In_2Cl_6	22.3	2.1	4.3	33.4	36.4	22.9	2.2	4.5	33.9	36.5
C In_2Br_6	14.2	1.7	3.6	54.8	26.1	16.5	1.6	3.2	54.8	26.2
C In_2I_6	12.6	1.5	2.2	64.3	19.4	12.2	1.2	2.4	64.7	19.6

(a) C = Me_2bipy^{2+} cation. (b) Halogen

TABLE 3

Analytical Results for Lower Indium Halides

Compound	Found %		Required %	
	In	Halogen	In	Halogen
InCl	76.7	23.4	76.4	23.6
InBr	58.7	41.2	59.0	41.0
InI	47.3	52.5	47.5	52.5
$InCl_2$	61.7	38.6	61.8	38.2
$InBr_2$	42.2	58.3	41.8	58.2
InI_2	31.3	68.9	31.1	68.9

TABLE 4

Conductivity results for the $Me_2bipy \cdot InX_n$ and $Me_2bipy \cdot In_2X_6$ complexes

(n = 3,4,5 ; X = Cl,Br or I)

Compound(a)	Molar Conductivity(b)	Solvent
$C \cdot InCl_3$	97	acetonitrile
$C \cdot InBr_3$	85	acetonitrile
$C \cdot InI_3$	25	nitrobenzene
$C \cdot InCl_4$	(c)	
$C \cdot InBr_4$	(c)	
$C \cdot InI_4$	(c)	
$C \cdot InCl_5$	175	acetonitrile
$C \cdot InBr_5$	355	acetonitrile
$C \cdot InI_5$	188	nitromethane
$C \cdot In_2Cl_6$	148	acetonitrile
$C \cdot In_2Br_6$	138	acetonitrile
$C \cdot In_2I_6$	143	acetonitrile

(a) C = Me_2bipy^{2+} cation

(b) Molar conductivities at room temperature; $ohm^{-1}cm^2$

(c) Insoluble in most solvents

2.7 Results and Discussion

(a) The Trihalogenoindate(I) Anions

Vibrational Spectroscopy

The Raman spectra of the solid indium monohalides showed the following bands (in cm^{-1})

InCl	86 sh,	102 w,	234 m		
InBr	38 w ,	47 s,	68 ms,	86 ms	
InI	39 mw,	78 vs,	105 mw,	135 w ,	211 s

No attempt to assign these bands was made;the important point is that the InX_3^{2-} (X = Cl,Br or I) anions have very different spectra in this region (see table 5).

By comparison with some isoelectronic species such as the trihalogeno-tin(II) anions and the trihalides of antimony,the Raman spectra of the InX_3^{2-} species were assigned on a C_{3v} symmetry. The assignment of a C_{3v} symmetry for $SnBr_3^-$ and SnI_3^- anions in the solid state has been questioned by Wharf and Shriver[87] who suggested C_s symmetry. For a pyramidal MX_3 molecule with C_{3v} symmetry,group theoretical methods predict four,both Raman and infrared active bands: ν_1 and ν_2 of A_1 symmetry and ν_3 and ν_4 of E symmetry (see table 6). An ether extract of a solution of stannous chloride in hydrochloric acid gives a Raman spectrum which is attributed to the pyramidal $SnCl_3^-$ ion. Similarly the $SnBr_3^-$ ion extracted from a solution of stannous bromide in aqueous hydrobromic

TABLE 5

Raman spectra of the trihalogenoindate(I) anions$^{(a)}$ in the solid state (in cm^{-1})

C $InCl_3$	C $InBr_3$	C InI_3
252 m	177 w	136 m
185 m	149 w	110 w
102 mw	74 w	64 w
97 w	46 w	40 sh

(a) C = Me_2bipy^{2+} cation

Abreviations for this and subsequent tables: m = medium; mw = medium weak; w = weak; sh = shoulder.

TABLE 6

Relationship between C_{3v} and C_s symmetries

Point group	ν_1	ν_2	ν_3	ν_4
C_{3v} (MX_3)	A_1(I,R) ν_s(MX)	A_1(I,R) δ_s(XMX)	E(I,R) ν_a(MX)	E(I,R) δ_a(XMX)
C_s (MX_2Y)	A'(I,R) ν_s(MY)	A'(I,R) δ_s(XMY)	A'(I,R) + A"(I,R) ν_s(MX) ν_a(MX)	A'(I,R) + A"(I,R) δ_s(XMX) δ_a(YMX)

acid gives a spectrum consistent with a C_{3v} symmetry. The SnI_3^- species has not been obtained in solution,but its Raman spectrum in the solid state was reported by Wharf and Shriver and interpreted in terms of C_s symmetry in which the degeneracy of the C_{3v} E modes is removed,so that a splitting of ν_3 and ν_4 would be observed.

The vibrational spectra of the InX_3^{2-} anions (X = Cl, Br or I) were assigned in C_{3v} on the basis of the symmetry rules outlined in table 6. Since no splitting of the E modes was detected,it was concluded that unlike the $SnBr_3^-$ and SnI_3^- anions in the solid state no C_s symmetry can be inferred for the trihalogenoindate(I) anions.

The assignment of the observed bands to the vibrational modes of the pyramidal C_{3v} point group was made by comparison with the reported vibrational spectra of the isoelectronic tin(II) and antimony(III) analogues. Table 7 shows the assignment of all three trihalogenoindate(I) anions,together with the appropriate results for the isoelectronic SnX_3^- [87,88] and SbX_3 [89] species.

The assignment of the vibrational spectra of the trihalogenoindate(I) anions given in table 7 is in keeping with the assignment of these ions to a C_{3v} pyramidal symmetry. The above assignment is also in agreement with the predicted decrease in the frequencies with the decrease of the oxidation state of the central atom. The decreasing in the fre-

TABLE 7

The assignment of the Raman spectra of $InX_3{}^{2-}$, and the vibrational spectra of $SnX_3{}^{-}$ and SbX_3 species (in cm^{-1})

	ν_1	ν_2	ν_3	ν_4
X = Cl				
In(I)	252	102	185	95
Sn(II)	297	128	256	103
Sb(III)	345	176	322+316	154+145+141
X = Br				
In(I)	177	74	149	46
Sn(II)	211	83	181	65
Sb(III)	246	113	229	92
X = I				
In(I)	136	78	110	40
Sn(II)(a)	152	60	128	50
Sb(III)	160	67	138	43

(a) Bands at 137 and 50 cm^{-1} are assigned to ν_5 and ν_6 in C_s symmetry by Wharf and Shriver[87].

quencies one can expect with the increasing of the mass of the substituents, i.e., going from chlorine to iodine, was also observed.

The correctness of these assignments for the InX_3^{2-} species have been strengthened by force constant calculations (see chapter III).

Conductivity Measurements

The conductivity measurements were carried out in different solvents as dictated by the solubility of the complexes.

For non-complex compounds in acetonitrile, 1:1 electrolytes such as tetraalkylammonium salts give values of about 159 ohm^{-1} cm^2 at 10^{-3} M solutions. In complex compounds values as low as 82 and as high as 199 $ohm^{-1}cm^2$ have been used to characterize 1:1 electrolytes[90].

The rather low values found for $Me_2bipy \cdot InCl_3$ and $Me_2bipy \cdot InBr_3$ in acetonitrile may be explained by the large size of the cation compared with the anion, leading to incomplete dissociation. For $Me_2bipy \cdot InI_3$ the molar conductivity at room temperature is in keeping with the average value for a 1:1 electrolyte type in nitrobenzene[90,91].

(b) The $Me_2bipy \cdot InX_5$ Complexes

Vibrational Spectroscopy

The Raman spectra of the tetrahalogenoindate(III) anions in solutions have been studied by Woodward et al[92 94]. Barrowcliffe et al[95] reported the vibrational spectra of

$InCl_6^{3-}$ and more recently Shriver and Wharf[96,97] published both solid and solution state infrared and Raman spectra of $[Et_4N]_2[InCl_5]$. Single crystal studies of this compound have also been reported[98,99]. The vibrational spectra of solids $C\ InX_4$, C_2InX_5, C_3InX_6 and C_4InX_7 where X = Cl, Br or I and C is a substituted ammonium cation have recently been published[86].

The Raman spectra of the solids $Me_2bipy \cdot InX_5$ are given in table 8. For crystalline $Me_2bipy.InCl_5$ the Raman spectrum correlates very well with the Raman spectrum reported[99] for the $[Et_4N]_2[InCl_5]$ which has been shown to contain the square based pyramidal C_{4v}, $InCl_5^{2-}$ anion[71]. Adams and Smardzewski report nine Raman active bands between 300 and 100 cm^{-1}, at 294, 287, 273, 193, 165, 145, 141 and 107 cm^{-1} assigned to $\nu_1(A_1)$, $\nu_4(B_1)$, $\nu_7(E)$, $\nu_5(B_1)$, $\nu_6(B_2)$, $\nu_8(E)$, $\nu_3(A_1)$ and $\nu_9(E)$ modes respectively.

From table 8 it is clear that the solid Raman spectrum of $Me_2bipy \cdot InCl_5$ is similar to the vibrational spectrum of $[Et_4N]_2[InCl_5]$ and hence the former compound also contains the C_{4v} $InCl_5^{2-}$ anion.

This conclusion is of some importance in terms of the earlier discussion on this anion[71], whose structure differs from the isoelectronic species $SnCl_5^-$ and $SbCl_5$ which have D_{3h} symmetry[100,101]. More recently the $CdCl_5^{3-}$ anion has been found to have a trigonal bipyramidal structure[103]

TABLE 8

The Raman spectra of $Me_2bipy \cdot InX_5$ complexes

(X = Cl,Br,I)

$Me_2bipy \cdot InCl_5$	$Me_2bipy \cdot InBr_5$	$Me_2bipy \cdot InI_5$
294 m	232 w	197 m
281 m	196 s	181 m
275 m	84 w	137 vs
194 w	78 w	56 w
142 w		42 w
124 w		
105 w		

Abreviations for this and subsequent table: vs = very strong; s = strong.

emphasising once again the anomalous structure of $InCl_5^{2-}$. The suggestion was made earlier[71] that the C_{4v} structure of the pentachloroindate(III) anion might have been the result of lattice effects associated with tetraethylammonium cation, although this proposal was not supported by some incomplete spectral studies[86] on salts with the cations Me_4N^+,$MePh_3N^+$ and $Bu_2Ph_3P^+$, where the C_{4v} symmetry also appears probable. The present data show clearly that a severe change of cation from Et_4N^+ to the large dipositive Me_2bipy^{2+} does not alter the C_{4v} symmetry of the $InCl_5^{2-}$ anion,and lattice effects can seemingly therefore be rejected in any discussion of this problem;the explanation for the fact that $InCl_5^{2-}$ is not isostructural with its isoelectronic d^{10} congeners is not apparent at the present time.

The situation for the bromide and iodide compounds is different. Salts of the $InBr_4^-$ ion have Raman bands at 200 s (ν_1,A_1),237 mw(ν_3,F_2) and 79 m (ν_4,F_2),whereas for InI_4^- the analogous modes are at 139 s,186 w and 58 w,cm^{-1}. From a comparison of these bands with those reported for $Me_2bipy\cdot InBr_5$ and $Me_2bipy\cdot InI_5$ (table 8) one can infer that the solid state lattice in these latter compounds are in fact Me_2bipy^{2+} + InX_4^- + X^- (X = Br or I),with the InX_4^- anion in some site symmetry lower than tetrahedral since some splitting of ν_3 occurs. This conclusion is in keeping with earlier work[86] in which the compound $[Me_4N]_2[InBr_5]$ was shown to consist of $2Me_4N^+ + InBr_4^- + Br^-$ by similar arguments. This situation has also been found in solids of the type C_4InX_7 (X = Cl or Br and C = $MeNH_3^+$,$Me_2NH_2^+$) for which a $4C^+ + InX_6^{3-} + X^-$ structure has been proposed[86].

The failure to obtain InI_5^{2-} is not surprising since it seems unlikely that iodo-complexes of indium(III) with coordination number greater than four exist in the solid state.

Conductivity Measurements

The conductivity results for the $Me_2bipy.InX_5$ complexes are given in table 4.

The molar conductivity of $Me_2bipy.InCl_5$ in acetonitrile is in keeping with the results obtained from the vibrational spectroscopy which showed the compound contains $InCl_5^{2-}$ species. In fact the value of 175 ohm^{-1} cm^2 is in the upper range for 1:1 electrolytes in this solvent,and therefore the compound can be formulated as $[Me_2bipy][InCl_5]$.

For $Me_2bipy\cdot InBr_5$ the measured value of the molar conductivity in acetonitrile agrees very well with the average value for 2:1 electrolyte;this is also in keeping with the conclusions inferred from the Raman spectra which showed this solid is best formulated as $Me_2bipy^{2+} + InBr_4^- + Br^-$.

A rather wide range of values for the molar conductivity in nitromethane has been found[90]. Values as low as 115 and as high as 250 ohm^{-1} cm^{2} have been found for a 2:1 electrolyte type,with an average value of 168 ohm^{-1}cm^{2}. For $Me_2bipy \cdot InI_5$ a value of 188 ohm^{-1}cm^{2} was found,in good agreement with its formulation as 2:1 electrolyte and also in keeping with the spectroscopic results.

(c) The $Me_2bipy \cdot InX_4$ Complexes

Vibrational Spectroscopy

The reaction of indium dihalides with the appropriate salt of the Me_2bipy^{2+} cation,gave in each case a crystalline material of stoichiometry $Me_2bipy \cdot InX_4$. Table 9 shows the Raman spectra of these compounds.

Looking at the Raman spectra of the trihalogenoindate(I) anions (table 5) and of the indium(III) halide complexes (table 8),it is clear that in the case of both $Me_2bipy \cdot InBr_4$ and $Me_2bipy \cdot InI_4$,the spectra can be interpreted on the assumption that the solid is an equimolar mixture of $2Me_2bipy^{2+}$ + InX_3^{2-} + InX_4^{-} + X^{-},taking into account the relative intensities of the emissions in question. For the chloride derivative,the spectrum is made up of the spectra of $InCl_3^{2-}$ and $InCl_5^{2-}$ leaving only one band,that at 321 cm^{-1},unassigned.

Table 10 shows the assignment of the bands found for the $Me_2bipy \cdot InX_4$ (X = Cl,Br or I) solids in terms of the Raman bands reported previously for the InX_3^{2-} anions and the indium(III) halide complexes.

TABLE 9

The Raman spectra of the $Me_2bipy \cdot InX_4$ solids

(X = Cl,Br or I)

$Me_2bipy \cdot InCl_4$	$Me_2bipy \cdot InBr_4$	$Me_2bipy \cdot InI_4$
321 m	237 w	196 s
284 m	199 w	181 s
196 m	148 w	136 s
185 m	106 w	106 w
148 w	72 w	79 sh
128 w		74 w
104 w		
102 mw		
98 w		

Table 10. Assignment of the Raman Bands (in cm^{-1}) of Compounds $Me_2Bipy \cdot InX_4$

X = Cl									
$InCl_3^{2-}$	98w	102vw				185m			
$InCl_5^{2-}$			104w	128w	148w		196m	284m	
not assigned									321m
X = Br									
$InBr_3^{2-}$	72w		106w	148w					
$InBr_4^-$						199w		237w	
X = I									
InI_3^{2-}	74w,79sh			106w		136s			
InI_4^-						136s	181s		196s

These results show that the anionic halide complexes derived from the dihalides are,in each case,a diamagnetic mixture of indium(I) and indium(III) species (molar susceptibilities at room temperature: -290(Cl), -120(Br), -445(I) x 10^{-6} cgs units). These conclusions are in keeping with the formulation of the indium dihalides as mixed oxidation state compounds,but beyond that can give no information as to their detailed structure.

(d) The Raman Spectra of Indium Dibromide and Diiodide

It was pointed out before that Raman spectroscopy of molten $InCl_2$ has shown the presence[40] or absence[41,43] of the $InCl_4^-$ anion. In the course of the present investigation it was found that much less attention has been given to indium dibromide and indium diodide than to the chloride and therefore there was no vibrational spectroscopy data available for these compounds. Hence it seemed worthwhile to obtain the Raman spectra of $InBr_2$ and InI_2 in order to see if the unsettled situation found for the dichloride was the same in these compounds.

The Raman spectrum of solid indium diiodide shows five emissions,and is readily correlated with the spectrum of the tetrahedral InI_4^- anion[86,93].

InI_4^- (T_d)	139(ν_1)	42(ν_2)	185(ν_3)	58(ν_4)
InI_2	138 vs	47 w	191m,177mw	72w,62mw

It is clear that indium diiodide lattice is made up of InI_4^- anions and can be formulated as In(I)[In(III)I_4]. The splitting of ν_3 and ν_4,the F_2 fundamental modes,show that the InI_4^- anion is in a site symmetry lower than T_d. On descending in symmetry from T_d to C_{3v},it is seen that the F_2 vibrational modes of T_d are split in two modes, A_1 + E both infrared and Raman active . The tetrahedral A_1 and E modes remain unchanged. From group theoretical methods,it can be inferred that a further descend in symmetry from C_{3v} to C_{2v} a further splitting of all the C_{3v} E vibrational modes would be expected. The Raman spectrum of InI_2 clearly shows that although there is a splitting of the F_2 fundamental modes,the symmetry is not as low as C_{2v} since no splitting of the ν_2(E) mode is observed. Therefore one can conclude that the InI_4^- anion is in a C_{3v} site symmetry.

This conclusion is in agreement with previous results which demonstrate that the high stability of the InI_4^- anion, which leads to ionic structures in such varying compounds as [$InI_2(dmso)_4$][InI_4][56] and [Me_2In][InI_4][27].

The Raman spectrum of $InBr_2$ again correlates well with that of the $InBr_4^-$ anion[86,92] and demonstrates the presence of this anion in a C_{3v} site symmetry.

$InBr_4^-$ (T_d)	197(ν_1)	55(ν_2)	239(ν_3)	79(ν_4)
$InBr_2$	196 vs	59 m	237w,227w	97,85 mw

In one experiment,the Raman spectrum showed doubling of the very strong ν_1 emission at 196 cm^{-1} and broadening of the other bands,suggesting the presence of two phases. Such a phenomenon might explain some of the apparently contradictory results obtained in phase studies of indium-chloride systems. Recently Waterworth and Worrall[103] have reported similar spectra to those given above for $InBr_2$ in the range 190-250 cm^{-1}.

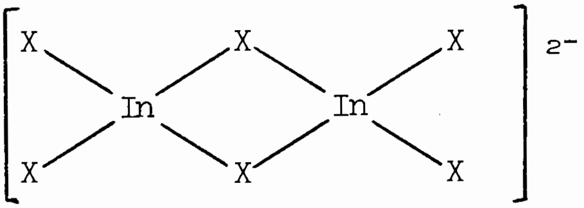
(e) The $Me_2bipy.In_2X_6$ Complexes

Vibrational Spectroscopy

Waterworth and Worrall[103] have reported that the solid phase of In_2Br_3 has the structure $In(I)_2[In(II)_2Br_6]$. By analogy with the work of Evans and Taylor[104] on the dinuclear halide complexes of gallium(II),which are of the type $[Me_4N]_2[Ga_2X_6]$ (X = Cl,Br or I),Waterworth and Worral[103] suggested the structure $[X_3In\text{-}InX_3]^{2-}$ for the presumed indium(II) complex anion in In_2Br_3. Raman bands at 241 m, 201 m and 139 vs cm^{-1} were reported for the anion,and of these the one at 139 cm^{-1} was assigned to the metal-metal stretching mode.

The Raman spectrum of the anion $In_2Br_6^{2-}$ in $Me_2bipy.In_2Br_6$ shows no such band (see table 11).

Comparison of these results with those for other indium species suggest strongly that these anions are in fact dihalogen bridged complexes of the type



(X = Cl,Br or I)

This is specially true for the iodide compound,where comparison can be made with In_2I_6[105-107] and the mono- and trimethyl derivatives $MeInI_2InI_2$ and $MeInI_2InMe_2$[27].

The ring breathing mode in these compounds lies between 135 (in In_2I_6) and 142 cm^{-1} (in $MeInI_2InMe_2$);ν(In-I) frequencies have been found in the range 216-136 cm^{-1},depending on the oxidation state of the central atom.

On this basis,the band at 138 cm^{-1} in $In_2I_6^{2-}$ was assigned to the ring vibration of InI_2In moiety,and the higher frequencies as the terminal ν(In-I) modes. The frequency ratio $\nu(In\text{-}I)_{bridge}/\nu(In\text{-}I)_{terminal}$ is about 0.75,close to that found in a wide range of dihalogeno bridged molecules[108]. It is worth noting that if the above assignment is correct, the $In_2I_6^{2-}$ anion cannot be planar with a D_{2h} symmetry since in this case two terminal (B_{2u} + B_{3u}) and two bridging (B_{2u} + B_{3u}) indium-iodine stretching modes in the infrared,

TABLE 11

The Raman spectra of $Me_2bipy \cdot In_2X_6$ complexes (in cm^{-1})

(X = Cl,Br or I)

$Me_2bipy \cdot In_2Cl_6$	$Me_2bipy \cdot In_2Br_6$	$Me_2bipy \cdot In_2I_6$
347 m	262 m	214 w
309 w	232 m	198 m
295 s	222 w	182 m
205 m	208 w	138 s

but not in the Raman, would be observed.

The assignment of the bridging and terminal indium-halogen vibrational modes for the bromide and chloride is less straightforward and the most it can be said is that the present evidence gives little support to any model requiring significant indium-indium bonding.

At the present the exact nature of the $Me_2bipy\cdot In_2X_6$ complexes is not very well understood and more structural information is required.

Conductivity Measurements

The molar conductivities of the solids $Me_2bipy\cdot In_2X_6$ (X = Cl, Br or I) in acetonitrile are listed in table 4.

The experimental values of the molar conductivity for these compounds agree well with the average value of 140 $ohm^{-1}cm^2$ found for 1:1 electrolyte[90], and therefore they can be formulated as $[Me_2bipy][In_2X_6]$.

2.8 Conclusions

From the results given above, it is clear that the compounds of the type $Me_2bipy\cdot InX_3$ (X = Cl, Br or I) are 1:1 electrolytes and can be formulated as $[Me_2bipy][InX_3]$. On the other hand the vibrational spectra of these compounds are in keeping with the group theoretical rules for a C_{3v} symmetry since no further splitting of the E modes was observed. Taking into account the experimental fact that an increase in the oxidation state of the central atom increases the metal-halogen frequencies, the assignment of the observed bands for these species is in keeping with the vibrational spectra reported for the isoelectronic $Sn(II)X_3^-$ and $Sb(III)X_3$ species. Molar susceptibilities of the three salts were -246, - 287 and -132 x 10^{-6} cgs units for the chloride, bromide and iodide respectively, values which confirm the expected diamagnetism of the compounds prepared.

The $Me_2bipy \cdot InX_5$ compounds are made up of the well known tetracoordinate InX_4^- species for X = Br or I, with the fifth halide ion somewhere in the lattice balancing the dipositive charge of the cation. For $Me_2bipy.InCl_5$, a true pentacoordinate species having C_{4v} symmetry is present.

Raman spectroscopic results on the $Me_2bipy \cdot InX_4$ solids (X = Cl, Br or I) clearly show that the lattice is made up of equimolar mixture of the $InX_3^{2-} + InX_4^- + X^- + 2Me_2bipy^{2+}$ for the bromide and iodide. In $Me_2bipy \cdot InCl_4$, the lattice is formed by the equimolar mixture of $InCl_3^{2-} + InCl_5^{2-} + 2Me_2bipy^{2+}$. These results point out the fact that the ionic dimer structure involving mixed oxidation states, is more likely to occur in the indium dihalides. This chemical evidence is reinforced by the Raman spectra of quenched samples of indium diiodide and dibromide for which the Raman spectroscopy showed the presence of InI_4^- and $InBr_4^-$ anions respectively.

The reaction of the potentially nucleophilic InX_3^{2-} species with the neutral indium(III) halides yields solids of the type $Me_2bipy \cdot In_2X_6$ (X = Cl,Br or I) containing the complex anions $In_2X_6^{2-}$. From the Raman spectra, it is inferred that these anions posses a halogen bridged structure rather than a one involving metal-metal bond in the fashion suggested for their gallium(II) analogues. It was found that the assignment of the iodide derivative agrees with previous vibrational studies on compounds of similar type, but no attempt was made to assign the Raman spectra of the bromide and chloride species.

It is suggested that if the assignment for the iodide is correct the molecule cannot be planar with a D_{2h} symmetry. The exact nature of these compounds is still unsettled.

C H A P T E R III

FORCE CONSTANT CALCULATIONS FOR ANIONIC INDIUM(I) AND (III) HALIDE COMPLEXES

3.1 The Vibrational Problem

The vibrational frequencies of a molecule having a given shape depend on: (a) the masses of the atoms in the molecule and (b) the forces restoring the atoms to their equilibrium positions when the vibrations take place. The strength of these restoring forces are measured by the force constants.

The importance of determining the force constants and normal coordinates for molecular vibrations is well accepted, as they provide the basic link between the electronic structure of the molecule and its observed vibrational frequencies and give a picture of the forces acting within a molecule. Therefore in the calculation of the vibrational frequencies, since it may be assumed that the atomic masses are known,the problem is reduced to finding the force constants for the molecule under study.

In practice,the problem is reversed;from the experimentally determined frequencies,the unknown force constants are calculated. There are,however,three main obstacles to their determination:

(a) for even a quadratic or harmonic potential function, the number of force constants required for the complete function is always larger than the number of frequencies available. Thus, for a secular equation of order N there are N(N+1)/2 independent force constants to be calculated, but only N vibrational frequencies. The classical solution to this problem is to use data on several isotopic substituted molecules and/or to use values of Coriolis coefficients, centrifugal stretching constants, mean amplitudes of vibration and vibrational intensities, all of which are related to force constants,

(b) the observed frequencies differ from the harmonic system partially because of anharmonicity and partially because of resonance perturbations. Corrections for anharmonicity and resonance perturbations are of the order of few percent and in practice these have been made successfully only for very few simple molecules such as CO_2, HCN and C_2H_2[109], and

(c) the amount of computation involved is sufficient to prevent in practice a detailed force constant calculation by conventional means, although the availability of electronic computers has obviously overcome this problem.

Despite most of the difficulties outlined above can be overcome for most of the molecules, the first two problems will always remain, and hence force constants can only be calculated under certain approximations. One of the most common practices is to restrict the number of force constants used in the potential function,so that they are less than or equal to the number of observed frequencies,and to neglect the effects of anharmonicity and resonance perturbations.

In the restriction of the number of force constants one has to be able to provide a realistic potential function and capable of meaningful comparison at least with similar molecules.

A complete mechanical treatment would cover the rotational-vibrational interaction as well as the motion of the electrons arround the nuclei. Because of the very great difference between the masses of the electron and the nucleus, it is permissible as a very good approximation to regard their respective motions as mechanically separable. This is referred to as the Born-Oppenheimer approximation. The rotational-vibrational interaction is generally quite weak and therefore the purely vibrational problem is a good approximation for free molecules.

The inclusion of the translational motion of the molecule as a whole has been expressly neglected since it produces no changes in the equilibrium positions of the atoms making up the molecule,and therefore no change in the potential energy occurs.

3.2 Potential Force Fields

It was pointed out above that in order to reduce the number of parameters to calculate the vibrational frequencies some restrictions in the potential function have to be accepted. For the sake of simplicity,the terms of third,fourth and higher order in the potential energy expression are neglected and hence the potential energy V is written as[110]

$$2V = \sum_{t,t'=1}^{3N-6} F_{tt'} S_t S_{t'} \qquad (3\text{-}1)$$

where $F_{tt'}$ is a force constant and S_t and $S_{t'}$ are internal coordinates. This is called the "general quadratic potential function". Since this function is rarely derivable except for molecules of high symmetry or linear triatomic molecules and since the number of force constants is always greater than the number of fundamental frequencies,many intermediate functions have been used.

(a) The Central Force Field

In a central force field,the potential energy can be written as

$$2V = \sum K_{AB} \cdot \Delta R^2_{AB} \qquad (3\text{-}2)$$

where ΔR_{AB} is the change in the bond distance between the atoms A and B and K_{AB} is a force constant. The summation over all the atoms of the molecule.

This force field has not been used successfully because it does not account for bending and out-of-plane forces.

(b) The Valence Force Field

Another approximation to express the potential energy is that called valence force field. The valence force field model takes into account the bending forces and therefore V can be written as

$$2V = \sum K_A \cdot \Delta R^2_A + \sum K_M \cdot \Delta\alpha^2_M \qquad (3\text{-}3)$$

where K_A, ΔR_A have the same meaning than those in the central force field and K_M and $\Delta\alpha$ account for the bending force constant and the corresponding internal coordinate respectively. The summation is extended over all bonds and angles. The number of force constants is usually less than the number of fundamental frequencies.

(c) The Generalized Valence Force Field

The generalized valence force field is one of the most commonly force field used. It results as an extention of the valence force field to which some interaction constants have been added. The potential energy takes the form

$$2V = \sum K_A \cdot \Delta R_A^2 + \sum K_M \cdot \Delta\alpha_M^2 + \sum K_{AB} \cdot \Delta R_A \cdot \Delta R_B +$$

$$+ \sum K_{MN} \cdot \Delta\alpha_M \cdot \Delta\alpha_N + \sum K_{AM} \cdot \Delta R_A \cdot \Delta\alpha_M \qquad (3\text{-}4)$$

The generalized valence force field uses stretching,bending and interaction constants between them. It has the advantage over the central and valence force fields that is more realistic in reproducing the frequencies,but it has the defect that it is difficult to decide which and how many force constants can be used if one wants to set some of them equal to zero. Usually,one is required to calculate more force constants than there are frequencies available.

(d) The Urey-Bradley Force Field

The Urey-Bradley force field[111] is basicly a generalized valence force field which has superimposed on it some repulsive force constants between non-bonded atoms. The repulsive forces are such that their magnitudes diminish as the distance between the atoms increases. Its introduction is a clear attempt to account for the Van der Waals interaction. The potential energy takes the form

$$2V = \sum[K_i(\Delta r_i)^2 + K'_i(\Delta r_i)] + \sum[H_i r_{i\alpha}^2(\Delta\alpha_i)^2 + + H'_i r_{i\alpha}^2(\Delta\alpha_i)] + \sum[F_i(\Delta q_i)^2 + F'_i q_i \Delta q_i] \qquad (3\text{-}5)$$

where Δr_i,$\Delta\alpha_i$ and Δq_i are the changes in bond length,bond angle and distance between non-bonded atoms,respectively. K,K',H,H',F and F' represent the stretching,bending and repulsive force constants,respectively. The introduction of r_i, $r_{i\alpha}$ and q_i,the values of the equilibrium distances,account to make the force constants dimensionally similar.

This field has the advantage over the others that usually the number of force constants required is equal to the observed frequencies,but one cannot lose sight of the fact that this field is only a fair approximation to the actual force field of the molecule.

(e) Other Force Fields

A small number of clearly defined force fields have been used,although their application and validity have not been extensively explored. They are: hybrid orbital force field[112] and orbital valence force field[113,114].

3.3 The Internal Coordinates

In the treatment of the purely vibrational problem it is advantageous to introduce a set of internal coordinates which describe the relative positions of the atoms without being concerned with the position of the molecule as a whole. In general, for a molecule made up of N atoms there will be 3N-6 (or 3N-5 for a linear molecule) internal coordinates. Let B be a matrix which generates the internal coordinates D from the rectangular coordinates x, y and z for each atom, then

$$D = B \cdot X \qquad (3\text{-}6)$$

where D is a one column matrix whose elements are the internal coordinates and having 3N rows (including those concerned with translational and rotational displacements). On the right hand side of equation (3-6), X is a one column matrix also, containing 3N rows and B is a square matrix of dimension 3N x 3N. From equation (3-6) it can be seen that the cartesian coordinates can be expressed by the relationship

$$X = A \cdot D \qquad (3\text{-}7)$$

where A is the inverse matrix of B.

The total kinetic energy of the system, including translations and rotations as well as the vibrational kinetic energy, expressed in terms of the time derivatives of the cartesian displacements $\dot{x}_i$,will be

$$2\bar{T} = (m_1\dot{x}_1^2 + m_1\dot{y}_1^2 + m_1\dot{z}_1^2) + (m_2\dot{x}_2^2 + m_2\dot{y}_2^2 + m_2\dot{z}_2^2) + + \dots + (m_N\dot{x}_N^2 + m_N\dot{y}_N^2 + m_N\dot{z}_N^2) \qquad (3\text{-}8)$$

which in matrix notation becomes

$$2\bar{T} = \dot{X}^* M \dot{X} \qquad (3\text{-}9)$$

where $\dot{X}$ is a single-column matrix whose elements are the time derivatives of the 3N cartesian coordinates and M is a square diagonal matrix containing the masses of the atoms (three times each). The symbol * stands for the transposed matrix.

Substituting (3-7) into (3-9) we have

$$2\bar{T} = \dot{D}^* \cdot A^* M \cdot A \dot{D} \qquad (3\text{-}10)$$

If the square matrix B in equation (3-6) is partitioned into B and B_o,where B accounts for the purely vibrational problem and B_o for the six coordinates involving translations and rotations,equation (3-10) can be expanded into

$$2\bar{T} = \dot{D}^* A^* M A \dot{D} + \dot{D}^* A^* M A_o \dot{D}_o + \dot{D}_o^* A_o^* M A \dot{D} + \dot{D}_o^* A^* M A_o \dot{D}_o \qquad (3\text{-}11)$$

From equation (3-11) it can be inferred that the first term of the total kinetic energy is concerned with the vibrational internal coordinates, whereas the other terms contain D_o and A_o, which involve the translational and rotational coordinates. In the treatment of the vibrational problem, the first term of the total kinetic energy will be used and therefore equation (3-11) reduces to

$$2K = \dot{D}^* A^* M A \dot{D} \tag{3-12}$$

which represents the vibrational kinetic energy.

According to Wilson[115], the total purely vibrational kinetic energy given in equation (3-12) can be expressed by the so called $\underline{g}$ matrix, defined by

$$\underline{g} = B M^{-1} B^* \tag{3-13}$$

where B is the matrix already considered in equation (3-6) and M^{-1} is the inverse matrix of M. The vibrational kinetic energy becomes

$$2K = \dot{D}^* \underline{g}^{-1} \dot{D} \tag{3-14}$$

where $\underline{g}^{-1}$ is the inverse matrix of $\underline{g}$.

In the same way the vibrational potential energy of the molecule can be written as

$$2V = D^* \underline{f} D \tag{3-15}$$

where $\underline{f}$ is a square matrix whose elements are the force constants f_{ij}. The construction of the G and F matrices from the $\underline{g}$ and $\underline{f}$ matrices respectively will be outlined later. Once the G and F matrices have been obtained, the next step is to solve the matrix secular equation

$$|\, G\, F - E\lambda \,| = 0 \qquad (3\text{-}16)$$

where E is the unitary matrix and λ are the eigenvalues of the secular equation, related with the frequencies by the relationship[108]

$$\lambda = 0.58915\cdot(\bar{\nu} \times 10^{-3})^2 \qquad (3\text{-}17)$$

3.4 The Symmetry Coordinates

In the preceding section, the internal coordinates, namely changes in bond lengths and bond angles, were used to solve the vibrational problem. From the set of internal coordinates, it is now possible to generate a new set of coordinates, each of which belongs to a particular symmetry species of the molecular point group. The new coordinates, called internal symmetry coordinates or simply symmetry coordinates S, are symmetrized linear combinations of the internal coordinates D, and likewise there will be a transformation from them to the set of normal coordinates Q_i, each of which will be expressed as a linear combination of the S coordinates.

Let $\hat{P}(S^i)$ be the projector operator for the species S; the equation defining such operator will be

$$\hat{P}(S^i) = \sum_R \chi^i(R)\hat{R} \qquad (3\text{-}18)$$

where $\chi^i(R)$ is the character of the matrix representing the symmetry operation R and $\hat{R}$ its operator. There will be one $\hat{P}(S^i)$ operator for each symmetry species of the molecular point group[116]. For example, let $\hat{P}(S^i)$ operate on the internal coordinates Δr_1 of a MX_3 C_{3v} molecule

$$\hat{P}(S^i)\Delta r_1 = \sum_R \chi^i(R)\hat{R}\Delta r_1$$

Table 12 gives the details of the use of the operator $\hat{P}(S^i)$ on Δr_1. From table 12, it is clear that $\sum \chi^i(R)\hat{R}\Delta r_1$ for the A_1 vibrational species is $2\Delta r_1 + 2\Delta r_2 + 2\Delta r_3$ which after normalizing becomes the normalized vector S^{A_1}, i.e., the symmetry coordinate for the symmetry species A_1 of the C_{3v} molecular point group. The summation for the A_2 species is of course zero as no fundamental vibration of that symmetry exists. The summation for the E species after normalizing gives the normalized vector $S^{Ea} = \sqrt{6}(2\Delta r_1 - \Delta r_2 - \Delta r_3)$. Since the E species spans a 2-dimensional sub-space, the S^{A_1} and S^{Ea} vectors can be used to generate the S^{Eb} vector. Bearing in mind that the set of symmetry coordinates must be orthonormal, if b_1, b_2 and b_3 are the coefficients of the linear combination of the internal coordinates in S^{Eb}, one can write

$$b_1^2 + b_2^2 + b_3^2 = 1$$

$$\sqrt{3}(b_1 + b_2 + b_3) = 0$$

$$\sqrt{6}(2b_1 + b_2 + b_3) = 0$$

Solving for b_1,b_2 and b_3 and normalizing,S^{Eb} becomes $S^{Eb} = \sqrt{2}(\Delta r_2 - \Delta r_3)$.

In the same way and using other internal coordinates such as $\Delta\alpha$,the change in the X-M-X angle,it is possible to generate all six symmetry coordinates;two for the A_1 symmetry species and four for the E species. Therefore the transformation of the internal coordinates to the symmetry coordinates is obtained from

$$S = U\ D \tag{3-19}$$

where U is a square matrix whose elements are the coefficients of the linear combination of the internal coordinates in the symmetry coordinates.

3.5 The G and F Matrices

It was pointed out before that the vibrational kinetic and potential energies can be expressed in terms of the internal coordinates and the $\underline{g}$ and $\underline{f}$ matrices. The introduction of the symmetry coordinates allows to express these energies as

TABLE 12

Projector operator on Δr_1 of a C_{3v} MX_3 molecule

C_{3v}	E	C_3^+	C_3^-	σv_1	σv_2	σv_3
$\hat{R}\Delta r_1$	Δr_1	Δr_3	Δr_2	Δr_1	Δr_3	Δr_2
$\chi(R)(A_1)$	1	1	1	1	1	1
$\chi(R)(A_2)$	1	1	1	-1	-1	-1
$\chi(R)(E)$	2	-1	-1	0	0	0
$\chi(A_1)\hat{R}\Delta r_1$	Δr_1	Δr_3	Δr_2	Δr_1	Δr_3	Δr_2
$\chi(A_2)\hat{R}\Delta r_1$	Δr_1	Δr_3	Δr_2	$-\Delta r_1$	$-\Delta r_3$	$-\Delta r_2$
$\chi(E)\hat{R}\Delta r_1$	$2\Delta r_1$	$-\Delta r_3$	$-\Delta r_2$	0	0	0

$$2K = \dot{S}^* G^{-1} \dot{S} \qquad (3\text{-}20)$$

and

$$2V = S^* F S \qquad (3\text{-}21)$$

respectively,where G and F are given by the transformations

$$G = U \underline{g} U^* \qquad (3\text{-}22)$$

and

$$F = U \underline{f} U^* \qquad (3\text{-}23)$$

Equations (3-22) and (3-23) allow us to calculate the G and F matrices required to solve the secular equation $| G F - E\lambda | = 0$.

The introduction of the symmetry coordinates in the solution of the vibrational problem causes the secular equation to becomes factorised into a number of differents parts,each of which corresponds to a given symmetry species of the molecular point group. As a consequence the G and F matrices also factorise. Thus,for the case of the MX_3 molecule with C_{3v} symmetry,the secular equation factorises into three blocks; one containing the A_1 symmetry coordinates and two E blocks. In fact,since the two blocks belonging to the E species must be identical with one another,only one of them need be considered.

The setting up of the f matrix required to obtain the F matrix is straightforward and it will be given for each case worked out in this chapter. The setting of the G matrix requires the setting of the g matrix;for not very large molecules this can be done by hand. The relationship (3-13) is specially suitable for computer calculation,which is the way usually adopted when working with large molecules. In our case the G matrices were calculated outside the program and read in as input. The method used to set the g matrix was that given by Decius[117]. Each matrix element is given by

$$g_{ij} = \sum_{k=1}^{N} S_{ik} S_{jk} \mu_k$$

where g_{ij} is the g matrix element associated with the internal coordinates i and j, S_{ik} is a vector representing the contribution of the kth atom to the coordinate i, μ_k is the reciprocal mass of the kth atom,and the summation is extended over all N atoms of the molecule. The g_{ij} matrix elements for both the general and special cases in which all the valence angles of the configuration are assumed to be 90°, 109°28' and 120° respectively are given in references 117 and 118.

3.6 The Potential Energy Distribution and Band Assignment

It is well known that a given group of atoms absorbs over a narrow range of frequencies regardless of the rest of the molecule to which is attached. In this sense "group frequency charts" are very useful in identifying atomic groups in inorganic and organic compounds. The concept of group frequency is based on the assumption that all nuclei perform their harmonic oscillations in a normal vibration in a relatively independent way. This is perfectly acceptable,and the individualization of a given vibration is easily done,if both atoms in the chemical bond have very different masses. If both atoms have comparable masses the amplitudes of oscillation are similar for each atom and therefore the characterization or "isolation" of the frequency is not easy,as the motions might couple strongly.

If the coupling between various groups of frequencies is expected,the theoretical analysis of each individual frequency is absolutely necessary[108].

Let L be a matrix conecting the internal coordinates with the normal coordinates,then

$$\begin{bmatrix} D_1 \\ D_2 \\ \cdot \\ \cdot \\ D_i \end{bmatrix} = \begin{bmatrix} l_{11} & l_{12} & \cdot & \cdot & \cdot & l_{1N} \\ l_{21} & l_{22} & \cdot & \cdot & \cdot & l_{2N} \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ l_{i1} & l_{i2} & \cdot & \cdot & \cdot & l_{iN} \end{bmatrix} \begin{bmatrix} Q_1 \\ Q_2 \\ \cdot \\ \cdot \\ Q_N \end{bmatrix} \qquad (3\text{-}24)$$

where $Q_1, Q_2 \ldots Q_N$ are the normal coordinates changing with the frequencies $\nu_1, \nu_2 \ldots \nu_N$ respectively when the normal vibrations take place. All the D internal coordinates change with the same frequencies, but the amplitudes of the oscillation are different for each internal coordinate. The ratio $l_{1N} : l_{2N} : \ldots : l_{iN}$ gives the relative ratio of the amplitudes of the internal coordinates D associated with a given normal coordinate Q_N.

For a given set of Q_N, the ratios of the different l_{ij} elements can be obtained as a matrix from the relationship

$$G\,F\,L = L\,\Lambda \tag{3-25}$$

where the G, F and L matrices are those previously discussed and Λ is a square diagonal matrix whose elements are the eigenvalues of the GF matrix. It is clear that if one considers the L matrix as made up by succesive columns $L_1, L_2 \ldots L_N$, equation (3-25) can be written as

$$\begin{aligned} G\,F\,L_1 &= L_1\,\Lambda_1 \\ G\,F\,L_2 &= L_2\,\Lambda_2 \\ \cdots\ &\quad \cdot\ \cdot \\ \cdots\ &\quad \cdot\ \cdot \\ G\,F\,L_N &= L_N\,\Lambda_N \end{aligned}$$

where the columns L_N are the eigenvectors of the GF matrix corresponding to the eigenvalues $\Lambda_1, \Lambda_2, \ldots, \Lambda_N$, respectively

The eigenvectors derived in this way contain some undetermined multiplicative factors which require to be determined. This process is called the normalization of the eigenvectors. The normalization process can be performed by normalizing conditions such as

$$L^* L = G \tag{3-26}$$

An entirely equivalent way to normalize the eigenvectors is by making use of the relationship[119,120]

$$L^* F L = \Lambda \tag{3-27}$$

From the normalized eigenvectors one would be able to infer which internal coordinate predominates in the normal vibration under study;if one of the l_{ij} values is relatively large compared with the others,the normal vibration is said to be mainly due to the vibration caused by the change of this coordinate. However,sometimes the eigenvectors do not provide a sure guide in the assignment of the bands. Morino and Kuchitsu[121] have proposed that the potential energy distribution for each normal mode Q_N is given by the expresion

$$V(Q_N) = \tfrac{1}{2} Q_N^2 \sum F_{ij} l_{iN} l_{jN} \tag{3-28}$$

In this way the $F_{ii}l^2_{iN}$ terms are greater than those where $i \neq j$ and therefore contribute more strongly to the potential energy distribution. If any $F_{ii}l^2_{iN}$ is large compared with the others,the vibration is assigned to that particular mode associated with that internal coordinate.

A more convenient way to express the potential energy distribution is to calculate the percentage of contribution of each mode to the vibration. The potential energy distribution % is given by

$$\frac{F_{ii}\, l^2_{iN}}{\sum F_{ii}l^2_{iN}} \times 100 \qquad (3\text{-}29)$$

for each coordinate.

3.7 The Method of Calculation

The calculations were performed with programs written at Simon Fraser University with the valuable cooperation of the staff of the computer center,whose assistance is acknowledged with thanks. The program was set up in symmetry coordinates,therefore the basic input of the program were the U and G matrix elements which were created separately.

In this way the F matrix was formed internally after the set of force constants was read in. The secular equations were separately solved according with the symmetry of the normal mode involved in the molecular point group to which the molecule under study belonged. The unnormalized eigenvectors were calculated with the same subroutine.

The normalization of the eingenvectors was made by using the relationship (3-26) and checked with the relationship (3-27). The potential energy distribution for each normal mode was calculated by using relationships (3-28) and (3-29).

The fit of the calculated frequencies was made by an iterative procedure. In a latter stage of these calculations the program devised by Schachtschneider[122] was available. The results for InI_4^- obtained with this program agree well with those obtained with the program used in this work.

3.8 The Indium Halide Complexes

In chapter II it was pointed out that one of the interesting features of the chemistry of the coordination compounds of indium is that three,four,five and six coordinate complexes can be prepared even with the same ligand. Slight changes in experimental conditions bring about changes in the coordination number;for example both four and five coordinate chloride species are stabilized by tetraethylammonium cation,depending on the solvent from which the complex is recrystallized[86].

A discussion of these phenomena is hampered both by the lack of a reliable model of the bonding involved and by the absence of appropriate energetic data,in particular bond strengths.

As part of this thesis,we carried out normal coordinate analysis for all those anionic indium(III) halide complexes for which complete vibrational spectra are available,as well as for the indium(I) halide complexes prepared and reported in chapter II.

The calculations were based on a simplified general quadratic valence force field (SGQVFF) which has generally accepted as a good approximation for expressing the potential energy of small molecules. Force field models do not lead to a unique expression of the potential energy,but this approximation does allow meaningful comparison to be made with previous results on isostructural molecules. In all cases Wilson's F and G matrix method was used.

3.9 Results

(a) The Trihalogenoindate(I) Anions

The vibrational spectra of $InX_3{}^{2-}$ anions (X = Cl,Br,I) have been shown in chapter II to be consistent with a C_{3v} molecular symmetry. The Raman spectra of these anions are given in table 7.

For a C_{3v} molecule of the type MX_3,group theoretical methods predict six genuine vibrational modes: $2A_1 + 2E$, all of which are infrared and Raman active . The A_1 modes correspond to the symmetric M-X stretching mode and the symmetric X-M-X bending mode,whereas the E modes correspond to the corresponding antisymmetric modes.

The internal coordinates,shown in figure 1,were taken as the changes in the bond lengths and bond angles. The symmetry coordinates were generated as described (see section 3.4). The symmetry coordinates are listed in table 13.

TABLE 13

Normalized symmetry coordinates for InX_3^{2-} anions in C_{3v} molecular symmetry

$S_1(A_1) = \sqrt{3}(\Delta r_1 + \Delta r_2 + \Delta r_3)$

$S_2(A_1) = \sqrt{3}(\Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{31})$

$S_{3_a}(E) = \sqrt{6}(2\Delta r_1 - \Delta r_2 - \Delta r_3)$

$S_{3_b}(E) = \sqrt{2}(\Delta r_2 - \Delta r_3)$

$S_{4_a}(E) = \sqrt{6}(2\Delta\alpha_{12} - \Delta\alpha_{23} - \Delta\alpha_{31})$

$S_{4_b}(E) = \sqrt{2}(\Delta\alpha_{23} - \Delta\alpha_{31})$

The potential function for the InX_3^{2-} anions has the form

$$2V = 3f_r(\Delta r)^2 + 3r^2 f_\alpha(\Delta\alpha)^2 + 6f_{rr}(\Delta r_i)(\Delta r_j) + \\ + 12rf_{r\alpha}(\Delta r)(\Delta\alpha) + 6r^2 f_{\alpha\alpha}(\Delta\alpha_i)(\Delta\alpha_j) \tag{3-30}$$

where the definition of the f interaction constants are as follows:

r equilibrium In-X bond length

f_{rr} bond with a bond at angle α to it

$f_{r\alpha}$ angle with one bond forming its sides

$f_{\alpha\alpha}$ angle with an angle adjacent

and f_r and f_α are the main stretching and bending force constants respectively.

From equation (3-30) it is clear that the number of force constants to be calculated is greater than the number of frequencies available. Following Donaldson et al[123],the approximation $f_{r\alpha} = f_\alpha$ was used. This reduces the number of constants from five to four,i.e.,to the number of observed frequencies.

Values of bond lengths and bond angles are not available for these species,so that in constructing the G matrix elements, the bond angles found for the isoelectronic SbX_3 species[124] and bond lengths from reference 125 were taken. Table 14 lists the G-matrix elements for the trihalogenoindate(I) anions and the structural parameters used in their construction.

Table 15 lists the derived force constants,the observed and calculated frequencies.

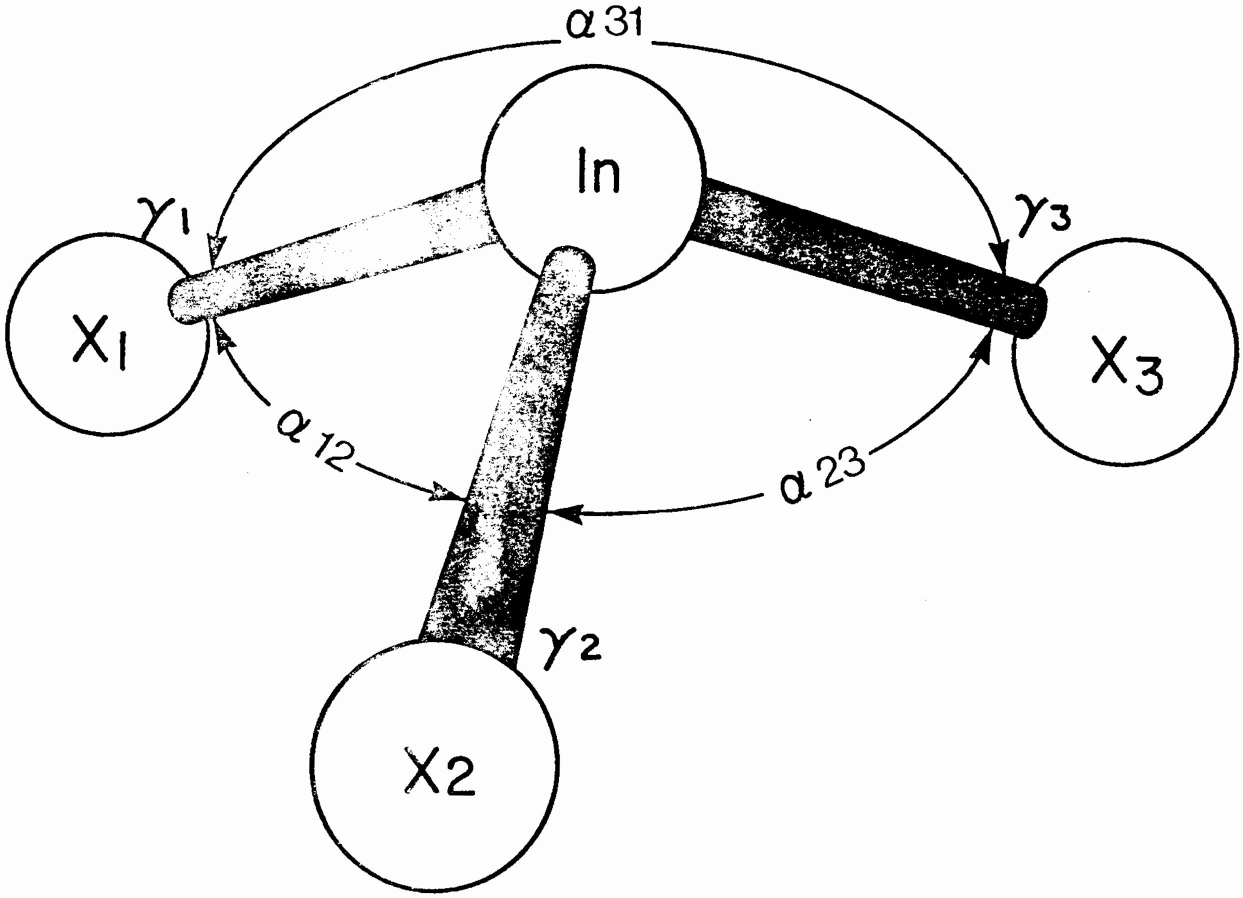


Figure 1. The internal coordinates for the $InX_3{}^{2-}$ species

TABLE 14

The G-matrix elements for the $InX_3{}^{2-}$ anions$^{(a)}$

Species	r(Å)	α (deg)	G_{11}	G_{12}	G_{22}	G_{33}	G_{34}	G_{44}
$InCl_3{}^{2-}$	2.42	99	0.03418	-0.00579	0.01344	0.03827	0.00487	0.01288
$InBr_3{}^{2-}$	2.54	97	0.01909	-0.00586	0.00855	0.02228	0.00434	0.00608
$InI_3{}^{2-}$	2.86	99	0.01386	-0.00489	0.00558	0.01794	0.00412	0.00379

(a) $G_{ij} = G_{ji}$

TABLE 15

Force constants (10^{-5} dynes cm^{-1}) and calculated and observed frequencies (in cm^{-1}) for $InX_3{}^{2-}$ species

Species	f_r	f_{rr}	$f_{r\alpha}$	f_α	$f_{\alpha\alpha}$	ν_1	ν_2	ν_3	ν_4	
$InCl_3{}^{2-}$	0.760	0.205	0.101	0.101	0.006	251	103	185	98	calc.
						252	102	185	97	observ.
$InBr_3{}^{2-}$	0.750	0.160	0.050	0.050	0.012	177	73	145	45	calc.
						177	74	149	46	observ.
$InI_3{}^{2-}$	0.625	0.170	0.071	0.071	0.026	137	80	108	40	calc.
						136	78	110	40	Observ.

Analysis of the potential energy distribution (see table 16) leads to the conclusion that the vibrations are fairly pure, although the coupling of the eigenvectors S_1 and S_2 in ν_1 becomes more important going from the chloride to the iodide. While in $InCl_3^{2-}$ ν_1 is a 100 % S_1, $InBr_3^{2-}$ contains 3 % S_2 and InI_3^{2-} 10 % S_2. The reverse is observed in the other A_1 mode; there is a decreasing of the coupling of the eigenvectors going from the chloride to iodide in which the vibration is almost 100 % S_2.

The E modes are less coupled. In InI_3^{2-}, ν_3 contains only 3 % of S_4 whereas for the chloride and bromide, ν_3 is almost 100 % S_3. For $InCl_3^{2-}$, ν_4 contains about 17 % of S_3 compared with a 5 % in $InBr_3^{2-}$ and 12 % in InI_3^{2-}.

The small coupling of the normal modes is also reflected in the potential energy distribution among force constants. In $InCl_3^{2-}$, ν_1 contains no important contribution of any bending or bending-stretching interaction constant, whereas the same vibration shows the presence of a 16 % of $f_{r\alpha}$ in $InBr_3^{2-}$ and a 20 % in InI_3^{2-}. The vibration ν_2 contains about 10 % of f_r in $InCl_3^{2-}$ and no contribution to the same vibration in $InBr_3^{2-}$ and InI_3^{2-} in keeping with the observation that the coupling of the eigenvectors decreases going from the chloride to the iodide.

On the other hand, ν_3 is a pure stretching mode as no

TABLE 16

Potential energy distribution for $InX_3{}^{2-}$ anions

		Eigenvectors % S_i	Force Constant % f
$InCl_3{}^{2-}$	ν_1	100% S_1	$65\% f_r + 35\% f_{rr}$
	ν_2	23% S_1 + 77% S_2	$10\% f_r + 32\% f_{r\alpha} + 47\% f_\alpha$
	ν_3	100% S_3	$77\% f_r + 21\% f_{rr}$
	ν_4	17% S_3 + 83% S_4	$16\% f_r + 55\% f_\alpha$
$InBr_3{}^{2-}$	ν_1	97% S_1 + 3% S_2	$61\% f_r + 26\% f_{rr} + 11\% f_{r\alpha}$
	ν_2	4% S_1 + 96% S_2	$12\% f_r + 58\% f_\alpha + 28\% f_{\alpha\alpha}$
	ν_3	99% S_3	$78\% f_r + 17\% f_{rr}$
	ν_4	5% S_3 + 95% S_4	$70\% f_\alpha + 17\% f_{\alpha\alpha}$
$InI_3{}^{2-}$	ν_1	90% S_1 + 10% S_2	$47\% f_r + 25\% f_{rr} + 20\% f_{r\alpha}$
	ν_2	99% S_2	$11\% f_{r\alpha} + 81\% f_\alpha$
	ν_3	97% S_3 + 3% S_4	$70\% f_r + 19\% f_{rr}$
	ν_4	12% S_3 + 88% S_4	$13\% f_{r\alpha} + 57\% f_\alpha + 21\% f_{\alpha\alpha}$

contribution of any force constant, but f_r and f_{rr} appear in all three cases. Again, the potential energy distribution for ν_4 seems to follow no simple relationship.

(b) The Tetrahalogenoindate(III) Anions

A number of salts containing the tetrahalogenoindate(III) anions (X = Cl, Br or I) have been prepared[68,86]. The infrared and Raman results on the crystalline solids are in good agreement with the Raman spectra reported by Woodward and his coworkers[92-94] for extract solutions of these species. The solution spectra were assigned on the assumption of T_d symmetry, with four fundamental vibrations (A_1 + E + $2F_2$); some splitting of the F modes in the solid state has been observed.

The tetrahedral symmetry has been confirmed by X-ray crystallographic methods for $InCl_4^-$ [69] and more recently, for InI_4^- [70], both in simple salts and in the ionic dimer $[InI_2(dmso)_4][InI_4]$[56]. The spectral data used in the calculation of the force constants for these species are those reported by Woodward et al[92-94], for the solution species.

The internal coordinates for the tetrahedral InX_4^- anions are shown in figure 2; they are the changes in bond lengths and angles. The normalized symmetry coordinates are listed in table 17.

The symmetry coordinate $S_{1_b}(A_1)$ was taken as redundant, since all six angles cannot change simultaneously during the

TABLE 17

Normalized symmetry coordinates for the InX_4^- species

$$S_1(A_1) = \tfrac{1}{2}(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4)$$

$$S^{*}_{1_b}(A_1) = \surd 6(\Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{31} + \Delta\alpha_{14} + \Delta\alpha_{24} + + \Delta\alpha_{34})$$

$$S_{2_a}(E) = \surd 12(2\Delta\alpha_{12} - \Delta\alpha_{23} - \Delta\alpha_{31} - \Delta\alpha_{14} - \Delta\alpha_{24} + +2\Delta\alpha_{34})$$

$$S_{2_b}(E) = \tfrac{1}{2}(\Delta\alpha_{14} - \Delta\alpha_{31} + \Delta\alpha_{23} - \Delta\alpha_{24})$$

$$S_{3_a}(F_2) = \surd 12(2\Delta\alpha_{12} - \Delta\alpha_{23} - \Delta\alpha_{31} + \Delta\alpha_{14} + \Delta\alpha_{24} - -2\Delta\alpha_{34})$$

$$S_{3_b}(F_2) = \surd 6(\Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{31} - \Delta\alpha_{14} - \Delta\alpha_{24} - -\Delta\alpha_{34})$$

$$S_{3_c}(F_2) = \tfrac{1}{2}(\Delta\alpha_{23} - \Delta\alpha_{31} - \Delta\alpha_{14} + \Delta\alpha_{24})$$

$$S_{4_a}(F_2) = \surd 6(\Delta r_1 + \Delta r_2 - 2\Delta r_3)$$

$$S_{4_b}(F_2) = \surd 12(\Delta r_1 + \Delta r_2 + \Delta r_3 - 3\Delta r_4)$$

$$S_{4_c}(F_2) = \surd 2(\Delta r_2 - \Delta r_1)$$

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* redundant coordinate

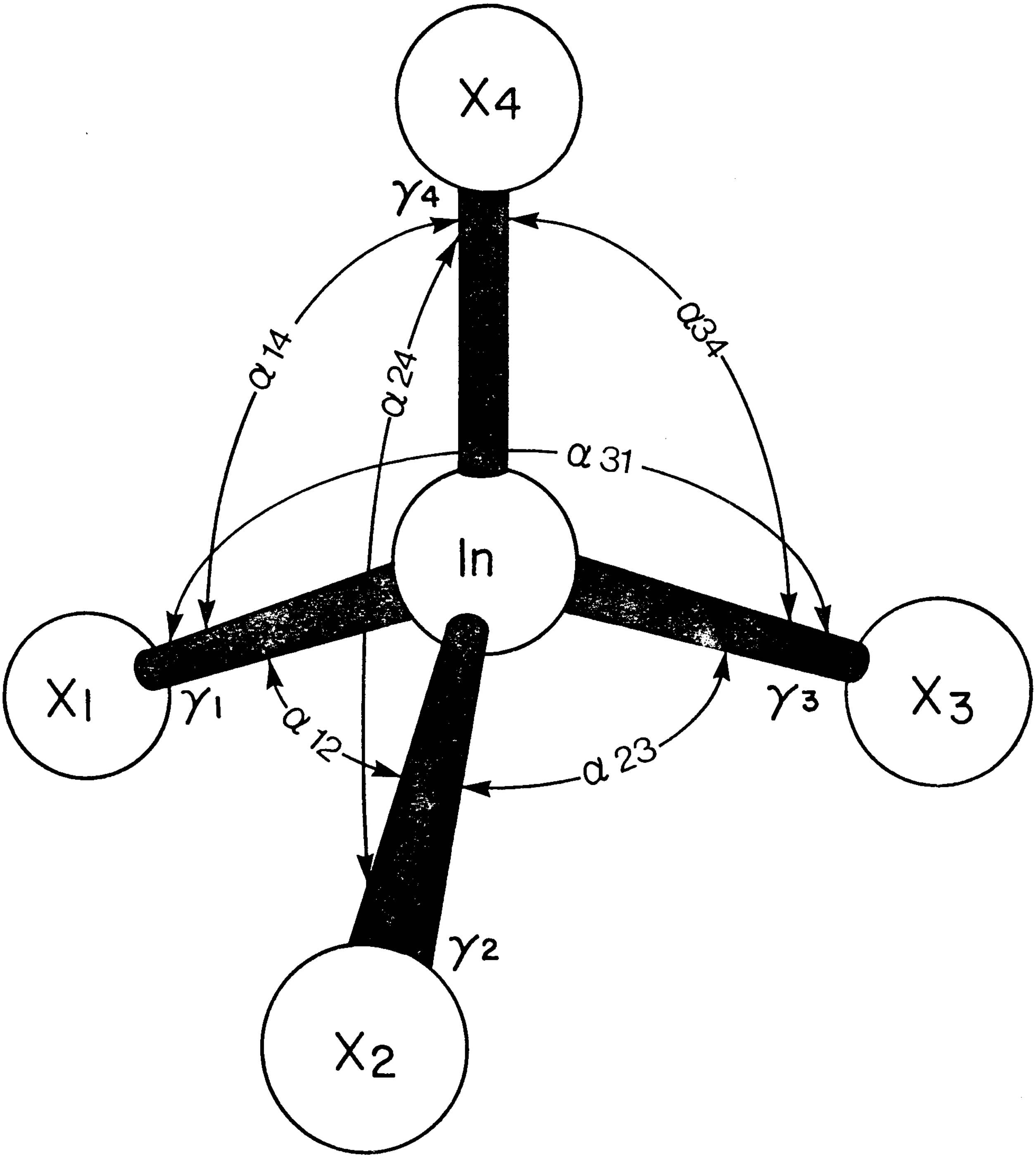


Figure 2. Internal coordinates for the InX_4^- species

the vibration.

Following the usual practice,the force constants associated with stretching-bending interaction and bending-bending interaction were assumed to be zero when no common bond is involved. The potential function for the InX_4^- tetrahedral species has the form

$$2V = 4f_r(\Delta r_i)^2 + 6r^2 f_\alpha(\Delta\alpha)^2 + 12f_{rr}(\Delta r_i)(\Delta r_j) + $$

$$+ 24rf_{r\alpha}(\Delta r)(\Delta\alpha) + 12r^2 f_{\alpha\alpha}(\Delta\alpha_i)(\Delta\alpha_j)$$

The term $f_{r\alpha}$ refers to the interaction involving one bond and the angle;all the other terms have their usual meaning.

Examination of the potential function reveals that the number of force constants to be calculated is again greater than the number of frequencies available. As in the case of the normal coordinate treatment for InX_3^{2-} species,the approximation $f_{r\alpha} = f_\alpha$ was used.

Table 18 gives the bond lengths and the G-matrix elements for the InX_4^- (X = Cl,Br or I) species.

Table 19 shows the derived force constants and the calculated and observed frequencies for these tetrahedral anions.

Woodward et al [92-94] used an approximate method to obtain values of 2.16, 1.83 and 1.44 x 10^{-5} dynes cm^{-1} for the primary stretching force constants for $InCl_4^-$, $InBr_4^-$ and InI_4^- respectively. These values differ considerably from those

TABLE 18

Structural parameters and G-matrix elements for InX_4^- species

Species[(a)]	r(Å)	G_{11}	G_{22}	G_{33}	G_{34}[(b)]	G_{44}
$InCl_4^-$	2.33	0.02820	0.01558	0.03981	-0.00996	0.01894
$InBr_4^-$	2.47	0.01251	0.00615	0.02412	-0.00940	0.01171
InI_4^-	2.70	0.00787	0.00324	0.01949	-0.00860	0.00853

(a) All angles were tetrahedral

(b) $G_{34} = G_{43}$

TABLE 19

Force constants (10^{-5} dynes cm^{-1}) and calculated and observed frequencies (in cm^{-1}) for the InX_4^- anions

Species	f_r	f_{rr}	$f_{r\alpha}$	f_α	$f_{\alpha\alpha}$	ν_1	ν_2	ν_3	ν_4	
$InCl_4^-$	1.865	0.095	0.086	0.086	0.015	321	89	336	112	calc.
						321	89	337	112	observ.
$InBr_4^-$	1.598	0.067	0.076	0.076	0.013	196	56	239	79	calc.
						197	55	239	79	observ.
InI_4^-	1.199	0.079	0.058	0.058	0.007	139	42	183	58	calc.
						139	42	185	58	observ.

calculated in the present work, mainly because the authors assumed that all other force constants would be neglected. More recently, Muller and Krebs also calculated force constants for these species, using a modified force field and assuming that $F_{34} = 0$ which leads to the conclusion that $f_{r\alpha}$ is zero[126]. Their values for the primary stretching force constants are about 0.1 - 0.2 units lower than those given in table 19, but the agreement between the two calculations for the bending forces is reasonably good, with differences of less than 0.05 units.

In related work based on a general valence force field model, Krebs et al[127] obtained the primary stretching force constants for the InX_4^- anions, but did not calculate any bending force constants. These calculations gave values close to, but still different from those in table 19. It is worth noting that Krebs et al only obtained the difference $f_\alpha - f_{\alpha\alpha}$ for the bending interaction, with values of 0.7, 0.6 and 0.5 x 10^{-5} dynes cm^{-1} for the chloride, bromide and iodide respectively, surprisingly similar to those which can be derived from the present work.

Table 20 gives the potential energy distribution for the InX_4^- species, interms of the eigenvectors and force constants.

The calculated eigenvectors and potential energy distribution for the F_2 vibrational modes show that the eigen-

TABLE 20

Potential energy distribution for the normal vibrations of InX_4^- species

		Eigenvectors % S_i	Force Constant % f
$InCl_4^-$	ν_1	100% S_1	$87\% f_r + 13\% f_{rr}$
	ν_2	100% S_2	$74\% f_\alpha + 26\% f_{\alpha\alpha}$
	ν_3	99% S_3	$89\% f_r$
	ν_4	4% S_3 + 96% S_4	$90\% f_\alpha$
$InBr_4^-$	ν_1	100% S_1	$89\% f_r + 11\% f_{rr}$
	ν_2	100% S_2	$75\% f_\alpha + 25\% f_{\alpha\alpha}$
	ν_3	96% S_3 + 4% S_4	$84\% f_r + 10\% f_{r\alpha}$
	ν_4	2% S_3 + 98% S_4	$91\% f_\alpha$
InI_4^-	ν_1	100% S_1	$83\% f_r + 17\% f_{rr}$
	ν_2	100% S_2	$81\% f_\alpha + 19\% f_{\alpha\alpha}$
	ν_3	93% S_3 + 7% S_4	$78\% f_r + 12\% f_{r\alpha}$
	ν_4	100% S_4	$96\% f_\alpha$

vectors S_3 and S_4 undergo slight increased coupling along the series $InCl_4^-$,$InBr_4^-$ and InI_4^-; ν_3 contains less than 0.5% of S_4 in $InCl_4^-$,4% in the bromide and 7% in the iodide. The opposite situation is found for ν_4,where S_3 is present to about 4% in the chloride and 2% in the bromide,whereas in InI_4^-,the vibration is 100% pure.

The increasing coupling in ν_3 is also reflected in the potential energy distribution among force constants. While in $InCl_4^-$,ν_3 is 89% f_r and the other force constants contributing very little,in $InBr_4^-$ there is an important contribution of the $f_{r\alpha}$ constant. InI_4^-,this force constant contributes 12%. On the other hand,ν_4 is increasingly more pure f_α,the primary bending force constant.

(c) The Pentachloroindate(III) Anion

Raman,polarized single-crystal Raman[98,99] and polarized far-infrared[99] spectra of the $InCl_5^{2-}$ anion have been reported. In the calculation carried out on this anion,the data reported by Adams and Smardzewski[99] were used.

The various internal coordinates are shown in figure 3 and are defined as follows: r_i ($i=1,2,3,4$) = $In\text{-}Cl_{basal}$, r_5 = $In\text{-}Cl_{axial}$, α_{ij} is the angle between bonds in the basal plane and β_{ij} the angle between the axial bond r_5 and any of the bonds in the basal plane.

In the calculation of the force constants,the potential

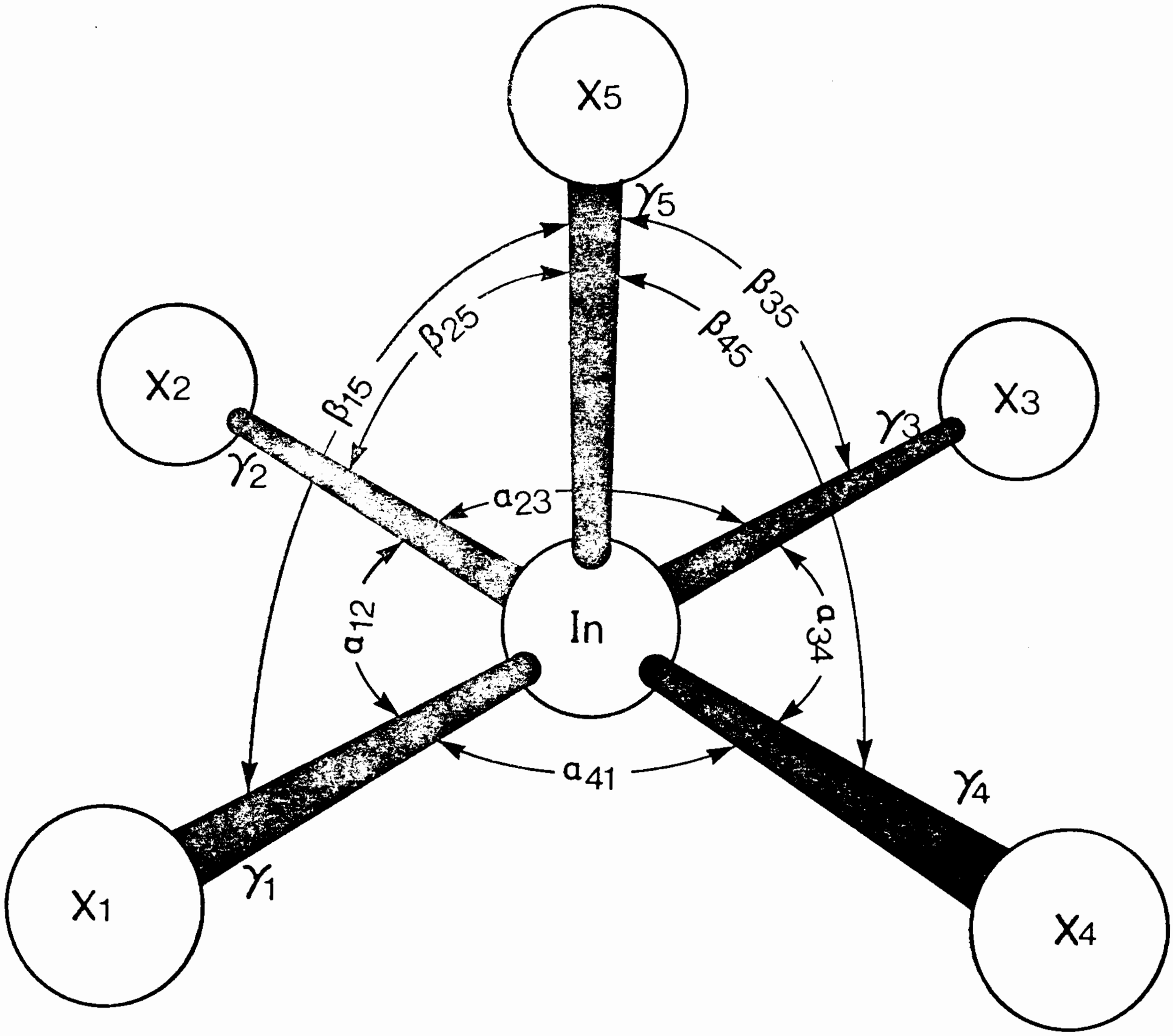


Figure 3. Internal coordinates for $InCl_5^{2-}$ anion

function for the C_{4v} $InCl_5{}^{2-}$ anion was

$$\begin{aligned} 2V \;=\; & f_R(\Delta r_5)^2 + 4f_r(\Delta r_i)^2 + 4r^2 f_\alpha(\Delta\alpha)^2 + \\ & + 8f_{rr}(\Delta r_i)(\Delta r_j) + 8f'_{rr}(\Delta r_i)(\Delta r_j) + \\ & + 8r^2 f_{\alpha\alpha}(\Delta\alpha_i)(\Delta\alpha_j) + 8r^2 f_{\beta\beta}(\Delta\beta_i)(\Delta\beta_j) + \\ & + 4r^2 f_\beta(\Delta\beta)^2 \qquad (3\text{-}32) \end{aligned}$$

where f_{rr} refers to the interaction force constant of two bonds in the basal plane having a common angle, f'_{rr}, accounts for the interaction between two bonds without a common angle. The symmetry coordinates listed by Begun et al[128] were used.

The potential function chosen leads to eight force constants to be calculated from nine fundamental frequencies. As the other force constants were assumed to be zero no cross term in the F matrix exists.

Single-crystal X-ray structure determination of $[Et_4N]_2[InCl_5]$ shows that the anion has a C_{4v} symmetry in this salt[71]. The unique apical In-Cl bond is slightly shorter (2.415 ± 0.012 Å) than the four basal bonds (2.456 ± 0.007 Å), and an average bond length of 2.45 Å was used in the calculation of the G-matrix elements. Table 21 shows the force constants derived for this anion; the observed and calculated

TABLE 21

Force constants (10^{-5} dynes cm^{-1}) and calculated and observed frequencies (in cm^{-1}) for $InCl_5^{2-}$ anion

Force Constant	Calc.Freq.	Obs.Freq.[a]	G-Matrix Elements
f_R = 1.378	293	294,$\nu_1(A_1)$	G_{11} = 0.03691
f_r = 1.305	283	283,$\nu_2(A_1)$	G_{22} = 0.03020
f_{rr} = 0.335	140	140,$\nu_3(A_1)$	G_{33} = 0.00544
f'_{rr} = -0.039	286	287,$\nu_4(B_1)$	G_{44} = 0.02820
f_α = 0.016	183	183,$\nu_5(B_1)$	G_{55} = 0.07718
$f_{\alpha\alpha}$ = -0.010	164	165,$\nu_6(B_2)$	G_{66} = 0.07463
f_β = 0.033	274	274,$\nu_7(E)$	G_{77} = 0.04560
$f_{\beta\beta}$ = 0.09	143	143,$\nu_8(E)$	G_{88} = 0.08247
	108	108,$\nu_9(E)$	G_{99} = 0.07281

(a) assignment from reference 99

frequencies and their assignment. The G-matrix elements are also given.

The potential energy distribution was not calculated on the basis of the eigenvectors as no off-diagonal terms in the GF matrix are present and therefore the vibrations are 100% pure. The potential energy distribution among force constants reveals that the assignment of Adams and Smardzewski is correct. Table 22 gives the potential energy distribution among force constants for $InCl_5^{2-}$ anion.

Examination of table 21 shows that f_R, the force constant for the $In\text{-}Cl_{axial}$ stretching mode is slightly greater than the corresponding force constant for the basal chlorides. This is in keeping with the fact that $InCl_5^{2-}$ is a very slightly distorted C_{4v} species in which the indium atom is slightly above the basal plane of the four chlorides.

(d) The Hexachloroindate(III) Anion

The vibrational spectrum of the $InCl_6^{3-}$ anion has been recorded for salts with both organic[86] and inorganic[95] cations. There is reasonable agreement between these two sets of results, leading to the assignment shown in table 23. No crystal structure determination has been reported, but the number and activity of the bands in the vibrational spectrum confirm the expected octahedral symmetry. An octahedral MX_6 molecule possesses three Raman-active vibrations ($A_{1g} + E_g + F_{2g}$),

TABLE 22

Potential energy distribution among force constant %
for $InCl_5^{2-}$ species$^{(a)}$

Frequency	Description	f_R	f_r	f_{rr}	f'_{rr}	f_α	$f_{\alpha\alpha}$	f_β	$f_{\beta\beta}$
ν_1	$\nu(In\text{-}Cl^a)$	100							
ν_2	$\nu_s(In\text{-}Cl_4)$		76	5	19				
ν_3	$\pi(In\text{-}Cl_4)$					20	26	42	11
ν_4	$\nu_a(In\text{-}Cl_4)$		76	4	20				
ν_5	$\pi(In\text{-}Cl_4)$							79	21
ν_6	$\delta(In\text{-}Cl_4)$					44	56		
ν_7	$\nu_a(In\text{-}Cl_4)$		80		20				
ν_8	$\pi(In\text{-}Cl^a)$							78	21
ν_9	$\delta_a(In\text{-}Cl_4)$					100			

(a) $In\text{-}Cl^a$ refers to vibrational modes involving the axial chloride.

two infrared-active vibrations ($2F_{1u}$) and one inactive (F_{2u}) mode.

The symmetry coordinates were constructed from the internal coordinates shown in figure 4,and are given in table 23.

The potential function has the form

$$2V = 6f_r(\Delta r)^2 + 12r^2 f_\alpha(\Delta\alpha)^2 + 24f_{rr}(\Delta r_i)(\Delta r_j) + \\ + 6f'_{rr}(\Delta r_i)(\Delta r_j) + 24rf_{r\alpha}(\Delta r)(\Delta\alpha) + \\ + 24r^2 f_{\alpha\alpha}(\Delta\alpha_i)(\Delta\alpha_j) \qquad (3\text{-}33)$$

where f'_{rr} refers to the interaction force constant of two mutually perpendicular bonds,and the other terms have the usual meaning. Like in the calculations performed for the trihalogenoindate(I) and tetrahalogenoindate(III) anions,the approximation $f_{r\alpha} = f_\alpha$ was used in order to reduce the number of force constants to be calculated.

Table 24 shows the derived force constants for $InCl_6{}^{3-}$, the calculated and observed frequencies,and the G-matrix elements constructed with an In-Cl bond length of 2.61 Å,based on the data for $[InCl_5(H_2O)]^{2-}$ [125].

Taking into account the change in the mass of the central atom and the oxidation state,the f_r force constant for

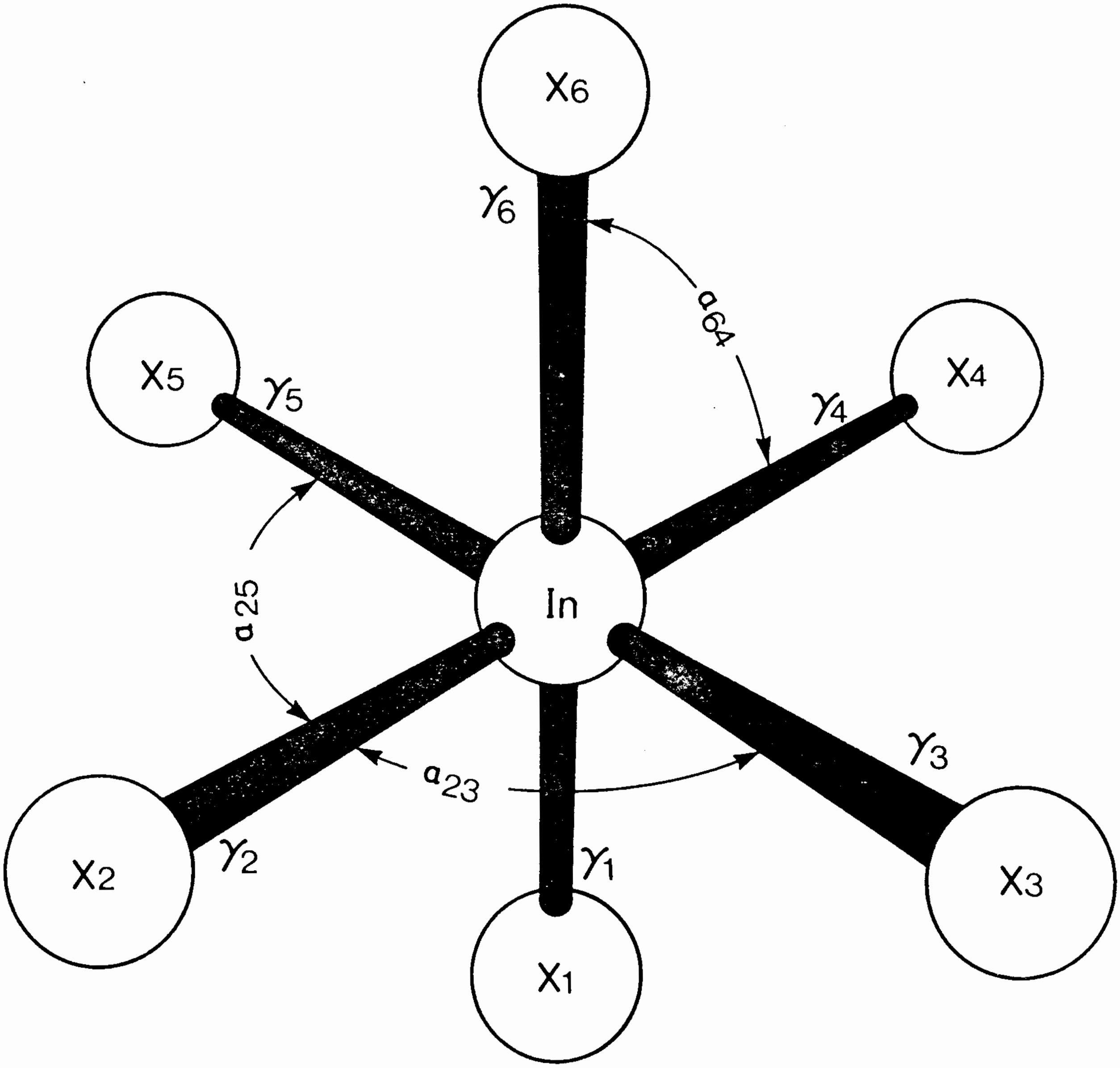


Figure 4. Internal coordinates for $InCl_6^{3-}$ anion

TABLE 23

Symmetry coordinates for $InCl_6^{3-}$ anion

$$S_{1_a}(A_{1_g}) = \sqrt{6}(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4 + \Delta r_5 + + \Delta r_6)$$

$$S^*_{1_b}(A_{1_g}) = \tfrac{1}{2}(\Delta\alpha_{56} + \Delta\alpha_{26} + \Delta\alpha_{13} + \Delta\alpha_{36})$$

$$S^*_{1_c}(A_{1_g}) = \tfrac{1}{2}(\Delta\alpha_{12} + \Delta\alpha_{26} + \Delta\alpha_{46} + \Delta\alpha_{14})$$

$$S^*_{1_d}(A_{1_g}) = \tfrac{1}{2}(\Delta\alpha_{43} + \Delta\alpha_{45} + \Delta\alpha_{25} + \Delta\alpha_{23})$$

$$S_{2_a}(E) = \sqrt{12}(\Delta r_1 + \Delta r_3 - 2\Delta r_2 - 2\Delta r_4 + \Delta r_5 + + \Delta r_6)$$

$$S_{2_b}(E) = \tfrac{1}{2}(\Delta r_1 + \Delta r_6 - \Delta r_2 - \Delta r_4)$$

$$S_{3_a}(F_{1_u}) = \sqrt{2}(\Delta r_6 - \Delta r_1)$$

$$S_{3_b}(F_{1_u}) = \sqrt{2}(\Delta r_2 - \Delta r_4)$$

$$S_{3_c}(F_{1_u}) = \sqrt{2}(\Delta r_5 - \Delta r_3)$$

$$S_{4_a}(F_{1_u}) = \sqrt{8}(\Delta\alpha_{46} + \Delta\alpha_{36} + \Delta\alpha_{26} + \Delta\alpha_{56} + \Delta\alpha_{14} - - \Delta\alpha_{13} - \Delta\alpha_{12} - \Delta\alpha_{15})$$

$$S_{4_b}(F_{1_u}) = \sqrt{8}(\Delta\alpha_{43} + \Delta\alpha_{45} + \Delta\alpha_{14} + \Delta\alpha_{46} - \Delta\alpha_{25} - - \Delta\alpha_{23} - \Delta\alpha_{12} - \Delta\alpha_{26})$$

$$S_{4_c}(F_{1_u}) = \sqrt{8}(\Delta\alpha_{36} + \Delta\alpha_{23} + \Delta\alpha_{13} + \Delta\alpha_{34} - \Delta\alpha_{56} - - \Delta\alpha_{25} - \Delta\alpha_{15} - \Delta\alpha_{45})$$

table 23 (continued)

$$S_{5_a}(F_{2_g}) = \tfrac{1}{2}(\Delta\alpha_{34} + \Delta\alpha_{25} - \Delta\alpha_{45} - \Delta\alpha_{23})$$

$$S_{5_b}(F_{2_g}) = \tfrac{1}{2}(\Delta\alpha_{36} + \Delta\alpha_{15} - \Delta\alpha_{56} - \Delta\alpha_{13})$$

$$S_{5_c}(F_{2_g}) = \tfrac{1}{2}(\Delta\alpha_{12} + \Delta\alpha_{46} - \Delta\alpha_{26} - \Delta\alpha_{14})$$

$$S_{6_a}(F_{2_u}) = \sqrt{8}(\Delta\alpha_{36} + \Delta\alpha_{56} + \Delta\alpha_{14} + \Delta\alpha_{12} - \Delta\alpha_{46} - - \Delta\alpha_{26} - \Delta\alpha_{13} - \Delta\alpha_{15})$$

$$S_{6_b}(F_{2_u}) = \sqrt{8}(\Delta\alpha_{56} + \Delta\alpha_{15} + \Delta\alpha_{23} + \Delta\alpha_{34} - \Delta\alpha_{36} - - \Delta\alpha_{13} - \Delta\alpha_{25} - \Delta\alpha_{45})$$

$$S_{6_c}(F_{2_u}) = \sqrt{8}(\Delta\alpha_{23} + \Delta\alpha_{25} + \Delta\alpha_{46} + \Delta\alpha_{14} - \Delta\alpha_{34} - - \Delta\alpha_{45} - \Delta\alpha_{26} - \Delta\alpha_{12})$$

* Redundant coordinates

$InCl_6^{3-}$ is in reasonable agreement with that reported by Wharf and Shriver[87] for the $SnCl_6^{2-}$ anion (1.435×10^{-5} dynes cm^{-}).

The eigenvectors and potential energy distribution for the F_{1u} vibrations show that ν_3 is quite pure, whereas ν_4 contains about 10% of S_3. For the other vibrational modes each eigenvector contributes 100%, since no off-diagonal element in the GF matrix exists.

The potential energy distribution among force constants for the $InCl_6^{3-}$ species is shown in table 25. The calculated eigenvectors for the F_{1u} modes are also given.

The assignment of the bands given in table 24 agrees well with the approximate description obtained from the potential energy distribution among force constants. The coupling of S_3 and S_4 eigenvectors in ν_4 is also reflected in the potential energy distribution among force constants since f_r contributes 9% to ν_4, but the vibration is still a fairly pure bending motion.

No salts of the corresponding InI_6^{3-} anion have been prepared, but the $InBr_6^{3-}$ complex anion has been identified in the crystalline lattice of $[MeNH_3]_4InBr_7$ and $[Me_2NH_2]_4InBr_7$, which have been shown to be the equimolar mixture of $4R_4N^+$ + $InBr_6^{3-}$ + Br^- [86]. The ν_3 and ν_4 absorption of this complex anion are at 179 and 170 cm^{-1} respectively, but unfortunately these results do not constitute a sufficient basis for calculation of the force constants for this species.

TABLE 24

Force constants (10^{-5} dynes cm^{-1}) and calculated and observed frequencies (in cm^{-1}) for $InCl_6^{3-}$

Force Constant	Calc.Freq.	Observ.Freq.	G-Matrix Element
$f_r = 0.949$	275	275, $\nu_1(A_{1g})$	$G_{11} = 0.02820$
$f_{rr} = 0.154$	245	245, $\nu_3(F_{1u})$	$G_{22} = 0.02820$
$f'_{rr} = 0.010$	176	175, $\nu_2(E_g)$	$G_{33} = 0.04561$
$f_{r\alpha} = 0.089$	151	150, $\nu_4(F_{1u})$	$G_{34} = -0.01334$
$f_\alpha = 0.089$	130	130, $\nu_5(F_{2g})$	$G_{44} = 0.01850$
$f_{\alpha\alpha} = 0.028$			$G_{55} = 0.01655$
			$G_{66} = 0.00827$

TABLE 25

Potential energy distribution among force constants % for $InCl_6^{3-}$

Frequency	Description	f_r	f_{rr}	f'_{rr}	$f_{r\alpha}$	f_α	$f_{\alpha\alpha}$
ν_1	ν(In-Cl)	60	39				
ν_2	ν(In-Cl)	75	24				
ν_3	ν(In-Cl)	89			7		
ν_4	δ(Cl-In-Cl)	9				48	30
ν_5	δ(Cl-In-Cl)					61	38

Eigenvectors for the F_{1u} modes

ν_3	97% S_3 + 3% S_4
ν_4	10% S_3 + 90% S_4

3.10 Discussion

The results of the force constants reveal some interesting relationships between these constants for the various indium complexes, and in some cases between the values for the complexes of indium and related compounds.

As noted in section 3.6, direct evidence on the type of bonding in anionic halide complexes of indium is lacking, but two nuclear quadrupole resonance (nqr) studies strongly imply that the bonding is in fact ionic in character. The nqr spectra (^{115}In and ^{31}Cl) of $InCl_5(H_2O)^{2-}$ species have been interpreted in terms of ionic In-Cl bonds[129], and similar studies[130] on SnX_6^{2-} anions (X = Cl, Br and I) lead to the conclusion that the percentage of ionic character varies from 60% in $SnCl_6^{2-}$ to 55% in SnI_6^{2-}, with a linear dependence on the difference in the electronegativities ($X_{hal} - X_{Sn}$). Finally, and of more immediate relevance, Wharf and Shriver[87] showed that calculations based on ionic models gave the correct ratio of stretching force constants for $SnCl_4$ and $SnCl_6^{2-}$. It therefore seems a reasonable working hypothesis that the bonding in the isoelectronic indium(III) halide is significantly ionic.

Considering the primary stretching force constants (f_r) for the tetrahalogenoindate(III) anions, it is seen that f_r decreases smoothly from $InCl_4^-$ to InI_4^-. It seems likely that these changes in f_r arise from concomitant (but not necessarily proportional) changes in bond strength and,in the light of the above discussion,changes in f_r might be related to changes in the electronegativity difference ΔX ($= X_{hal} - X_{In}$).

In fact,if one takes the Pauling electronegativities used in establishing the relationship between percentage of ionic character and ΔX in the nqr studies[129],f_r is linearly dependent on ΔX (= 1.38, 1.18 and 0.88 for Cl,Br and I, respectively). In order to put such a relationship in its proper context,it must be pointed out that with either Sanderson or Allred-Rochow values for ΔX,a plot of f_r against ΔX is markedly curved (and presumably this also applies to the nqr results).

The general conclusion,however,seems valid,namely,that with such ionic-bonded species the stretching force constant, and hence presumably the bond strength,depends on the electronegativity of the ligand.

Recent work[131] has shown that a similar relationship exists for the stretching modes of MCl_4 and MBr_4 molecules (M = C,Si,Ge and Sn). For these species,ν_1 and ν_3 are found to be dependent upon the ionic character of the M-X bond,but again the nature of the relationship depends on the set of electronegativity values used. There seems to be little profit in discussing the detailed nature of such dependences at this point.

Wharf and Shriver[87] noted an interesting effect of oxidation state in their work,which covered both tin(II) and tin(IV) halide complexes. They defined a parameter Ω = oxidation state/coordination number,and showed that Ω is proportional to f_r in tin-chloride complexes,in which the ratio of the stretching force constants for SnX_3^- to SnX_4 species varies from 0.48 to 0.59 with an average value of 0.54 which is in good agreement with the ratio $\Omega(SnX_3^-)/\Omega(SnX_4) = 0.67$. This relationship was tested for the compounds worked out in this thesis find that the ratio of the stretching force constants for pairs of InX_3^{2-} and InX_4^- anions varies from 0.41 to 0.52 with an average value of 0.46,which is somewhat closer to the ratio $\Omega(InX_3^{2-})/\Omega(InX_4^-) = 0.44$ that in the case for the analogous ratios for the tin complexes. Unfortunately the dependence of f_r on Ω does not hold within the indium(III) halide complexes in which the coordination number varies from four to six. The relevant values are

	Ω	$f_r \times 10^{-5}$ dynes cm^{-1}
$InCl_4^-$	0.75	1.865
$InCl_5^{2-}$	0.60	1.378 and 1.305
$InCl_6^{3-}$	0.50	0.949

Despite the absence of proportionality between Ω and f_r for these three species,a relative simple relationship does exist,as is shown by the plot of f_r against the coordination number (figure 5). Again it is difficult to place any detailed interpretation on these relationships,except that an ionic model would require a gradual weakening of bond with the increasing of the coordination number.

Figure 6 shows another relationship between the log of tne primary stretching force constants for the isoelectronic species InX_3^{2-}, SnX_3^- and SbX_3[132,133] and the oxidation state of the central element.

There is some uncertainty in the point for the $SbBr_3$, arising from the range of values reported[132] for f_r (1.338 - 1.686 x 10^{-5} dynes cm^{-1}). Relationships between stretching frequencies and oxidation state are well known[134],but figure 6 implies the existence of a more precise dependence than is usually acknowledged.

In summary,the primary stretching frequencies on the indium(I) and indium(III) anionic halide complexes depend on ligand electronegativity,coordination number and oxidation state of the metal in a manner which is qualitatively in keeping with a model of significantly ionic indium-halide bond,the details of which remain to be elucidated.

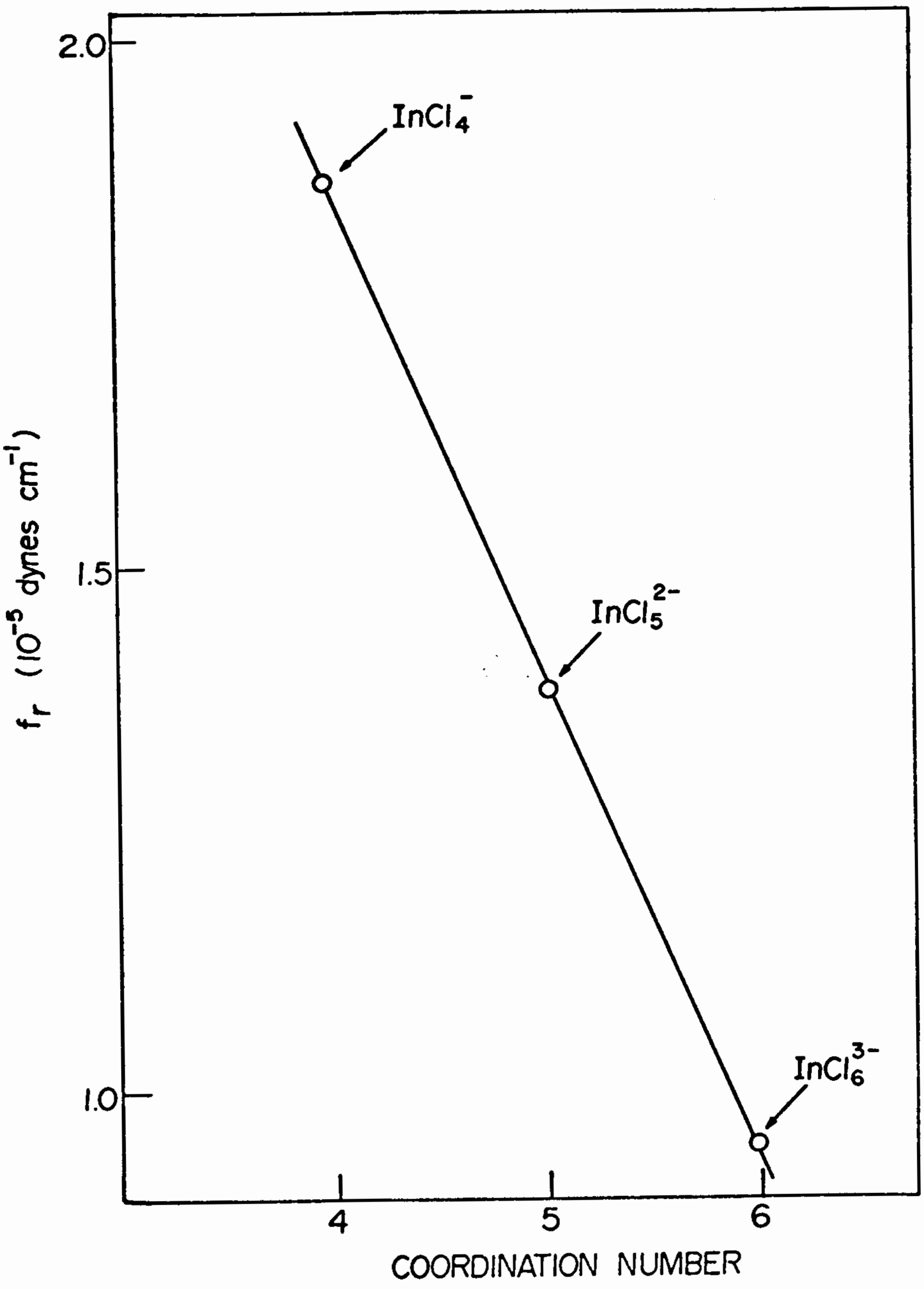


Figure 5. The dependence of the primary stretching force constant (f_r) on the coordination number in some halide complexes of indium(III)

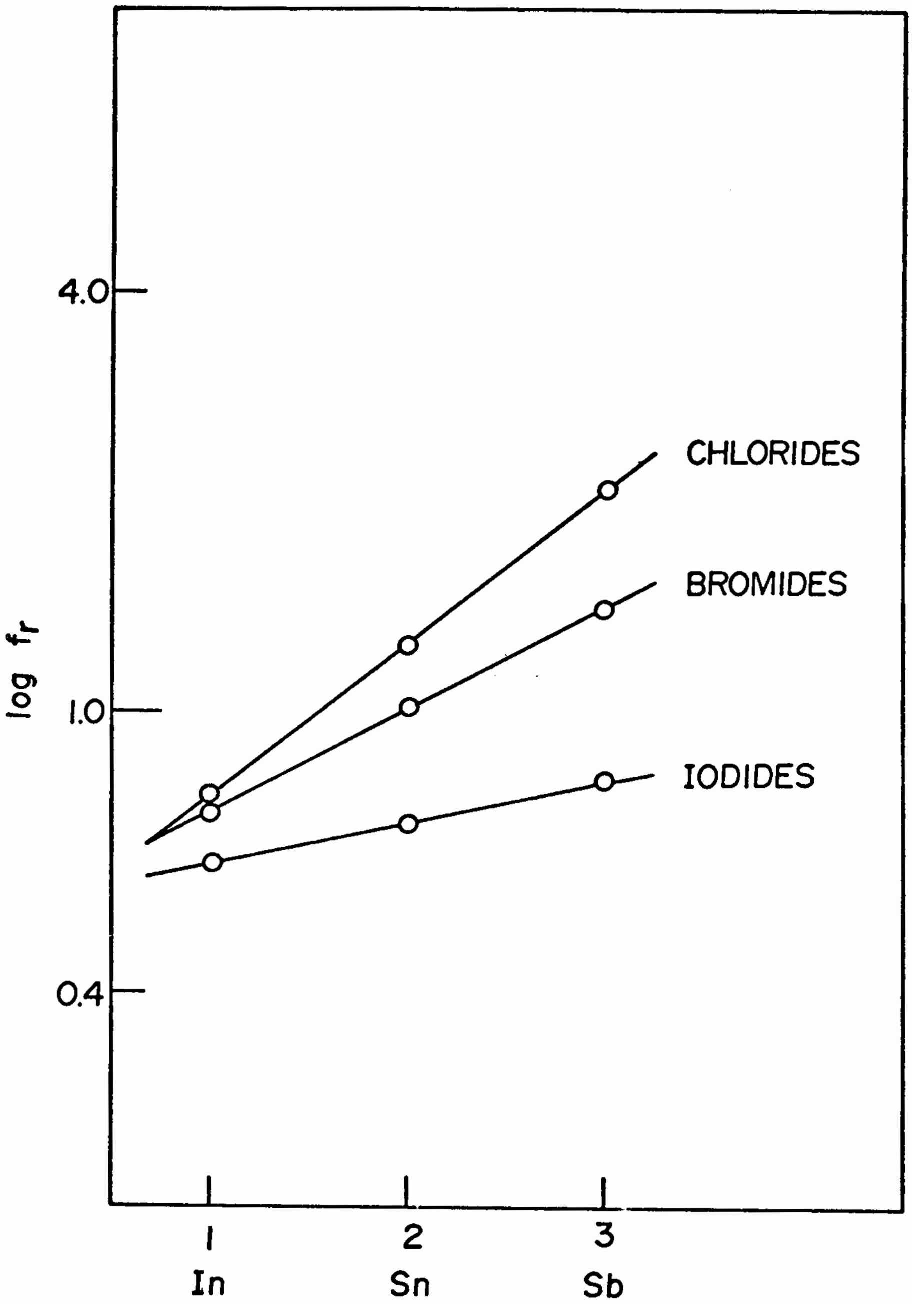


Figure 6. The dependence of log f_r on the oxidation state of the metal for MX_3 halides of some main group metals

CHAPTER IV

SOME REACTIONS OF CYCLOPENTADIENYLINDIUM(I)

4.1 Introduction

The chemistry of indium(I) has been less studied than of the more easily accessible (III) state and the number of compounds presently known is small (see chapter I), and little structural information is available.

Cyclopentadienylindium(I) was first prepared by Fischer and Hofmann[17]. This cyclopentadienyl compound is the only reasonable stable organo-indium(I) compound presently available, the corresponding methylcyclopentadienyl species being much more difficult to handle[18].

The bonding in this unusual "half sandwich" structure[135] has been the subject of a number of discussions[136-138]. Some authors have favoured ionic bonding[136,137], others covalent[138,139]. Cotton and Reynolds[137], who were the first to provide experimental evidence for the half sandwich structure of cyclopentadienylindium(I), critized the Fischer-Hofmann model because it would lack the symmetry demanded by the C_{5v} molecular symmetry and secondly because the calculated overlap integrals showed that the molecule must be ionic. Shibata et al[139] found that Cotton's first objection fails when the Fischer representation is viewed in terms of the resonance theory, whereas the second objection vanishes with the discovery that Cotton and Reynolds miscalculated both the sign and magnitude of the overlap integrals. In fact the molecule seems to be quite covalent, with the metal-ring bonding made up by the overlap of the π a_1 molecular orbital of the C_5H_5 ring and pure p metal orbitals. Shibata et al[139] have also pointed out that although the overlap of the π orbital with the indium sp hybrid orbitals is very large, the energy required for promotion of the 5s lone pair of electrons in bonding would be too large to pay for extensive hybridization. The centrally bonded ring structure has been confirmed in both solid[135] and gas[139] phases.

The trihalogenoindate(I) anionic complexes reported in chapters II and III are isoelectronic with the trigonal pyramidal SnX_3^- species. The donor interactions of these latter complexes with transition metal ions are well established[140]; adduct formation with boron trifluoride is apparently followed by ligand rearrangement reaction[141,142]. More recently it was found that dicyclopentadienyltin(II) also forms a 1:1 adduct with boron trifluoride[143].

Following the close analogy between indium(I) and tin(II) species it seemed worthwhile to study the donor properties of the indium(I) species reported in chapter II and the easily available cyclopentadienylindium(I).

4.2 Adducts of Cyclopentadienylindium(I) with Boron Trihalides and Trimethyl Boron

Cyclopentadienylindium(I) (CpIn) in chloroform reacts with gaseous BX_3 (X = F,Cl,Br or CH_3) to yield solids of stoichiometry $CpIn{\cdot}BX_3$,whose structures have been investigated by means of vibrational spectroscopy. Vibrational spectroscopy shows that the BX_3 group has the expected trigonal pyramidal structure similar to that found for some acetonitrile[141,142] and dicyclopentadienyltin(II) adducts[143]. On the other hand,the spectra also show that the cyclopentadienyl ring is in the monohapto (σ-bonded diene) form,in marked contrast to the stereochemistry of the parent CpIn.

In an attempt to obtain more information about the structure of the cyclopentadienyl ring the reaction of both CpIn and $CpIn{\cdot}BCl_3$ with maleic anhydride were carried out; Diels-Alder addition occurs in both cases,suggesting that an equilibrium between the pentahapto and monohapto forms of CpIn may exist in solution.

The interaction between cyclopentadienylindium(I) and the two Lewis acids chloroform and trifluoroiodomethane was also investigated,with the aim of determining the basicity of CpIn relative to other donors. Significantly, there appears to be no evidence of any such interaction, a point relevant to the energetics of the formation of the CpIn·BX_3 adducts.

4.3 Some Iodide Complexes of Cyclopentadienylindium(III)

In previous section it was found that the cyclopentadienyl ligand changes its bonding mode from the pentahapto form in CpIn to the monohapto form upon adduct formation with boron trihalides and boron trimethyl. It was also found that the pentahapto CpIn undergoes Diels-Alder addition with maleic anhydride. On the other hand, CpIn does not interact appreciably with weak Lewis acids such as chloroform and trifluoroiodomethane previously used to measure the basicity of other donor molecules[144-147]. The above results suggested that an equilibrium between the pentahapto and monohapto forms would exist in solution, which is readily displaced to the monohapto form as a function of the strength of the acceptor molecule. In an attempt to obtain more information about the suggested equilibrium and the mechanism by means the change in the bonding mode of the cyclopentadienyl ligand occurs, the interaction between CpIn and a moderate Lewis acid, namely, iodine was studied.

Cyclopentadienylindium(I) in chloroform reacts with iodine to yield the polymeric yellow solid $CpInI_2$, which is partially soluble in ether and light sensitive. The compound is stable for 3-4 days.

A number of rections of $CpInI_2$ with some nitrogen-donor ligands,triscylopentadienylindium(III) and tetra-propylammonium iodide,have been carried out.

The reaction of $CpInI_2$ in ether with 2,2'-bipyridyl and 1,10-phenanthroline yielded complexes of the type $CpInI_2L$ (L = bipy or phen),whereas with Cp_3In and Pr_4NI (Pr = propyl),the unstable Cp_2InI and the anionic species $[Pr_4N][CpInI_3]$ were obtained.

Vibrational spectra show that the cyclopentadienyl ring adopts the monohapto form in all these species.

The reaction of CpIn with methyliodide and trifluoroiodomethane yielded indium monoiodide,as did the reaction of CpIn with iodine in the presence of ethanol. A possible mechanism for these reactions is discussed.

4.4 Experimental

(a) Physical Measurements

Physical measurements were carried out using the procedures described in the previous chapters,with the following exceptions:

Nuclear Magnetic Resonance

^1H and ^{19}F nuclear magnetic resonance (nmr) spectra were recorded with a Varian A56/60 spectrometer,operating at frequencies of 60 and 56.4 MHz respectively.

Mass Spectra

Mass spectra were obtained with a Hitachi-Perkin Elmer RMU-6E operating in the single-focusing mode at an excitation potential of 80 eV.

Infrared Spectra

Infrared spectra were recorded with a Perkin Elmer 457 or a Beckman IR 12 spectrophotometers. Spectra were obtained with nujol and hexachlorobutadiene mulls using caesium iodide windows.

(b) Analytical Determinations

Analytical determinations were performed as described in chapter II. Boron analyses were carried out by a slight modification of the method described by Taylor[148].

(c) Solvents

The solvents were purified from moisture and impurities as described in chapter II.

Spectroscopic grade chloroform was washed twice with concentrate sulphuric acid and then washed twice with distilled water to remove any ethanol stabilizer. The chloroform was then allowed to stand overnight over anhydrous calcium sulphate and distilled prior to use from a fresh sample of calcium sulphate.

(d) Preparative Chemistry

The indium(I) compounds readily disproportionate in the air, and therefore all reactions and operations were performed under dry nitrogen using conventional dry-box techniques.

Cyclopentadienylindium(I) and cyclopentadienylindium (III) diodide are light sensitive and although their manipulations were carried out in normal light, over -exposure was avoided.

Preparation of Cyclopentadienylindium(I)

Freshly distilled cyclopentadiene was added to finely cut sodium (~ 3 g.) in dry ether and the mixture stirred at 0°C until all the sodium had reacted. The mixture was refluxed for one hour and then anhydrous indium trichloride (7.25 g.) in the ratio CpNa:$InCl_3$ = 4:1, was added to the resultant heavy white precipitate of CpNa. The reaction mixture turned yellow and reflux continued for four hours after which the ether was removed under vacuum and the cyclopentadienylindium(I) collected by sublimation at 150°C from the mixture. It was stored in the dark in a nitrogen-filled dry-box.

Preparation of Cyclopentadienylindium(I)-BX_3 Adducts

(X = F, Cl, Br or CH_3)

Cyclopentadienylindium(I) was dissolved in freshly distilled dry chloroform, and a small excess of boron trihalide condensed into the vessel in vacuo. The mixture was then allowed to warm up to room temperature, and stirred for approximately 30 minutes, after which the solvent and unreacted boron trihalide were removed by evaporation. The solid products, which were identified as the appropriate cyclopentadienylindium(I)-boron trihalide (or trimethylboron) adducts, were insoluble in all the common organic solvents, and sensitive to moisture; the ease of hydrolysis judged qualitatively, as $CpIn{\cdot}BBr_3 > CpIn{\cdot}BCl_3 > CpIn{\cdot}BMe_3 > CpIn{\cdot}BF_3$. Analytical and other results for these adducts are given in table 26.

Reaction of $Me_2bipyInX_3$ with Boron Trihalides

$Me_2bipyInX_3$ (X = Cl, Br or I) were treated in a similar manner with an excess of BF_3 or BCl_3. After removal of the excess of the boron trihalide by pumping, the initial indium(I) compound was recovered unchanged.

Reaction of Cyclopentadienylindium(I) with Maleic Anhydride

One mmole of maleic anhydride in freshly distilled chloroform was reacted with an equimolar quantity of CpIn in chloroform. The solution was stirred for 24 hours at room temperature in dry atmosphere. The yellow-brown solid was filtered off, washed with chloroform and dried.

The presence of chloroform in the solid was confirmed by infrared absorptions at 2400 m, 2260 s, 1485 s and 391 vw cm^{-1}. The stoichiometry $C_9H_7O_3In$ is that expected from a 1:1 Diels-Alder addition of CpIn and maleic anhydride.

TABLE 26

Analytical results for $CpIn\cdot BX_3$ and some maleic anhydride adducts

		Required %					Found %				
Compound	m.pt(°C)	C	H	In	B	X	C	H	In	B	X
$CpIn\cdot BF_3$	270 dec.			46.4	4.4				46.5	4.6	
$CpIn\cdot BCl_3$	190 dec.	20.2	1.7	38.6	3.7	35.8	19.9	1.7	38.6	3.7	35.2
$CpIn\cdot BBr_3$	286	13.9	1.6	26.7	2.6	55.7	12.3	1.1	26.5	2.6	55.4
$CpIn\cdot BMe_3$	164 dec.			48.7	4.7				48.3	4.8	
$CpIn\cdot C_4H_2O_3\cdot CHCl_3$	>300	30.1	2.0	28.5			30.2	2.0	29.0		
$CpIn\cdot BCl_3\cdot C_4H_2O_3$	>300	27.7	1.8	29.4	2.6	26.6	27.3	1.8	29.1	2.7	27.0

$C_4H_2O_3$ = Maleic anhydride

The compound is insoluble in all the common organic solvents.

Reaction of CpIn·BCl$_3$ with Maleic Anhydride

A suspension of CpIn·BCl$_3$ in a chloroform solution of the anhydride (1mmole of each reactant) was stirred at room temperature for 24 hours. The orange-red solid was filtered off,washed with chloroform and dried. The solid analyses for $C_9H_7O_3InBCl_3$,corresponding to the boron trichloride adduct of 7-indium(I)-bicyclo [2.2.1] hept-5-ene-1,2-dicarboxylic acid anhydride. The compound is insoluble in all common organic solvents,except ether.

Preparation of Cyclopentadienylindium(III) Diodide

Iodine (1mmole) in freshly distilled chloroform was added dropwise to a solution containing 1 mmole of CpIn in chloroform. A yellow precipitate inmediately formed;this was filtered off,washed with chloroform and dried. The solid is insoluble in all common organic solvents,but is partially soluble in ether. Analyses are shown in table 27.

Preparation of Cyclopentadienyl-2,2'-bipyridylindium(III) Diodide

1 mmole of 2,2'-bipyridyl dissolved in dry ether was added to a suspension of 1 mmole of CpInI$_2$. A yellow solid which precipitated was filtered off,washed with ether and dried. The solid is soluble in acetone,acetonitrile and nitromethane.

Preparation of Cyclopentadienyl-1,10-phenanthrolineindium(III) Diodide

1 mmole of 1,10-phenanthroline dissolved in dichloromethane was added to a suspension of 1 mmole of cyclopentadienylindium(III) diodide. The yellow precipitate was filtered off,washed with ether and dried. The solid is soluble in acetonitrile and nitromethane,and partially soluble in dichloromethane.

Preparation of Biscyclopentadienylindium(III) Iodide

Cyclopentadienylindium(III) diodide (1 mmole) was suspended in a solution prepared by dissolving triscyclopentadienylindium(III) in hot benzene. The suspension was refluxed for 10 hours. The brown solid was filtered off, washed with benzene and dried. Carbon and hydrogen analyses yielded constantly low values as the compound is rather unstable. However,indium and iodine analyses could be obtained with good results on sample weighed inmediately after preparation.

Preparation of Tetrapropylammonium Cyclopentadienylindiun(III) Triodide

1 mmole of tetrapropyl ammonium iodide dissolved in anhydrous methanol was added to a suspension of cyclopentadienylindium(III) diodide in ether. The resulting solution was stirred for 24 hours,and the solvent then removed. The

yellow solid is insoluble in most common solvents except nitrobenzene in which is partially soluble. This solvent was used in measuring the molar conductivity.

4.5 Results and Discussion

(a) Adducts of Cyclopentadienylindium(I) with Boron Trihalides and Trimethylboron

Vibrational Spectroscopy

The infrared spectra of the boron trihalides and trimethylboron adducts of CpIn were recorded in nujol and hexachlorobutadiene mulls. The assignment of the bands involved comparison with the bands reported for the boron trihalide adducts of acetonitrile[149,150],and for free trimethylboron[151]. Table 28 list the infrared bands of the boron trihalide and trimethylboron adducts of CpIn.

(i) The Boron Trihalide Moiety

The changes which take place in the vibrational spectra of BX_3 (X = F,Cl,Br or CH_3) species on complex formation,i.e., as the local molecular symmetry of BX_3 changes from D_{3h} to C_{3v},have been discussed in detail by a number of authors. Swanson and Shriver[149,150] have assigned the spectra of the boron trihalide adducts of acetonitrile and confirmed the assignment of the adducts by normal coordinate analysis. Such calculations are of considerable importance,in that the potential energy distribution allows

TABLE 27

Elemental analyses and molar conductivities for the CpIn derivatives

Compound	Found %					Required %					$\Lambda_M^{21^\circ C(a)}$
	C	H	N	In	I	C	H	N	In	I	($ohm^{-1}cm^2$)
$CpInI_2$	13.2	1.1		26.4	58.4	13.8	1.2		26.5	58.5	
$CpInI_2$·bipy	29.1	2.1	4.9	19.5	43.1	30.5	2.2	4.7	19.5	43.0	5.7
$CpInI_2$·phen	33.3	2.7	4.1	18.7	41.2	33.2	2.2	4.6	18.7	41.4	8.7
Cp_2InI				30.8	34.3				30.9	34.1	8.3
$CpInI_3$ C(b)	26.3	4.7	1.6	15.3	50.9	27.3	4.4	1.8	15.4	51.0	26.0(c)

(a)Molar Conductivities in acetonitrile. Concentration,ca.10^{-3} M.

(b) C = Tetrapropylammonium cation

(c) Molar conductivity in nitrobenzene. Concentration = 2.53 x 10^{-3} M.

the identification of those vibrations which are sufficiently pure for meaningful comparison to be made between different adducts. Table 29 lists the boron-halide vibrations in the $CpIn \cdot BX_3$ adducts, assigned by analogy with the work on the corresponding acetonitrile adducts. Because of the mixing which occurs in the B-X skeletal vibrations, no simple relationships relate the B-X frequencies to the strength of the B-N coordinate bond in a series of BF_3 adducts involving nitrogen donors[149]. Swanson and Shriver do however suggest that the frequency separation between ν_{as} and ν_s in such series decreases with the increasing basicity of the donor molecule. On this basis, the separation of approximately 310 cm^{-1} for the $CpIn \cdot BF_3$ adduct implies that CpIn is about as strong a donor to BF_3 as is acetonitrile. It does not seem possible to test this conclusion with the results for BCl_3 and BBr_3 because of the lack of suitable results for other donors; the difference $\nu_{as}-\nu_s$ in fact increases only slightly from $CpIn \cdot BF_3$ to $CpIn \cdot BCl_3$.

The spectrum of $CpIn \cdot BMe_3$ presents a more difficult problem, due to the lack of comparable information on the vibrational spectra of adducts of trimethylboron. Comparing the infrared spectra of $CpIn \cdot BX_3$ (X = F, Cl, Br) with that of $CpIn \cdot BMe_3$ one should be able to substract the cyclopentadienyl bands. After substraction of the cyclopentadienyl bands, those left were 1605 m, 1419 ms, 742 s, 410 w, 391 w, 307 mw

TABLE 28

Infrared spectra of the boron trihalide and trimethylboron adducts of CpIn (in cm^{-1})

$CpIn\cdot BF_3$	$CpIn\cdot BCl_3$	$CpIn\cdot BBr_3$	$CpIn\cdot BMe_3$
3042 w	3040 w	3035 w	3060 m
2958 m		2930 s	2925 m
2855 mw	2880 m,br	2870 s	2855 m
			1605 m
1578 vw	1565 m	1545 ms	1555 s
			1419 ms
1305 vw	1305 mw	1298 w	1305 w
1275 m	1263 mw	1252 s	1255 m
1212 vw	1198 mw	1135 s	1215 w
1101 s			
1065 s			
1009 s	1005 mw	1018 s	1005 s
	940 ms	935 m	
	911 ms		
	860 ms		888 m
808 m	807 ms		802 ms
776 mw			
758 w	760 mw	786 s,br	758 m
			742 s
721 ms	718 s	715 m	725 s
	692 m		
	675 m		
620 mw			

Table 28 (continued)

		580 m	
521 ms			
515 ms	515 m	515 m	
478 m,br	495 m	480 w	
		431 s	
			410 w
			391 w
	375 w		
		355 s	
			307 mw
285 w	285 m	285 w	282 ms
	260 s		

TABLE 29

Boron-halide vibrations in solid $CpIn\cdot BX_3$ adducts (in cm^{-1})

Vibration[(a)]	X = F	X = Cl	X = Br
$\nu_a(B-X)$	1101	692	580
	1065	675	
$\nu_s(B-X)$	776	375	431
$\delta_{as}(BX_3)$	521	260	355

(a) Approximate description

and 282 ms. Following Woodward et al[151], the bands at 742, 410, 391 and 307 cm^{-1} have been assigned to the antisymmetric and symmetric B-Me stretching modes and symmetric and antisymmetric BC_3 deformation modes, respectively. The frequency shifts with respect to the free BMe_3, are similar to those between BX_3 and $CpIn \cdot BX_3$.

In an attempt to obtain a better way to assign the bands due to the BMe_3 group in $CpIn \cdot BMe_3$, adducts with pyridine and its deutero derivative were prepared. Unfortunately their Raman and infrared spectra are too complicated to allow a sure assignment of the BMe_3 bands.

(ii) The B-In and In-C Vibrations

Each of the three boron trihalide adducts prepared has an infrared band at 515 cm^{-1}; in $CpIn.BMe_3$, this appears at 505 cm^{-1}. Since atomic mass of boron is not very different than that of the carbon atom, it is believed that this band is the stretching mode of the In-B coordinate bond; ν(In-C) for indium-carbon bonds involving simple alkyls groups have been found in the region of 500 cm^{-1} [27,81].

In Cp_3In and its adducts, ν(In-C) is at about 300 cm^{-1} and therefore the bands at 285 cm^{-1} in the $CpIn \cdot BX_3$ (X = F, Cl, Br) and at 282 cm^{-1} for $CpIn \cdot BMe_3$ adduct were assigned to this vibrational mode.

(iii) The Cyclopentadienyl-Indium Moiety

The identification of the bonding mode of the cyclopentadienyl ligand by means of vibrational spectroscopy has been the subject of a number of papers[152-154]. Three types of bonding modes of the cyclopentadienyl ring have been observed[152]: (a) ionic,(b) centrally bonded or pentahapto form and (c) the diene or monohapto form. The centrally bonded form possesses C_{5v} symmetry and the 27 fundamental vibrations are grouped in $4A_1 + A_2 + 5E_1 + 6E_2$. Due to the aromatic character of the C_5 ring,all the C-H stretching frequencies should lie above 3000 cm^{-1},whereas one of the two C-H out-of-plane deformation vibrations is expected to lie at 700 to 800 cm^{-1}. On the other hand, a monohapto form having a C_s symmetry (see figure 7),the vibrational modes are grouped in $15A' + 12A''$ and the aliphatic carbon frequency should lie between 2800 to 3000 cm^{-1}. The C_1-H out-of-plane deformation frequency should lie arround 700 cm^{-1}. This same vibration for C_2-H and C_3-H modes will also show up between 700-800 cm^{-1}.

The infrared spectrum[27] of CpIn shows bands at 3070 vw, 1430 w,br, 998 m, 765 s, 737 m and 720 ms cm^{-1}. This spectrum is that expected for a pentahapto (centrally bonded) structure,according to Fritz[152],and thus in agreement with the known structure[135,139] of CpIn. These results imply that

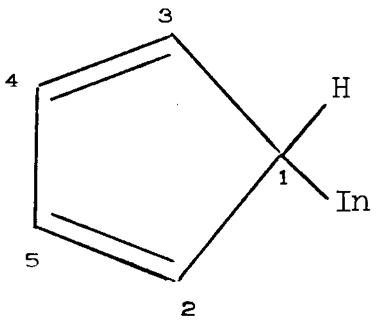


Figure 7. The monohapto form of cyclopentadienylindium(I)

the conclusion of Samuel and Bigorne[153,154] with respect to the ability of the out-of-plane deformation modes to infer the bonding mode of the cyclopentadienyl ring,vanishes,as CpIn shows three bands in the range 700-800 cm^{-1}.

More recently Mink et al[155] have shown that for Cp_2Hg a band at 2970 cm^{-1} is the fundamental C-H stretching of the "aliphatic" carbon in the monohapto form of this compound. Isotopic substitution showed that this band shifts to 2218 cm^{-1} and therefore cannot be a conbination band,since in that case it should be observed at 1518 + 1380 = 2898 cm^{-1}.

The spectrum of Cp_3In,on the other hand,is more complex, and in agreement with the σ-bonded diene (monohapto) structure for the ligand subsequently demonstrated by X-ray structure analysis[80].

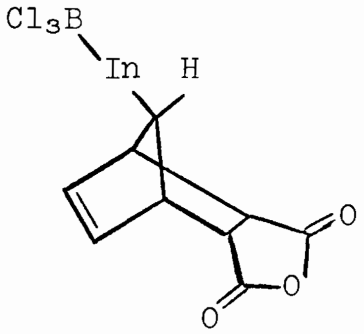
Those bands in the infrared spectra of the $CpIn{\cdot}BX_3$ (X = F,Cl,Br or Me) adducts attributed to the vibrations of the cyclopentadienyl ligand are listed in table 30.

These spectra are similar to those reported earlier[27] for Cp_3In and to the spectrum of Cp_2Hg[155,156], for which a σ-bonded diene structure is favoured. It is, therefore reasonable to conclude that the cyclopentadienyl group in $CpIn\cdot BX_3$ is in the monohapto form.

(iv) The Maleic Anhydride Adducts

Mink et al[155] have shown that biscyclopentadienylmercury undergoes Diels-Alder addition with both maleic anhydride and benzoquinone. In each case, the reaction involves addition of the dione across the diene system of each of the cyclopentadienyl rings, and it has been suggested that this reaction constitutes evidence for the diene structure of the ring.

Accordingly the reaction of maleic anhydride with $CpIn\cdot BCl_3$ was carried out. It was found that the reaction occurs easily to give product I identified analytically as the 1:1 Diels-Alder adduct presumably with the structure



I

TABLE 30

Vibrations of the cyclopentadienyl group in solid $CpIn \cdot BX_3$ adducts (frequencies in cm^{-1})

X = F	X = Cl	X = Br	$X = CH_3$
3042 w	3040 w	3035 w	3060 m
2958 m		2930 s	2925 m
2855 mw	2880 m,br	2870 s	2855 m
1578 vw	1565 m	1545 ms	1555 s
1305 vw	1305 mw	1297 w	1305 w
1275 m	1263 mw	1252 s	1255 m
1212 vw	1198 mw	1135 s	1215 w
1009 s	1005 mw	1018 s	1005 s
	940 ms	935 m	
	911 ms		
	860 m		888 m
808 m	807 ms		802 ms
758 w	760 mw	786 s,br	758 m
721 ms	718 s	715 m	725 s

The infrared spectrum (see table 31) has absorptions at 1775 and 1855 cm^{-1} due to the C=O stretching modes, ν(In-B) at 475, and bands at 762 + 425 and 325 cm^{-1} presumably due to the B-Cl stretching modes. It is interesting that the $CpIn{\cdot}BCl_3$ species is significantly stable, since the In-B bond is preserved throughout the Diels-Alder reaction of the ligand.

The diagnostic reliability of this reaction is however considerable lessened by the finding that maleic anhydride also reacts with cyclopentadienylindium(I) itself, again yielding a 1:1 adduct. The infrared spectrum of this substance (see table 31) is almost identical with that obtained from I as far as the vibrations of the organic groups are concerned.

The structure of this reaction product must remain a matter for speculation at present. Unfortunately, solubility problems prevented an investigation of the nuclear magnetic resonance spectra of either this substance or of the adduct I .

Irrespective of the details of the structure, it seems clear that in the indium case at least, reaction with maleic anhydride is not a satisfactory test of the presence of the diene form of cyclopentadienyl ligand. Since the activation energy for the Diels-Alder reaction of maleic anhydride and

TABLE 31

Infrared bands (in cm^{-1}) of the maleic anhydride adducts of CpIn and CpIn·BCl$_3$

$CpIn \cdot C_4H_2O_3$	$CpInBCl_3 \cdot C_4H_2O_3$
3060 w	3045 mw
2965 mw	2930 ms
2880 w	2880 ms
2400 m	
2260 s	
1855 ms	1855 ms
1778 s	1775 s
1660 ms	1662 ms
1631 ms	1631 s
1485 s	
1360 mw	1375 s,br
1305 mw	
	1262 m
1005 w	1002 w
970 ms	970 mw
940 s	930 ms
915 s	912 s
847 w	835 w
	762 s
722 mw	721 mw
675 w	675 w
665 mw	665 w
623 m	622 mw
	475 mw
	422 m
391 vw	325 w

cyclopentadiene is small, it is possible that the reaction with CpIn is evidence of an equilibrium in solution which normally lies strongly to the left. Such equilibrium would be

h^5-CpIn $\rightleftarrows$ h^1-CpIn

Mass Spectrometric Studies

The mass spectra of CpIn·BX_3 (X = F,Cl,Br or Me) showed no molecular ion. In each case, an intense peak was detected at m/e 115 due to indium. The mass spectra of these adducts are shown in tables 32 to 35.

The high temperature required to achieve sufficient vapor pressure for the halide species clearly causes profound molecular decomposition and ligand redistribution before ionization, since only in the case of the trimethylboron adduct is $CpIn^+$ detected in an appreciable intensity, whereas this ion is the principal mass peak in the spectrum of cyclopentadienylindium(I)[27].

The CpIn·BMe_3 compound apparently undergoes simple dissociation into its parent molecules on heating.

Discussion

The vibrational spectra of the CpIn·BX_3 (X = F,Cl,Br or Me) adducts leads to the formulation of these compounds on the basis of a monomer.

TABLE 32

The mass spectrum of CpIn·BF_3

(Spectrum normalized to base peak m/e 115 = 100%)

Excitation Voltage : 80 eV

Source Temperature : 160°C

m/e	Intensity %	Assignment
180	33	$CpIn^+$
159	15	?
136	41	InF_2^+
126	21	InB^+
115	100	In^+
82	24	CpB^+
74	11	
68	15	BF_3^+
65	25	Cp^+
49	22	BF_2^+
48	27	

TABLE 33

The mass spectrum of $CpIn \cdot BCl_3$

(Spectrum normalized to base peak m/e 115 = 100%)

Excitation Voltage : 80 eV

Source Temperature : 200°C

m/e	Intensity %	Assignment
180	10	$CpIn^+$
150	13	$InCl^+$
118	20	BCl_3^+
117	21	
116	25	
115	100	In^+
112	98	?
82	17	BCl_2^+
81	27	
65	22	Cp^+

TABLE 34

The mass spectrum of $CpIn \cdot BBr_3$

(Spectrum normalized to base peak m/e 275 = 100%)

Excitation Voltage : 80 eV

Source Temperature : 250°C

m/e	Intensity %	Assignment
277	48	$InBr_2^+$
275	100	
273	56	
205	27	$InBBr^+$
203	58	
201	28	
194	11	$InBr^+$
173	16	BBr_2^+
171	33	
139	48	?
137	48	
115	19	In^+
80	34	Br^+
79	22	

TABLE 35

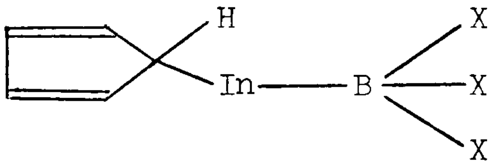
The mass spectrum of $CpIn \cdot BMe_3$

(Spectrum normalized to base peak m/e 115 = 100%)

Excitation Voltage : 80 eV

Source Temperature : 25°C

m/e	Intensity %	Assignment
180	99	$CpIn^+$
115	100	In^+
113	13	
66	21	Cp^+
65	22	
41	20	BMe_2^+



One obvious uncertainty is the magnitude of the C-In-B angle. It seems probable from the solubility behaviour of these substances that there are appreciable intermolecular interaction between the monomeric unit in the solid phase,probably due to dipole-dipole interaction. An alternative posibility is bonding from the cyclopentadienyl ring of one molecule to the indium of another;such a ring-metal interaction has been shown to play an important part in the structure of the benzene-$AlCl_3$ adduct and similar compounds[157].

The change in the mode of CpIn bonding on adduct formation is specially interesting .Cyclopentadienylindium(I) does not undergo an acid-base interaction with weak Lewis acids such as chloroform and trifluoroiodomethane,but does with stronger Lewis acids such as BX_3 (X = F,Cl,Br or Me).

Abel et al [144] have shown that the interaction between chloroform and electron pair donor molecules leads to significant changes in both,the ^1H-n.m.r. resonance and the C-H (or C-D) stretching frequency[145,146]. A solution of CpIn in chloroform had the solvent ^1H resonance at 436 Hz from TMS (c.f. 434 Hz for the pure solvent). Similarly, the C-D stretching frequency of a solution of CpIn in $CDCl_3$ was at 2262 cm^{-1},virtually unchanged from the frequency of pure $CDCl_3$. From these results,it can be concluded that CpIn is too weak a Lewis base to interact significantly with $CHCl_3$. Similar studies were carried out with solutions of CpIn and trifluoroiodomethane,which has also been used as a standdard Lewis acid in comparison of relative basicities of donor molecules[147]. An important complication in this work was the possible insertion reaction which eventually gives rise to indium monoiodide,but the use of freshly distilled CF_3I prevented this reaction from becoming significant within the time of the measurement. As in the work discussed above,it was found that the ^{19}F resonance of the pure CF_3I (-0.2421 KHz from external $CFCl_3$) and of the mixture (-0.2425 KHz) are the same within experimental error. In both cases then,CpIn is apparently too weak an electron pair donor to disturb significantly the electron density of the ground state of the acceptor molecules at the concentrations accessible.

Calculations on the energy levels in cyclopentadienyl have shown that the diene form is significantly higher in energy than the symmetrical ground state[158],and it is clear that h^1-CpIn must also lie some way above the h^5-CpIn ground state. At the same time,the structural evidence demonstrates that only in this higher energy structure can sufficient electron donation take place to yield stable adducts with BX_3. The total stabilization achieved in forming $CpIn{\cdot}BX_3$ compensates from the energy required to promote the cyclopentadienyl group into the diene form (and the BX_3 group into trigonal pyramidal symmetry). On the present evidence, CpIn can only act as an electron pair donor if the interaction is sufficiently strong to give access to the diene structure of the ligand. With weaker acids such as chloroform,this is energetically impossible and no acid-base interaction is observed.

One final point is that the cyclopentadienyl ligand apparently favours the monohapto configuration with electropositive main group elements,and adopts this structure in indium(III) complexes[27,80,159]. Donation from indium(I) to boron trihalides presumably has the effect of raising the effective positive charge on the metal atom,thus causing the ligand to reorganise into the diene form.

Harrison and Zuckerman[143] have prepared the adduct $Cp_2Sn{\cdot}BF_3$ analogous to $CpIn{\cdot}BF_3$. The infrared evidence again demonstrates that the BF_3 group has C_{3v} symmetry in this adduct,but these authors conclude that the cyclopentadienyl group is in the pentahapto form in both Cp_2Sn and the adduct. Mossbauer studies of the tin nucleus show very little change in the tin σ-orbital hybridisation on donation,and further indicate that the tin lone pair and the cyclopentadienyl ring are at the same relative distance from the tin nucleus in both species. There are therefore significant differences between the Cp_2Sn and CpIn adducts with BF_3,but the reasons for these differences are not inmediately clear at present.

(b) Some Iodide Derivatives of Cyclopentadienylindium(I)

Vibrational Spectroscopy

The reaction of CpIn with iodine in freshly distilled chloroform yields the compound $CpInI_2$. The physical properties of this compound,namely insolubility in most common solvents,suggest a polymeric nature of this solid. The Raman spectrum (see table 36) of this solid shows two peaks at 139 and 155 cm^{-1} probably due to the bridging and terminal indium-iodide stretching modes. The ratio $\nu(In\text{-}I)_{bridge}/\nu(In\text{-}I)_{terminal}$ is 0.89 in good agreement with that found in some iodide bridges containing compounds of indium (see section 2.7 d ,chapter II). Adduct formation occurs with 2,2'-bipyridyl and 1,10-phenanthroline. The molar conductivities of these adducts shown that they are non-electrolytes probably involving five-coordinate indium(III).

The reaction of $CpInI_2$ with Cp_3In in hot benzene yielded a not very stable compound of stoichiometry Cp_2InI. On the other hand,reaction of $CpInI_2$ with tetrapropylammonium iodide yielded the anionic $[Pr_4N][CpInI_3]$ in keeping with the preparation of the anions of the type $MeInX_3^-$ (X = Cl,Br or I) in this laboratory[160]. The molar conductivity of this compound in nitrobenzene shows that it can be formulated as a 1:1 electrolyte.

Inspection of the vibrational spectra of these solids shows that the cyclopentadienyl ring is σ-bonded since a band between 2900-2960 cm^{-1}due to the C_1-H stretching mode (see figure 7) is present in all cases. All five compounds show three bands between 800-620 cm^{-1} which would be due to the out-of-plane C-H deformation modes.

The bipyridyl and phenanthroline bands in $CpInI_2$·bipy and $CpInI_2$·phen respectively,showed the expected changes with respect to the free ligands,upon complexation and therefore they have been substracted from those bands listed in table 36. In the bipyridyl and phenanthroline adducts of $CpInI_2$,the In-N stretching vibrations are at 305 and 299 cm^{-1} in good agreement with those found for some complexes of the type $In(acac)LX_2$ where L = bipy or phen and X = Cl, Br or I (see chapter V). The In-I stretching frequencies for the bipyridyl adduct were found to lie at 176 cm^{-1} for the antisymmetric stretching mode and at 143 and 138 cm^{-1} for the symmetric stretching vibration. The latter mode appears split probably for some solid state effect. In the phenanthroline adduct,both antisymmetric and symmetric stretching modes appear to be split;ν_a(In-I) and ν_s(In-I) were found at 192+186 and 139+130 cm^{-1},respectively. No splitting of these bands was observed in Cp_2InI neither in $CpInI_3^-$ species. For this latter anionic species the In-I stretching modes are at 190 and 140 cm^{-1} in good agreement with those reported for InI_4^- (185 and 139 cm^{-1})[93] and in $MeInI_3^-$ (186 and 139 cm^{-1})[160].

Nuclear Magnetic Resonance

The rather low solubility of most of the compounds prevented to obtain the ^{1}H-n.m.r. spectra of them. However, the spectrum of $CpInI_2$·bipy in acetone shows the typical resonances of the bipyridyl protons and a single peak at 349 cps due to the cyclopentadienyl moiety. A similar situation was found in the n.m.r. spectrum of the phenanthroline adduct in dichloromethane in which the cyclopentadienyl resonance comes out at 350 cps.

The conclusions one can draw from the vibrational spectra would contradict those one can infer from the n.m.r. spectra. However,the ring whizzing process seems to be a very important process in the cyclopentadienylindium(III) derivatives[27],since the n.m.r. spectrum of Cp_3In shows a single peak at 356 cps even at low temperatures and the X-ray molecular structure determination has shown the cyclopentadienyl rings are σ-bonded[80].

TABLE 36

Infrared and Raman bands (in cm^{-1}) for the cyclopentadienylindium(III) derivatives$^{(a,b)}$

$CpInI_2$	$CpInI_2 \cdot bipy$	$CpInI_2 \cdot phen$	$CpInI_3^-$	Cp_2InI	Assignment
c	3072 ms	3070 ms	3045 w	3035 w	$\nu(=C-H)$
	2965 mw	2990 mw	2965 s	2955 ms	$\nu(C_1-H)$
2923 w	2925 mw	2925 mw	2940 s	2925 s	
1388 ms	1408 s				$\delta(C-H)$
1342 s	1385 s	1385 m	c	1305 w	
1155 w	1105 m	1105 s	1095 ms	1100 mw	
1070 m	1072 w	1078 w			$\nu(C-C)$
1058 m	1042 mw			1031 s	
1002 w	1015 ms		c	c	
983 s	c	c	982 s	980 ms	$\nu(C-C)$
905 w	892 w			890 m	ring deformation
863 s	871 w	869 m	c		
835 w	836 m		c		$\delta(CH_2)$

Table 36 (continued)

805 s	803 m	813 m	800 s	804 s	$\gamma(C_3\text{-}H)$
762 s	746 s	748 ms	751 s	740 ms	$\gamma(C_2\text{-}H)$
665 mw	622 m	627 w	660 mw	673 m	$\gamma(C_1\text{-}H)$
598 s					
315 w	325 m	329 m	321 w	288 w	$\nu(\text{In-C})$
				277 w	
	305 m	292 m		211 s	$\nu(\text{In-N})$
		192 m	190 mw	178 w	$\nu_a(\text{In-I})$
155 ms(b)	176 mw	186 m			
139 m(b)	143 m	139 mw	140 vs	145 w	$\nu_s(\text{In-I})$
	138 m	130 mw			
	115 mw	113 mw	114 m	106 m	
	111 m	96 mw			
	77 w	79 w		76 m	

(a) For $CpInI_2 \cdot bipy$ and $CpInI_2 \cdot phen$, the bands due to the bipyridyl and phenanthroline have been substracted.

(b) The bands bellow 211 cm^{-1} are Raman bands. For $CpInI_2$ the bands at 155 and 139 are assigned to the terminal and bridging In-I stretching modes respectively.

(c) Those bands marked c are covered by other bands.

Mass Spectral Studies

The mass spectra of all the compounds except $[Pr_4N][CpInI_3]$ are given in tables 37 to 40 .

From tables 38 and 39 it can be inferred that the mass spectra of the bipyridyl and phenanthroline adducts of $CpInI_2$ are quite similar. The main feature of the spectra is that no peak due to InI^+ ions was observed,the peak due to In^+ion is rather low in intensity and that the main peak is due to the nitrogen-donor ligand. No peaks due to the InL^+ (L = bipy or phen) ions or to the molecular ion were detected.

The mass spectra of $CpInI_2$ and Cp_2InI (tables 37 and 40) show some interesting differences. In the former,a peak of low intensity located at 496 (m/e) due to the InI_3^+ ions was detected,besides the peak of the InI_2^+ at 369. These peaks were not observed in the spectrum of Cp_2InI. As was suggested before,both solids could involve polymeric structures in view of their low solubilities. The Raman spectra of these solids clearly show the difference in the In-I stretching modes. Whereas $CpInI_2$ shows only two bands,i.e., 155 and 139 cm^{-1} which have been assigned to the terminal and bridging In-I stretching modes,these vibrations are observed at 178 and 145 cm^{-1} in Cp_2InI. Taking into account that an increase in the mass of the substitutuent would produce a decrease of these frequencies,the In-I stretching

TABLE 37

The mass spectrum of $CpInI_2$

(Spectrum normalized to base peak m/e 63 = 100%)

Excitation Voltage : 80 eV

Source Temperature : 100°C

m/e	Intensity %	Assignment
496	7	InI_3^+
369	15	InI_2^+
242	18	InI^+
130	10	Cp_2^+
129	13	I^+
128	13	
127	13	
115	36	In^+
83	12	?
78	11	?
77	17	?
66	29	Cp^+
65	29	
63	100	

TABLE 38

The mass spectrum of $\mathrm{CpInI_2 \cdot bipy}$

(Spectrum normalized to base peak m/e 156 = 100%)

Excitation Voltage : 80 eV

Source Temperature : 220°C

m/e	Intensity %	Assignment
156	100	bipy$^+$
128	12	I^+
127	18	
115	10	In$^+$
78	24	?
66	22	Cp$^+$

TABLE 39

The mass spectrum of $CpInI_2 \cdot phen$

(Spectrum normalized to base peak m/e 180 = 100%)

Excitation Voltage : 80 eV

Source Temperature : 220°C

m/e	Intensity %	Assignment
180	100	$phen^+$
154	19	?
115	10	In^+
90	13	?
66	40	Cp^+

TABLE 40

The mass spectrum of Cp_2InI

(Spectrum normalized to base peak m/e 66 = 100%)

Excitation Voltage : 80 eV

Source Temperature : 280°C

m/e	Intensity %	Assignment
242	16	InI^+
130	16	Cp_2^+
127	17	I^+
115	17	In^+
91	17	?
66	100	Cp^+

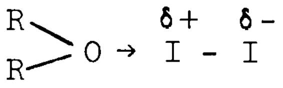
stretching frequencies for Cp_2InI would be expected to lie at higher frequencies,as in fact it is observed. In this sense it seems likely that the polymeric nature of $CpInI_2$ is different than the polymerization occurring in Cp_2InI. This suggestion is supported by the mass spectrum of Cp_2InI which shows no peak due to InI_2^+ and InI_3^+ ions. The halogen bridging structure proposed for $CpInI_2$ certainly allows the possibility that the molecule can be broken up in such way as to give rise to InI_2^+ and InI_3^+ ions. This possibility would be precluded for Cp_2InI,where the polymerization may be similar to that in the solid triscyclopentadienylindium (III)[80].

Discussion

The reaction of cyclopentadienylindium(I) with iodine in chloroform to yield $CpInI_2$ involves the oxidation of indium(I) to indium(III). The present work served to clarify the mechanism by which the reaction takes place,and also the way in which the cyclopentadienyl ligand changes its bonding mode from a pentahapto to a monohapto form. It was observed that if the above reaction is carried out in the presence of a small amount of ethanol the resulting product is not the desired $CpInI_2$,but indium monoiodide. Indium(I) iodide was obtained in quantitative yield (99%) and identified by its Raman and mass spectra.

Similar reaction were carried out using either methyliodide or trifluoroiodomethane instead of iodine. In all cases, indium(I) iodide was obtained in 100% yield in both the presence or absence of ethanol.

The important bonding orbitals in CpIn, following the work of Shibata et al[139] are those involving indium p_z (or sp hybrid) overlaping with the ring carbon orbitals (a_1), and the p_x and p_y (e_1) overlaping the appropriate Cp π-orbitals. It seems reasonable to assume that the formation of $CpInI_2$ occurs via the interaction of the e_1 molecular orbital of the CpIn and the π^* orbital of iodine. The formation of a transition state in which electrons can flow from the CpIn into an iodine antibonding molecular orbital, allows the formation of In-I bond as a result of the weakening of the I-I bond.

The effect of ethanol on the reaction is explicable in terms of the formation of a charge transfer complex between ethanol and iodine, of the type  $\begin{matrix}\mathrm{R}\\\mathrm{R}\end{matrix}\!\!>\mathrm{O} \rightarrow \overset{\delta+}{\mathrm{I}} - \overset{\delta-}{\mathrm{I}}$ in which the iodine molecule is already polarized, and hence it would alter the orbital levels of the iodine. More importantly, the presence of a dipole in I_2 would encourage the formation of a linear transition state Cp-In-I-I, from which indium(I) iodide could be eliminated. The polarization of the C-I bond is a permanent feature of the CH_3I and CF_3I

molecules and the linear transition state is again favoured needing no ethanol to eliminate InI.

In the reaction of cyclopentadienylindium(I) with iodine in the presence of ethanol or with methyl iodide,the indium(I) iodide formed was filtered off and the filtrate evaporated to dryness. In both cases a brown pasty solid was obtained which could not be characterized. Dissolving the solids in $CDCl_3$,the ^1H-n.m.r. spectra were recorded. The spectra showed no resonance due to the diene protons, but a number of peaks due to the CH_3-CH_2-O group,and to C-CH_2-C cyclic protons. No infrared absorptions due to the C = C stretching modes,were observed. In both cases a strong and broad band at about 3380 cm^{-1} was observed which may be evidence of association via intermolecular hydrogen bonding. At the present the way in which the ring would become saturated as well as the nature of these products are not well understood.

The mass spectra of these solids taken at 300°C yielded very little information. The brown pasty solid obtained from the reaction of CpIn with iodine yielded only one peak at m/e 45 assignable to the CH_3-CH_2O^+ ions,whereas the product of the reaction with methyl iodide shows an intense peak at m/e 31 due to the CH_3O^+ ions,45 due to $CH_3CH_2O^+$ and 46 due to $CH_3CH_2OH^+$ ions. Very weak peaks (relative intensities 4-5%) were detected at 113,127 and 128 m/e.

Attempts to isolate the product of the reaction of cyclopentadienylindium(I) with bromine in chloroform were unsuccesful. The reaction of stoichiometric ammounts of CpIn with bromine in the presence of bipyridyl in dilute solution of chloroform yielded a solid with the ratio Br/In $\approx$ 5,suggesting bromination of either the Cp ring or the bipyridyl,or both.

CHAPTER V

SOME MONOACETYLACETONATOINDIUM(III) COMPLEXES

5.1 General

There are not many complexes of indium(III) involving chelate oxygen-donor ligands reported in the literature. The nuclear magnetic resonance and vibrational spectra of indium(III) complexes of tropolonate and 3-hydroxy-2-methyl-4-pyronate have been studied[72]. The complex $In(oxine)_3$[161] (oxine = 8-hydroxyquinolato ion) has also been prepared.

Complexes formed by transition and non-transition metal ions with acetylacetone have been known for a long time. A common feature of these complexes is that the number of molecules of acetylacetone bonded to the metal is equal to the oxidation state of the central atom; when the ratio ligand to metal is increased or decreased, anionic or cationic species are obtained.

Gallium(III), indium(III) like aluminium(III) forms neutral ML_3 chelates with acetylacetone (acac)[162]. Polarographic studies[72,163] on $In(acac)_3$ in polar organic media have shown that the reduction occurs in one-electron steps, giving evidence for formally indium(II) species. Investigation of the indium(III)/acetylacetonate system in aqueous media[163] showed that the reduction of indium(III) species is dependent upon pH. X-ray powder techniques have shown that $In(acac)_3$ is isostructural with the iron(III) analog[63]. The infrared and Raman spectra[164], and force constant calculations on $In(acac)_3$[165] have also been reported.

Although a number of complexes of the type $M(acac)_nL_m$ where M = Co, Pt, Sn or Ga , L = NH_3, en, bipy, py[166], phen[167], Cl[168,169] and Br[170] and n = 1 or 2 and m = 2 or 4, have been reported, there is no indium(III) complex where the number of acetylacetonato ligand is less than three, except the organometallic $Me_2In(acac)$ derivative obtained by Clark and Pickard[75] by reacting Me_3In with the β-diketone.

As part of this thesis, complexes of the type $In(acac)LX_2$ where L = bipy, phen, py or d_5-py and X = Cl, Br or I have been prepared, characterized and their infrared and Raman spectra in the region 600 - 100 cm^{-1} studied.

5.2 The Monoacetylacetonatoindium(III) Complexes

The reaction of indium(I) halides with an excess of acetylacetone yielded a brown pasty solid soluble in ethanol, and treating this solution with the corresponding nitrogen-donor ligand, a series of crystalline solids were obtained.

Extraction of the brown pasty solid with chloroform lead to the identification of $In(acac)_3$ species in solution. The undissolved solid was found to be $In(acac)X_2 \cdot 2H_2O$.

In the process of dissolution of the indium(I) halides in acetylacetone some disproportionation leading to indium metal was observed for the chloride but not for the bromide and iodide. After one hour refluxing, this indium metal was completely dissolved. It is believed that the oxidative process occurs in three steps

i) $InX + Hacac = H[In(I)(acac)X]$

ii) $H[In(I)(acac)X] + InX = [In(III)(acac)X_2] + In + \frac{1}{2}H_2$

iii) $In + 3Hacac = In(acac)_3 + 3/2H_2$

From semiquantitative experiments it was found that the species giving rise to the $In(acac)LX_2$ complexes is $In(acac)X_2$ species and not $In(acac)_3$.

The study of the infrared and Raman spectra of these complexes in the region 600-100 cm^{-1} permitted the assignment of the indium-oxygen, indium-nitrogen and indium-halide stretching vibrations. The vibrational spectra of the d_5-py derivative was useful in unequivocally assigning some bands due to the nitrogen-donor ligands and acetylacetone in the low frequency region of the spectra.

Vibrational spectroscopy does not, in this case, allow a clear distinction between cis or trans arrangement of the halide ligands. In the trans $InO_2N_2X_2$ chromophore the symmetry is C_{2v}, and the indium-halide stretching modes $(a_1 + b_2)$ are infrared and Raman actives. For a cis structure (C_1 symmetry) all vibrational modes are also infrared and Raman actives.

5.3 Experimental

(a) Physical Measurements

Physical measurements were performed as described previously in chapters II and IV.

The infrared spectra were recorded on a Beckman IR-12 spectrophotometer on vaseline mulls using polyethylene windows.

Conductivity measurements were carried out with mM acetonitrile solutions.

(b) Preparative Chemistry

Preparation of In(acac)LX_2 Complexes

L = bipy,phen,py or d_5-py

X = Cl,Br or I

2mmole of indium(I) halide were refluxed with an excess (~10 ml.) of acetylacetone for 24 hours. A brown solution was obtained. The excess of acetylacetone was removed by pumping and then the pasty brown solid dissolved in ethanol. The corresponding nitrogen-donor ligand dissolved in ether (bipyridyl),dichloromethane (phenanthroline) or neat (pyridine or d_5-pyridine) was added.

After few minutes with stirring a crystalline solid precipitated,filtered off,washed with ether and dried at vacuum at 80°C. The solids are partially soluble in acetonitrile and in the mixture acetonitrile/methanol and complete soluble in the mixture acetonitrile/acetylacetone.

The presence of ethanol in the crystalline lattice of these complexes was confirmed by infrared absorptions at 3356 s, 2985 s, 1098 ms, 880 m and 802 ms cm^{-1}. The reasons why ethanol stays so firmely bonded in the crystalline lattice of these complexes is not well understood at present.

Attempts to prepare complexes with ligands other than nitrogen-donor,such as dmso,phosphines,diphosphines and halides were unsuccessful.

Table 41 shows the analytical,melting point and conductivity data for the compounds reported in this chapter.

5.4 Results

The reaction of the brown pasty solid,obtained from the dissolution of indium(I) halides in acetylacetone,in ethanol with 2,2'-bipyridyl,1,10-phenanthroline,pyridine and d_5-pyridine gave complexes of the type $In(acac)LX_2 \cdot C_2H_5OH$ where X = Cl,Br or I. All the complexes are air stable,light

TABLE 41

Analytical and conductivity data for the $In(acac)LX_2 \cdot S$(a) complexes(b)

Compound	Required %					Found %					$\Lambda_M^{25^\circ C}$(c)
	C	H	N	In	X	C	H	N	In	X	
$In(acac)bipyCl_2 \cdot S$	41.3	4.3	5.8	23.6	14.6	41.9	4.0	5.3	23.5	14.7	1.56
$In(acac)bipyBr_2.S$	35.4	3.6	4.9	19.9	27.8	35.0	3.1	5.0	19.9	27.7	1.46
$In(acac)bipyI_2 \cdot S$	30.5	3.1	4.2	17.1	37.9	30.9	2.8	4.0	17.1	37.8	1.01
$In(acac)phenCl_2 \cdot S$	44.6	4.1	5.5	22.5	13.9	44.3	3.5	5.8	22.6	13.7	1.70
$In(acac)phenBr_2 \cdot S$	38.0	3.5	4.7	19.1	26.6	38.2	3.1	4.8	19.4	26.7	1.00
$In(acac)phenI_2 \cdot S$	32.9	3.0	4.0	16.5	36.6	32.8	2.9	4.0	16.5	36.5	1.80
$In(acac)(py)_2Cl_2 \cdot S$	41.8	4.7	5.7	23.5	14.5	41.3	4.9	5.8	23.4	14.6	1.00
$In(acac)(py)_2Br_2 \cdot S$	35.3	3.9	4.8	19.9	27.7	35.6	3.5	4.9	20.0	27.8	1.70

Table 41 (continued)

In(acac)(py)$_2$I$_2$·S	30.4	3.4	4.2	17.1	37.8	30.3	3.0	4.4	17.1	37.9	2.11
In(acac)(d$_5$py)$_2$Cl$_2$·S	40.9	3.6	5.6	23.0	14.2	40.6	3.9	5.9	23.0	14.2	1.08
In(acac)(d$_5$py)$_2$Br$_2$·S	34.7	3.1	4.8	19.5	27.2	34.8	3.4	4.7	19.7	27.3	1.03
In(acac)(d$_5$py)$_2$I$_2$·S	29.9	2.7	4.1	16.8	37.2	29.3	2.8	4.2	16.9	37.4	1.23

(a) S = C_2H_5OH

(b) Melting points: In(acac)bipyX$_2$: 252(Cl),248(Br),218(I); In(acac)phenX$_2$: 293(Cl), decompose without melting(Br and I); In(acac)(py)$_2$X$_2$: 244(Cl),234(Br),186(I); In(acac)(d$_5$py)$_2$X$_2$: 248(Cl),239(Br),191(I).

(c) Molar conductivities in acetonitrile;soln. 10^{-3} M.

yellow and crystalline solids. In(acac)phen$I_2 \cdot C_2H_5OH$ is a green-yellow solid. The conductivity measurements confirm the formulation of these compounds as non-electrolytes. All the complexes appear to have a molecule of ethanol in the crystalline lattice which could not be removed by vacuum evaporation and heating. The mass spectrum of a sample taken at different temperatures showed the presence of peak at m/e 43 to 47 that could be due to the $C_2H_5OH^+$ ions.

Vibrational Spectroscopy

The vibrational spectra of these compounds have been studied in the region of 2000 to 100 cm^{-1} by infrared and Raman spectroscopy. The infrared spectra of the trischelate complexes of bipyridyl and phenanthroline with first-row transition metal ions have been reported by several investigators. Schilt and Taylor[171] studied the infrared spectra of these complexes in the region of 2000-600 cm^{-1}, whereas Inskeep[172] studied the region 2000-250 cm^{-1}. Clark and Williams[173] extended the infrared measurements down to 60 cm^{-1}.

Much less attention have received the bipyridyl and phenanthroline complexes of the group III elements. Carty[174] has studied the far infrared spectra of the complexes of gallium(III) halides with bipyridyl of the type GaX_3(bipy) (X = Cl, I), GaBr(bipy)$_2$ and GaX_2(bipy)$_2$A where A = BF_4^- or PF_6^-. The infrared absorption spectra of some complexes of the type GaX_3L_3 where X = Cl,Br and ClO_4^- and L = bipy or phen have been discussed by Kul'ba et al[175].

Walton[58] has measured the Raman spectra of complexes of indium(III) chloride with bipy,phen,py and pyrazine. He found that the complexes of the type $InCl_2L_2^+$ have a cis configuration.

Since the bands observed in the high-frequency region are mainly due to the ligands vibrations slightly perturbed by coordination and cannot be correlated with the stereochemistry,attention will be paid to the region of 600-100 cm^{-1},except in the pyridine complexes where according to Gill et al[176],the splitting of some vibrational modes can be correlated with the stereochemistry of the compound.

Table 42 lists the infrared and Raman bands of the complexes $In(acac)bipyX_2 \cdot C_2H_5OH$ (X = Cl,Br or I) and their assignments.

The bands at 309 and 283 cm^{-1} in the far-infrared spectrum of the chloride must arise from the ν(In-Cl) stretching mode since they do not appear in the bromide and iodide spectra. The Raman spectrum of the bromide shows a band of medium intensity at 182 cm^{-1},which can be assigned to the symmetric In-Br stretching mode since is absent in the other two complexes. The antisymmetric In-Br stretching mode comes out at 216 cm^{-1} in the infrared,but was not detected in the Raman. The two bands at 141 and 173 cm^{-1} in

TABLE 42

Infrared and Raman spectra (600-100 cm^{-1}) of In(acac)bipyX_2 (X = Cl,Br or I) complexes

X = Cl		X = Br		X = I		
Ir	Raman	Ir	Raman	Ir	Raman	Assignment
					102 w	
	116 w					
					141 s	ν_s(In-I)
					173 m	ν_a(In-I)
			182 m			ν_s(In-Br)
205 m			203 m	209 s	202 m	ν_s(In-O)
			216 s			ν_a(In-Br)
243 m	244 vw	241 s	238 w	238 ms	234 mw	ν_a(In-O)
258 mw	258 m		256 ms		259 ms	ν (In-N)
283 vs	284 ms					ν_s(In-Cl)
309 vs	304 ms					ν_a(In-Cl)
365 vw	363 s	365 vw	363 m		365 ms	bipy vibr.
408 m	405 w					?
417 s		416 s	416 mw	417 s	415 mw	acac vibr.
434 m	430 s	432 ms	431 s	430 ms	430 s	acac vibr.
528 m		528 vw				bipy vibr.
575 s	573 s	562 s	560 ms	558 s	560 ms	acac vibr.

the iodide can be undoubtly be assigned to the symmetric and antisymmetric In-I stretching modes.

Because the low symmetry of these complexes the selection rules for the vibrational spectra cannot be used to infer the stereochemistry of the complexes. A trans configuration(C_{2v}) requires the appearance of the two indium-halide stretching modes in the infrared and the Raman. On the other hand,for a cis configuration (C_1),no selection rules can be worked out as all the vibrations are both infrared and Raman actives.

A similar situation was found in the complexes with phenanthroline. Table 43 shows the vibrational spectra of the In(acac)phenX_2 (X = Cl,Br or I) complexes.

In the chloride the antisymmetric In-Cl stretching mode is at 302 cm^{-1} in the infrared. The symmetric mode was not observed,but it is probably covered by the strong and broad band at 284 cm^{-1} due to the ν_a(In-N) vibration. In the Raman these vibrational modes are also probably covered by the strong absorption at 295 cm^{-1}. In good agreement with the previously quoted assignment for the symmetric and antisymmetric indium-bromide and indium-iodide stretching modes in the bipyridyl complexes,in the phenanthroline derivatives these vibrations are at 187 and 207 cm^{-1} (212 cm^{-1} in the infrared) for the bromide and at 141 and 164 cm^{-1} for the iodide,respectively.

TABLE 43

Infrared and Raman spectra (600-100 cm^{-1}) of $In(acac)phenX_2$ (X = Cl,Br or I) complexes.

X = Cl		X = Br		X = I		
Ir	Raman	Ir	Raman	Ir	Raman	Assignment
					121 w	
					141 w	ν_s(In-I)
					164 w	ν_a(In-I)
			187 w			ν_s(In-Br)
		212 s	207 s			ν_a(In-Br)
232 w	252 w	238 w	248 mw	248 m	246 mw	ν_s(In-O)
284 s,br	282 vw		279 m		271 mw	ν_s(In-N)
	295 vs	293 m	293 s	296 s	298 s	ν_a(In-N)
302 s						ν_a(In-Cl)
411 ms	416 s	410 s	412 mw		413 mw	acac vibr.
427 s	433 vs	429 s	430 vs	426 s	428 vs	acac vibr.
482 mw		481 m		481 mw		phen vibr.
502 w		502 mw		502 mw		phen vibr.
513 mw		512 mw		515mw	512 vw	phen vibr.
566 s	562 m	562 s	558 ms	562 mw	562 m	acac vibr.

In the pyridine and d_5-pyridine complexes the In-Cl stretching modes were found at higher frequencies than in the bipyridyl and phenanthroline analogs . Thus, in the $In(acac)(py)_2Cl_2$,the antisymmetric In-Cl stretching mode was found at 328 cm^{-1} in the Raman,whereas the symmetric mode appears at 288 cm^{-1}. The far-infrared spectrum shows a broad band at 291 cm^{-1} which probably covers the band due to the antisymmetric stretching mode (see table 44). In the deuterated pyridine adduct these modes show up at 286 and 334 cm^{-1} in the Raman and as a rather broad band at 297 cm^{-1} in the infrared.

The assignment of the In-Br stretching modes is more difficult since the symmetric stretching mode should appear at about 190 cm^{-1} according to the frequencies found in the other complexes reported here. In that region all three complexes show a strong band probably due to the symmetric In-O stretching mode. The antisymmetric In-Br stretching was observed at 236 cm^{-1} in the Raman and at 227 cm^{-1} in the infrared.

The indium-iodine stretchings in the pyridine and d_5-pyridine adducts were observed in the Raman.The pyridine adduct shows three bands located at 132,152 and 161 cm^{-1} assignable to these vibrations.However the band at 161 cm^{-1} is also present in the bromide (159 cm^{-1}) and the chloride (158 cm^{-1}) and therefore can be ruled out. In the deuterated analogs

TABLE 44

Infrared and Raman spectra (1000-100 cm^{-1}) of $In(acac)(py)_2X_2$ (X = Cl,Br or I) complexes[(a)]

X = Cl		X = Br		X = I		
Ir	Raman	Ir	Raman	Ir	Raman	Assignment
					132 w	ν_s(In-I)
					152 ms	ν_a(In-I)
	158 mw		159 s		161 ms	
	189 mw		188 vs		188 s	ν_s(In-O)
217 m	211 mw	224 s	214 s	214 s	214 s	ν_a(In-O)
		236 mw	233 mw			ν_s(In-Br)
	256 mw		246 w		256 w	ν_s(In-N)
	272 mw		267 w		274 w	ν_a(In-N)
291 s	288 s					ν_s(In-Cl)
	328 mw					ν_a(In-Cl)
398 w	395 s	388 w	394 s	389 m	389 s	?
417 s	412 w	414 s		411 s		acac vibr.
430 s	424 s	430 s	426 s	427 ms	427 s	acac vibr.
	436 s		436 s		436 s	acac vibr.
567 s		562 s		565 s		acac vibr.
635 s	638 s	632 s	638 mw	632 s	638 mw	py vib,6a
652 m	655 s	650 ms	657 mw	652 ms	656 mw	acac vibr.
670 m		673 ms		678 ms		acac vibr.
697 s		697 s		695 s		py vib,11
762 s		756 s		757 s		py vib,4
813 s		807 s		800 s		acac vibr.
882 mw		878 w		875 m		acac vibr.
933 s	938 m	925 s	938 mw	927 s	940 mw	acac vibr.

(a) Notation for the pyridine bands is that given by Kline[177] a band between 157 and 146 cm^{-1} was observed which is probably due to some ring vibration of the deuterated pyridine. In the pyridine adducts this band was observed between 161 and 158 cm^{-1}.

The In-O stretching modes lie between 220-190 cm^{-1}, whereas the In-N modes are observed between 300-240 cm^{-1}in good agreement with the metal-nitrogen stretching frequencies found in complexes with bipyridyl and phenanthroline[178].

Hester and Plane[164] assigned as In-O stretching mode a band at 444 cm^{-1} in the complex $In(acac)_3$. That band probably contains some contribution of the In-O stretching mode,but it is too high in energy to be a pure stretching. In fact that band has been observed (with small variations) in most acetylacetonato complexes[179].

The assignment of a cis or trans configuration from the vibrational spectra it is not possible. The similarity of the vibrational spectra of all the complexes reported in this chapter,suggests a similar structure for all of them. According to Gill et al[176] since no splitting of the 4,5,11 and 16b vibrational modes in the pyridine and deuterated pyridine derivatives were observed a trans formulation seems to be likely,however the X-ray crystal and molecular structure determination of the non-solvated complex $In(acac)bipyCl_2$ (see chapter VI) shows that the chlorine atoms are cis in this complex. Probably this also

TABLE 45

Infrared and Raman spectra (1000-100 cm^{-1}) of $In(acac)(d_5py)_2X_2$ (X = Cl,Br or I) complexes

X = Cl		X = Br		X = I		
Ir	Raman	Ir	Raman	Ir	Raman	Assignment
					133 s	ν_s(In-I)
	151 s		146 m		157 s	
					176 ms	ν_a(In-I)
	188 s		188 s		198 ms	ν_s(In-O)
217 m	209 s	227 s	214 m	214 s		ν_a(In-O)
			246 s			ν_a(In-Br)
	268 m		267 m		264 w	ν_s(In-N)
	275 w		274 m		279 w	ν_a(In-N)
297s,br	286 s					ν_s(In-Cl)
	334 mw					ν_a(In-Cl)
395 s	389 mw	394 s	394 w	389 s	386 ms	?
419 s		416 s		410 s		acac vibr.
435 s	432 s	433 ms	429 s	426 ms	424 s	acac vibr.
509 ms		508 ms		508 ms		d_5py ,11
538 s		534 s		535 s		d_5py ,4
565 s		565 s		563 s		acac vibr.
608 s	614 m	603 s	618 w	604 ms	612 w	d_5py ,6b
	626 s		625 ms		626 w	d_5py ,6a
652 ms		650 s		652 ms		acac vibr.
667 ms		667 ms		667 ms		acac vibr.
782 ms		780 s		780 s		d_5py ,5
812 s		805 s		795 s		acac vibr.
825 s	824 m	828 s	831 ms	825 s	831 s	d_5py ,9a
831 s	848 m	842 s	842 w	840 s	843 ms	d_5py ,3
886 s	890 s	885 s	889 ms	886 s	891 s	acac vibr.
931 s	938 ms	930 s	936 mw	925 s	934 w	acac vibr.

apply to the other complexes prepared here.

Mass Spectral Studies

The main feature of the mass spectra of these complexes is a strong peak due to the nitrogen-donor ligand with a relative intensity of 100% and a number of peaks in the range m/e 44 - 47 probably due to the CH_3CO^+ and $C_2H_5OH^+$ ions. All spectra show a peak at m/e 115 due to In^+ ions. No peak due to the InL^+ ions were detected in any case,whereas in all spectra peaks from $In(acac)^+$ and $In(acac)X^+$ were found, although their relative intensities are rather low. In the bipyridyl and phenanthroline complexes peaks due to the $In(acac)_2^+$ ions were detected. Table 46 shows a typical spectrum for these complexes.

The peak due to the $acac^+$ ions show up at m/e 100 with very low intensity (<10%) implying that the acetylacetonato ligand remains bonded to the indium whereas the nitrogen-donor ligand comes out easily. For one of the pyridine complexes, $In(acac)(py)_2Cl_2$,the mass spectra were obtained at different temperatures starting at 70°C and up to 160°C. No changes in the spectrum were observed and the peak due to the pyridine (m/e = 79) was the main one all the times. This result implies that in fact the appearance of the nitrogen-donor ligand in the spectrum is not the result of thermal decomposition of the compound,but a simple ionizing process.

TABLE 46

The mass spectrum of In(acac)bipy$Cl_2 \cdot C_2H_5OH$

(Spectrum normalized to base peak m/e 156 = 100%)

Exciting Voltage : 80 eV

Source Temperature : 190°C

m/e	Intensity %	Assignment
412	11	$In(acac)_3^+$
314	86	$In(acac)_2^+$
249	38	$In(acac)Cl^+$
214	10	$In(acac)^+$
156	100	$bipy^+$
115	56	In^+
100	9	$acac^+$
78	24	?
47	29	
46	35	$C_2H_5OH^+$
45	39	
43	21	CH_3CO^+

All the compounds show an intense peak due to the $C_2H_5OH^+$ ions and a number of other peaks in this same region. Mass spectra obtained at 100°C showed those peaks as well as after heating the sample up to 250°C. Mass spectra of $In(acac)_3$ showed a single peak at m/e = 43 of rather low intensity,whereas in $In(acac)Cl_2 \cdot 2H_2O$ this peak comes out at m/e = 42. The spectrum of crystalline sample of $In(acac)bipyCl_2$ similar to that used in the X-ray crystal structure determination,which does not contain ethanol, showed also a single peak at 43 m/e assignable to the CH_3CO^+ ions. The presence of ethanol is therefore confirmed once again.

5.5 Discussion

Complexes of the type $In(acac)LX_2 \cdot C_2H_5OH$ where L = bipyridyl,phenanthroline,pyridine and d_5-pyridine and X = Cl,Br or I were prepared. From the vibrational spectra it can be inferred that the In-Cl vibrational frequencies lie about 300 and 288 cm^{-1} for the antisymmetric and symmetric stretching modes,respectively. In $In(acac)Cl_2 \cdot 2H_2O$ the infrared spectrum obtained in vaseline showed a strong band at about 300 cm^{-1} split by ca.11 cm^{-1}. On the other hand these modes lie at about 220 and 185 cm^{-1} for the In-Br vibrations and at about 140 and 175 cm^{-1} for the In-I vibrations,respectively. These frequencies agree well with the stretching frequencies found for other indium halide complexes (see chapter I and II).

The indium-oxygen stretching modes lie at about 200 and 215 cm^{-1},although these vibrations were found somewhat at higher frequencies for the bipyridyl complexes. In $In(acac)_3$[164] and $In(tropolonate)_3$,this vibration are found at about 230 and 246 cm^{-1},respectively. In all cases a band at about 410 cm^{-1} which probably involves an indium-oxygen stretching mode coupled with other vibration (probably a C-CH_3 stretching mode) was observed.

Indium-nitrogen stretching modes were detected at about 270 and 250 cm^{-1} in keeping with previous work on bipyridyl and phenanthroline complexes of indium[2,3].

In section 5.2 it was suggested that the oxidative reaction of the indium(I) halide with acetylacetone would involve the formation of H [In(I)(acac)X],[$In(acac)X_2$], [$In(acac)_3$] and H_2. The species H [In(I)(acac)X] must be very reactive and probably is consumed completely as no indication of its presence was found. The second and third species were readily identified by melting point determination,Raman and mass spectra. If the brown pasty solid, obtained from the dissolution of the indium(I) halides in acetylacetone,is dissolved in chloroform and the resulting solution filtered off,a white hygroscopic solid is left.

This solid was identified analytically as $In(acac)Cl_2{\cdot}2H_2O$ (analysis.Required%: C 18.7, H 3.4, In 35.8, Cl 22.1; Found%: C 18.7, H 3.3, In 35.6, Cl 22.2; melting point 132°C). The ^1H.n.m.r. spectrum of this solid in D_2O is quite similar to that of $In(acac)_3$ for which in $CDCl_3$[180] resonances at 8.00 and 4.50 τ with respect to T.M.S. were found. In $In(acac)Cl_2{\cdot}2H_2O$ these resonances are at 7.97 and 4.37 τ, respectively. It is believed that this species is an intermediate in the formation of the complexes of the type reported in this chapter since:

(a) attempts to prepare complexes from $In(acac)_3$ were unsuccessful.

(b) attempts to prepare complexes from the chloroform extract of the brown solid which contains $In(acac)_3$ (^1H-n.m.r. spectrum of this solution showed resonances at 8.01 and 4.50 τ) were also unsuccessful.

(c) reactions of $In(acac)Cl_2{\cdot}2H_2O$ in ethanol with the corresponding nitrogen-donor ligand yielde the desired compounds.

It is also believed that ethanol,which appears strongly bonded in the crystalline lattice of these complexes,plays an important role since attempts to prepare the complexes by reacting $In(acac)Cl_2{\cdot}2H_2O$ as well as the brown pasty solid,dissolved in water,acetonitrile,nitromethane and methanol,with the nitrogen-donor ligands did not yield the desired compounds and the reactants were recovered unchanged in each case.

Finally, because of the dissolution of indium(I) halides in acetylacetone requires refluxing the mixture for several hours, it was not possible to detect the presence of hydrogen in order to confirm completely the proposed mechanism.

CHAPTER VI

THE CRYSTAL AND MOLECULAR STRUCTURE OF ACETYLACETONATO-2,2'-BIPYRIDYLDICHLOROINDIUM(III)

6.1 Introduction

In the preceding chapter,the preparation,characterization and vibrational spectra of several complexes of indium(III) of the type In(acac)$LX_2 \cdot C_2H_5OH$ where L = bipy, phen,py or d_5-py and X = Cl,Br or I,were reported. By means of vibrational and mass spectra it was shown that the molecule of ethanol remains firmely bonded in the crystalline lattice of these complexes,even after drying under vacuum. Recrystallization of In(acac)bipy$Cl_2 \cdot C_2H_5OH$ in a mixture of acetylacetone/acetonitrile allowed to obtain the nonsolvated species whose crystal and molecular structure is reported in this chapter. It was also pointed out that because the low symmetry of the molecule,vibrational spectroscopy does not give a clear distinction between a cis or trans arrangement of the halide ligands and hence it seemed worthwhile to carry out the X-ray crystal and molecular structure determination of the In(acac)bipyCl_2.

6.2 Determination of the Structure

(a) Crystal Growing

Crystals of acetylacetonato-2,2'-bipyridyldichloroindium(III) were obtained in several different mixtures of solvents as dictated by its solubility. Crystals grown from acetonitrile/methanol and acetonitrile/nitromethane could not be used for Weissenberg and precession photographs. The appropriate single crystals were obtained from a 1:1 mixture of acetylacetone/acetonitrile.

(b) Crystal Mounting

A colourless crystal,parallelepiped in shape with dimensions of 0.55 x 0.26 x 0.30 mm. was used for Weissenberg,precession photographs and data collection.

(c) Photographs

Precession photographs of the h 0 1, h 1 ℓ, h 2 ℓ, 1 k 2h, 2 k 2h and h k -2h layers about the b axis and Weissenberg photographs indicated the Laue symmetry 2/m and the systematic absences h 0 ℓ, ℓ = 2n + 1 and 0 k 0 when k = 2n + 1. This allowed the space group to be unambiguously assigned as the monoclinic group $P2_1/c$. The approximate unit cell dimensions were a = 11.37, b = 12.21, c = 14.30 Å and β = 120°, V = 1720 Å^3.

(d) Data Collection

The crystal was mounted on a Picker FACS-1 computer controled four circle diffractometer,and optically aligned to position the crystal precisely at the point of intersection of the φ,χ and 2θ (ω is coincident with 2θ and therefore the crystal was also centered in ω).

Two reflections were carefully identified to determine the setting of the crystal. This was achieved by setting the 2θ value for one reflection with $\chi = 0^{\circ}$ and φ was driven until the reflection was located. A second reflection,with $\varphi \approx 90^{\circ}$ away from the first was then aligned by setting the 2θ angle and driving χ. The orientation matrix was then obtained from the two reflections and the approximate unit cell dimensions.

Accurate cell dimensions and their standard errors were determined from a least square fit to twenty strong reflections selected from the photographs and whose 2θ values were accurately measured on the diffractometer.

Reflection intensities for the unique set of data (one quarter of the limiting sphere of reflection with $25^{\circ} \geq 2\theta \leq 60^{\circ}$) were collected using the θ - 2θ scan method using niobium filtered Mo - K_{α} radiation,and a scintillation counter equipped with a pulse high discriminator.

For data collection the take-off angle was 1.0° and each reflection was scanned for 1.05° in 2θ, this extended for the $\alpha_1 - \alpha_2$ dispersion. The background was counted for 10 sec. at each end of the scan range. Two standard reflections were measured every 70 reflections and there was a systematic decreasing variation. The variation was ± 5% over the entire data.

(e) Solution of the Structure

The computer programs used in the solutions of the structure have been described elsewhere[181-183]. The raw intensity data was converted into unscaled structure factors $|F|$. The net intensities were corrected for Lorentz and polarization effects; absorption corrections were neglected. A reflection was considered unobserved if the net count was less than 3σ where

$$\sigma = [\text{total count}\cdot 10 + 4.5 + (t_s/t_b)^2(10(B_1 + B_2) + 9)]^{\frac{1}{2}}$$

where t_s and t_b are the total scanning time and the total time for the background respectively and B_1 and B_2 are the counts for the backgrounds. 4988 reflections were measured of which 3524 were considered as observed.

Examination of the three dimensional Patterson function allowed to determine the position of the indium since in the space group $P2_1/c$ the four equivalent positions x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $x, \frac{1}{2}-y, \frac{1}{2}+z$ and $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$ are related in the section of the unit cell by three vectors 2x, 2y, 2z; 2x, $\frac{1}{2}$, $\frac{1}{2}$-2z and 0, $\frac{1}{2}$-2y, -$\frac{1}{2}$. There were only three vectors meeting these requirements which indicated that the indium position to be approximately x = 0.1926, y = 0.2143 and z = -0.1906. Two other peaks were located within 2.5 Å from indium. Structure factors, $|F_c|$, were calculated from the atomic coordinates of indium and chlorine atoms. A full matrix least square refinement was done on the set of data in the range $25^{\circ} \geq 2\theta \leq 60^{\circ}$, varying the scale and the positional parameters. The residual index R $(= \sum(|F_o| - |F_c|)/\sum|F_o|)$ was 27.5% and the weighted residual index WR $(= (\sum W(|F_o| - |F_c|)^2/\sum W|F_o|)^{\frac{1}{2}})$ was 35.2%.

An electron density Fourier synthesis yielded 29 peaks which were used to calculate bond distances and bond angles between them. This allowed to locate the approximate coordinates of all non-hydrogen atoms. After a number of cycles of least square refinement with the indium and chlorine atoms assigned anisotropic thermal parameters of the form $\exp[-U_{11}\, a^{*2}h^2 + U_{22}\, b^{*2}k^2 + U_{33}\, c^{*}\ell^2 + 2U_{12}\, a^{*}\, b^{*}\, hk + 2U_{13}\, a^{*}c^{*}h\ell + 2U_{23}\, b^{*}c^{*}k\ell]$ and the other atoms isotropic, lead to a discrepancy index R = 5.7% and WR = 7.4%.

An electron density difference Fourier synthesis, computed at this stage, allowed to locate all hydrogen atoms, except those bonded to the C(12) and C(15), i.e., the methyl hydrogens. Two further least square refinement with all toms anisotropic except C(12) and C(15) and the hydrogen atoms,gave a residual index R = 4.7% and WR = 5.7%. A new difference Fourier function allowed to locate two methyl hydrogen atoms,whereas the other four were calculated from the coordinate position of the carbon atoms to which they have to be bonded and the previously found methyl hydrogen atoms. An examination of bond lengths and bond angles indicated that the calculated hydrogens were reasonable.

Further full matrix least square refinement with all non-hydrogen atoms anisotropic gave a final residual index R = 4.3% and WR = 5.0%. At no time the position or temperature factors of the hydrogen atoms were refined directly, although their positions were periodically redetermined as the carbon atom positions were refined.

An electron density difference map computed after refinement showed no positive or negative peak greater than 0.4 $e/\mathring{A}^3$.

The final atomic coordinates and temperature factors are listed in table 47 and the structure factors are given in table 48.

TABLE 47

Final factional coordinates and thermal parameters$^{(a,b,c)}$

Atom	X	Y	Z	U
In	0.19230(3)	0.28606(2)	0.30890(2)	
Cl(1)	0.4060(1)	0.1977(1)	0.4398(1)	
Cl(2)	0.1328(2)	0.1594(1)	0.1643(1)	
N(1)	0.2398(4)	0.4389(3)	0.4130(3)	
N(2)	0.3035(4)	0.4091(3)	0.2583(3)	
O(1)	0.0918(3)	0.2130(3)	0.3845(3)	
O(2)	0.0025(3)	0.3731(3)	0.2116(3)	
C(1)	0.1925(5)	0.4530(4)	0.4806(4)	
C(2)	0.2121(6)	0.5489(4)	0.5370(4)	
C(3)	0.2850(6)	0.6306(4)	0.5256(4)	
C(4)	0.3347(6)	0.6162(4)	0.4554(4)	
C(5)	0.3099(4)	0.5194(3)	0.3996(3)	
C(6)	0.3548(4)	0.4994(4)	0.3210(3)	
C(7)	0.4426(5)	0.5683(4)	0.3096(4)	
C(8)	0.4747(5)	0.5466(5)	0.2300(5)	
C(9)	0.4202(6)	0.4570(5)	0.1659(5)	
C(10)	0.3359(5)	0.3900(4)	0.1829(4)	
C(11)	-0.0339(5)	0.2166(4)	0.3548(4)	
C(12)	-0.0761(6)	0.1402(5)	0.4136(5)	
C(13)	-0.1301(5)	0.2839(4)	0.2738(4)	
C(14)	-0.1090(5)	0.3578(4)	0.2087(4)	
C(15)	-0.2260(6)	0.4240(5)	0.1267(5)	
H(1)	0.144	0.395	0.491	53
H(2)	0.174	0.557	0.582	61
H(3)	0.299	0.697	0.564	63
H(4)	0.387	0.673	0.447	58

H(7)	0.480	0.630	0.355	57
H(8)	0.534	0.593	0.220	71
H(9)	0.441	0.440	0.111	67
H(10)	0.299	0.327	0.140	55
H(12a)	-0.018	0.157	0.489	68
H(12b)	-0.169	0.151	0.393	68
H(12c)	-0.064	0.065	0.401	68
H(13)	-0.221	0.279	0.261	53
H(15a)	-0.188	0.488	0.115	70
H(15b)	-0.279	0.386	0.060	70
H(15c)	-0.288	0.445	0.151	70

Table 47 (continued)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
In	422(2)	374(2)	398(2)	-14(1)	235(1)	-7(1)
Cl(1)	439(6)	495(7)	666(8)	23(5)	183(6)	67(6)
Cl(2)	980(11)	643(8)	549(8)	-101(8)	405(8)	-203(7)
N(1)	48(2)	38(2)	45(2)	-6(2)	28(2)	-2(2)
N(2)	45(2)	47(2)	46(2)	3(2)	28(2)	5(2)
O(1)	54(2)	54(2)	58(2)	0(2)	33(3)	8(2)
O(2)	53(2)	53(2)	60(2)	7(2)	27(2)	11(2)
C(1)	69(3)	48(3)	58(3)	-5(2)	43(3)	-5(2)
C(2)	80(4)	59(3)	64(3)	2(3)	45(3)	-7(3)
C(3)	94(4)	45(3)	67(3)	4(3)	44(3)	-9(3)
C(4)	69(3)	42(2)	65(3)	-6(2)	32(3)	-1(2)
C(5)	41(2)	38(2)	43(2)	2(2)	19(2)	5(2)
C(6)	43(2)	40(2)	43(2)	3(2)	21(2)	7(2)
C(7)	54(3)	59(3)	61(3)	-5(2)	28(3)	11(3)
C(8)	66(4)	84(4)	79(4)	-2(3)	51(3)	20(4)
C(9)	79(4)	81(4)	75(4)	6(3)	58(3)	13(3)
C(10)	67(3)	61(3)	62(3)	3(2)	45(3)	6(2)
C(11)	53(3)	50(3)	52(3)	-13(2)	32(2)	-12(2)
C(12)	63(3)	78(3)	73(3)	-23(3)	40(3)	-3(3)
C(13)	45(3)	57(3)	63(3)	-6(2)	31(2)	-9(3)
C(14)	44(3)	42(2)	56(3)	2(2)	19(2)	-12(2)
C(15)	56(4)	65(4)	76(4)	13(3)	23(3)	4(3)

(a) The estimated standard deviations in the last significant figures are given in parentheses in this subsequent tables

(b) U are in 10^3 A^2

(c) U_{ij} for In,Cl(1) and Cl(2) are in 10^4 A^2,and in 10^3 A^2 for the subsequent atoms.

TABLE 48

Table of observed and calculated structure factors for $In(acac)bipyCl_2$

```
    H   FC   FC                                                      PAGE  1

K=   0, L= -20

    7   10   10
    8   12   12
    9   15   15

K=   1, L= -20

    7   13   12
    8   13   12
    9    8*   8

K=   2, L= -20

    7    4*   8
    8    5*  11
    9   16   16

K=   1, L= -19

    3    1*   1
    4    1*   3
    5    4*   7
    6    4*   1
    7    1*   3
    8    5*   5
    9    6*   2
   10    6*   5
   11    1*   4
   12    1*   1

K=   2, L= -19

    4    7*   7
    5    1*   7
    6    9*  11
    7    7*   5
    8    1*   5
    9   11   11
   10    1*   2
   11    7*   8

K=   3, L= -19

    4   13   13
    5   14   13
    6    4*   4
    7   11   11
    8   10   10
    9    8*   7
   10   17   16
   11    1*   1

K=   4, L= -19

    5   11   11
    6   20   19
    7    4*   5
    8   20   17
    9   15   15
   10    4*   6
   11   15   15

K=   5, L= -19

    6    6*   5
    7   21   22
    8    5*  11
    9   15   13
   10   13   14

K=   0, L= -18

    1   13   12
    2   11   11
    3   15   16
    4    4*   2
    5   24   24
    6   28   26
    7   15   14
    8   31   31
    9   19   17
   10   14   15
   11   29   30
   12    1*   1
   13   20   21

K=   1, L= -18

    1    8*  10
    2   11   14
    3    7*   7
    4   18   19
    5   14   12
    6   17   17
    7   24   26
    8    7*   2
    9   23   24
   10   26   26
   11    4*   7
   12   23   22
   13    8*   6

K=   2, L= -18

    2    1*   6
    3   12   14
    4    1*   1
    5   20   20
    6   21   20
    7    1*   7
    8   23   25
    9   11   13
   10   16   16
   11   22   21
   12    6*   2
   13   16   15

K=   3, L= -18

    2   14   15
    3    4*   2
    4   13   17
    5   15   13
    6   12   12
    7   20   21
    8    5*   2
    9   19   19
   10    9   10
   11    4*   6
   12   17   16

K=   4, L= -18

    2    6*   4
    3   13   13
    4    1*   4
    5   12   11
    6   21   19
    7    4*   2
    8   14   15
    9    1*   3
   10    6*   7
   11    9   10
   12    7*   2

K=   5, L= -18

    3    6*   1
    4    7*   8
    5    8*   7
    6    1*   1
    7   10    9
    8    5*   6
    9    1*   2
   10    8*   8
   11    1*   4

    H   FO   FC

K=   6, L= -18

    4    1*   2
    5    1*   5
    6    9    3
    7    1*   5
    8    6*   0
    9    8    5
   10    7*   2
   11    1*   3

K=   7, L= -18

    5    4*   3
    6    1*   2
    7    1*   0
    8    1*   3
    9    1*   1

K=   1, L= -17

    1    7*   5
    2    8*   5
    3    5*   4
    4    1*   4
    5    4*   1
    6    6*   1
    7    8    3
    8    1*   5
    9    9    4
   10    4*   2
   11    1*   2
   12    6*  10
   13    1*   4
   14    9    7

K=   2, L= -17

    1    7*   4
    2   10   12
    3   15   15
    4    4*   3
    5    1*   4
    6    9    8
    7    6*   2
    8    9    9
    9    8    0
   10    9    8
   11   11   11
   12    8*   6
   13   14   14
   14    1*   3

K=   3, L= -17

    1   14   10
    2   18   14
    3    1*   1
    4   17   19
    5    9    9
    6    5*   5
    7   12   12
    8    1*   3
    9   17   17
   10    7*   3
   11   17   14
   11   17   14
   12   15   13
   13    8    2

K=   4, L= -17

    1    8*   5
    2   10   10
    3   25   26
    4    1*   3
    5   19   20
    6    9   12
    7    9    8
    8   21   21
    9    5*   2
   10   16   16
   11   10    8
   12    8*   5
   13   19   19

K=   5, L= -17

    1   19   15
    2   18   18
    3    7*   9
    4   24   27
    5    8*   9
    6   18   17
    7   24   22
    8   11    8
    9   20   21
   10    1*   2
   11   11   14
   12   23   23
   13    7*   2

K=   6, L= -17

    2   17   15
    3   22   21
    4    1*   6
    5   23   23
    6   16   16
    7   15   12
    8   31   31
    9    4*   5
   10   18   20
   11   19   19
   12   11    7

K=   7, L= -17

    2   11    5
    3   15   13
    4   24   24
    5   10    2
    6   16   16
    7   21   21
    8    1*   1
    9   20   22
   10   10   10
   11   16   17

K=   8, L= -17

    3   15   15
    4    1*   5
    5   21   21
    6   13    5
    7   16   16
    8   25   25
    9    1*   5
   10   18   17

K=   9, L= -17

    5    1*   4
    6   14   15
    7   18   16
    8    1*   5

K=   0, L= -16

    1   13   10
    2   33   33
    3   16   16
    4   26   26
    5   43   43
    6   11   11
    7   32   31

    H   FO   FC

    8   37   36
    9    4*   1
   10   30   30
   11   17   18
   12   12   13
   13   23   23
   14    4*   5

K=   1, L= -16

    1   29   28
    2    1*   3
    3   21   21
    4   26   27
    5    8*   7
    6   43   42
    7   23   23
    8   21   20
    9   43   43
   10   10   12
   11   25   25
   12   19   19
   13   10    8
   14   21   23

K=   2, L= -16

    1    1*   3
    2   23   23
    3   17   17
    4   13   14
    5   45   46
    6    9    7
    7   30   30
    8   33   32
    9    1*   2
   10   36   36
   11    6*  12
   12    9   10
   13   13   14
   14    4*   3

K=   3, L= -16

    1   22   19
    2   11   11
    3   10   11
    4   22   23
    5    9    9
    6   34   33
    7   12   11
    8   13   14
    9   26   26
   10    4*   1
   11   18   19
   12   11   12
   13    7*   3
   14   15   17

K=   4, L= -16

    1    1*   5
    2   11   10
    3    1*   8
    4   10    8
    5   16   16
    6    1*   0
    7   21   15
    8   10   12
    9    8    5
   10   21   22
   11   15   13
   12    6*   6
   13   13   12
   14    6*   3

K=   5, L= -16

    1    8*  10
    2    9    7
    3    5*   4
    4    8    4
    5    5*   3
    6   12    9
    7    8    7
    8    6*   9
    9    7*   5
   10    5*   2
   11   15   16
   12    7*   8
   13    1*   8

K=   6, L= -16

    1    4*   3
    2    4*   2
    3    6*   4
    4    5*   1
    5    4*   5
    6    1*   0
    7    8    1
    8    1*   2
    9    5*   4
   10    9    5
   11    1*   3
   12   10    7
   13    1*   2

K=   7, L= -16

    1    1*   1
    2    6*   5
    3    1*   1
    4    1*   3
    5    7*   4
    6    5*   4
    7    7*   3
    8    1*   2
    9    1*   4
   10    4*   0
   11    6*   2
   12    6*   0

K=   8, L= -16

    1    7*   4
    2    1*   1
    3    1*   2
    4    4*   5
    5    9    5
    6    7*   3
    7    1*   4
    8    1*   5
    9    1*   2
   10    9*  11
   11    1*   5

K=   9, L= -16

    3    1*   4
    4    8*   6
    5    6*   4
    6   11   11
    7    6*   1
    8    4*   1
    9   13   11
   10    1*   2

K=  10, L= -16

    4    1*   2
    5   12   11
    6    1*   1
    7    7*  11
    8   14   11

K=   1, L= -15

    H   FO   FC

    1    4*   4
    2    1*   1
    3    8    7
    4    1*   5
    5    3*   1
    6    5*   3
    7    3*   4
    8   12   12
    9   10   10
   10    1*   0
   11   11   11
   12    9   10
   13   10   10
   14    4*   5
   15    7*   1

K=   2, L= -15

    1    1*   1
    2   12   13
    3    1*   2
    4    5*   8
    5    1*   6
    6    7*   6
    7   25   24
    8   11   11
    9   11   12
   10   14   13
   11    4*   1
   12   14   19
   13    8    8
   14    5*   4
   15    4*   8

K=   3, L= -15

    1   18   16
    2    7    1
    3   21   21
    4    8    8
    5    8   10
    6   23   23
    7    6*   7
    8   33   32
    9   18   18
   10   10    9
   11   28   28
   12    5*   8
   13    9    5
   14   16   16

K=   4, L= -15

    1    1*   1
    2   26   25
    3   10    8
    4   20   21
    5   25   26
    6    1*   2
    7   38   38
    8    9   11
    9   13   13
   10   25   26
   11    1*   2
   12   20   22
   13   17   16
   14    7*   3

K=   5, L= -15

    1   25   23
    2    1*   2
    3   29   29
    4   17   18
    5    8*   8
    6   36   34
    7    1*   1
    8   28   29
    9   17   17
   10    5*   7
   11   25   28
   12   13   12
   13   19   18
   14   17   17

K=   6, L= -15

    1    9    7
    2   31   30
    3    9    8
    4   25   25
    5   33   32
    6    5*   3
    7   32   30
    8   16   16
    9   16   18
   10   19   22
   11    7*   4
   12   25   26
   13   14   12

K=   7, L= -15

    1   18   19
    2    8*   2
    3   29   29
    4   24   26
    5    5*   7
    6   31   30
    7   18   16
    8   20   21
    9   23   22
   10    1*   3
   11   29   28
   12    7*   7
   13   18   17

K=   8, L= -15

    1    1*   7
    2   35   33
    3   11    5
    4   24   26
    5   28   29
    6    7*   4
    7   23   25
    8   17   18
    9    8*   5
   10   22   23
   11    5    1
   12   20   21

K=   9, L= -15

    1   23   22
    2    4*   6
    3   29   30
    4   20   16
    5    9    9
    6   25   25
    7    1*   7
    8   20   20
    9   16   17
   10    1*   6
   11   14   15

K=  10, L= -15

    2   14   13
    3    4*   6
    4   13   14
    5   22   20
    6    1*   1
    7   22   21
    8   15   14
    9   11    9

    H   FC   FC

   10    4*   8

K=  11, L= -15

    4   11    9
    5    7*   6
    6   12   10
    7    1*   1
    8    7*  11

K=   0, L= -14

    1   40   39
    2   55   59
    3   22   23
    4   44   45
    5   24   24
    6    8    4
    7   45   43
    8   28   28
    9   42   41
   10   27   29
   11    6*  10
   12   31   32
   13   13   13
   14   25   26
   15   13   12

K=   1, L= -14

    1   31   30
    2    1*   2
    3   45   47
    4   21   23
    5   37   37
    6   36   34
    7    1*   3
    8   45   44
    9   24   24
   10   30   30
   11   34   34
   12    8*   8
   13   26   27
   14   16   17
   15    7*   8

K=   2, L= -14

    1   31   29
    2   36   38
    3    6*   9
    4   39   41
    5   28   29
    6   22   24
    7   41   39
    8    9    9
    9   35   35
   10   25   25
   11    4*   6
   12   24   24
   13   11   10
   14   11   14
   15   20   19

K=   3, L= -14

    1   19   17
    2   11   12
    3   32   34
    5   34   34
    6   35   33
    7    6*   9
    8   41   41
    9   14   13
   10   22   21
   11   30   31
   12   10    8
   13   14   17
   14   12   14
   15    6*   6

K=   4, L= -14

    1   10    9
    2   13   13
    3    1*   2
    4   26   29
    5   19   19
    6   22   21
    7   33   33
    8    6*   5
    9   26   26
   10   26   25
   11    5*   1
   12   17   16
   13    4*   8
   14   10   13
   15   11    9

K=   5, L= -14

    1    6*   4
    2    9    6
    3    1*   4
    4    5*   2
    5   17   17
    6   15   15
    7    3*   3
    8   20   20
    9   13   14
   10   11   12
   11   17   17
   12    9    8
   13    9    9
   14    6*   5

K=   6, L= -14

    1    4*   1
    2    6*   1
    3    1*   3
    4    7*   9
    4    8    9
    5    1*   3
    6   16   15
    7   15   14
    8    3*   2
    9   11   10
   10   12   13
   11    4*   1
   12    4*   7
   13    6*   0
   14    4*   2

K=   7, L= -14

    1    8    3
    2    6*   1
    3    1*   2
    4   13   11
    5    1*   2
    6    1*   1
    7    5*   8
    8    1*   1
    9    7    4
   10    1*   2
   11    8*   7
   12    6*   5
   13    1*   1

K=   8, L= -14

    1    1*   1
    2    4*   1
    3   11   11
    4   19   19
    5    6*   9

    H   FO   FC

    6    1*   2
    7   10    7
    8    1*   5
    9    9    8
   10   10    7
   11    4*   1
   12    6*   5
   13    8    2

K=   9, L= -14

    1    8*   6
    2    6*   3
    3   17   18
    4    1*   1
    5   11   14
    6   12   10
    7    1*   2
    8   12   13
    9   13   13
   10   12   10
   11   15   14
   12    7*   4

K=  10, L= -14

    1   10   11
    2   13   12
    3    4*   7
    4   19   18
    5    4*   3
    6   12   13
    7   20   17
    8    8*   5
    9   20   17
   10    9*  11
   11    1*   1

K=  11, L= -14

    1    9    5
    2    1*   5
    3   13   13
    4    4*   2
    5   20   21
    6   12   13
    7    6*   3
    8   20   22
    9    7*   8
   10    9*  11

K=  12, L= -14

    4   15   14
    5    7*   7
    6   10   10
    7   19   19
    8    1*   6

K=   1, L= -13

    1   11    8
    2   14   13
    3    9   10
    4    7    6
    5   24   22
    6   17   15
    7    7*   8
    8   25   26
    9   16   16
   10   14   13
   11    8*   9
   12    5*   4
   13    1*   6
   14    1*   0
   15    9    4

K=   2, L= -13

    1   22   21
    2   18   19
    3   20   22
    4   35   38
    5   15   13
    6   35   34
    7   24   22
    8   18   18
    9   18   17
   10   16   17
   11   16   15
   12   13   14
   13    4*   4
   14    8    9
   15    6*   6

K=   3, L= -13

    1    6*   1
    2   27   26
    3   11   14
    4   11    9
    5   50   50
    6   23   23
    7   26   28
    8   40   39
    9   22   23
   10   20   18
   11   21   21
   12    7    5
   13   11   12
   14    8*  11
   15   11    8

K=   4, L= -13

    1   40   38
    2    6*   7
    3   30   32
    4   45   47
    5   14   15
    6   42   39
    7   41   43
    8    7    8
    9   28   28
   10   21   21
   11   20   20
   12   16   18
   13    4*   1
   14   18   16
   15   13   14

K=   5, L= -13

    1   15   14
    2   38   38
    3   23   23
    4    6*   3
    5   44   44
    6   37   36
    7   33   32
    8   40   40
    9   18   17
   10   31   30
   11   20   22
   12    8*   7
   13   21   23
   14   14   14

K=   6, L= -13

    1   27   26
    2   14   14
    3    9   10
    4   37   37
    5   38   39
    6   42   41
    7   34   34
```

```
   H   FO   FC
   8   6*    5
   9   40   40
  10   22   22
  11   14   15
  12   20   22
  13   4*    2
  14   21   21

K=   7, L= -13

   1   22   21
   2   16   17
   3   37   39
   4   6*    7
   5   46   46
   6   24   23
   7   18   21
   8   31   31
   9    5    9
  10   26   29
  11   24   24
  12   16   15
  13   25   25
  14   9*   11

K=   8, L= -13

   1   24   24
   2   29   30
   3   14   15
   4   32   33
   5   7*    9
   6   20   21
   7   24   22
   8    5    8
   9   27   27
  10   18   17
  11   22   23
  12   15   19
  13   7*    2

K=   9, L= -13

   1   19   17
   2   23   22
   3   20   20
   4   4*    2
   5   15   19
   6   17   18
   7   13   12
   8   22   22
   9    8    6
  10   17   17
  12    9    8

K=  10, L= -13

   1   21   20
   2   19   19
   3   1*    5
   4   25   25
   5   11   11
   6   10   11
   7   17   17
   8   1*    1
   9   14   15
  10   1*    4
  11   7*   10
  12   16   15

K=  11, L= -13

   1   7*    4
   2   6*    6
   3   17   16
   4   4*    1
   5   16   15
   6   14   14
   7   10    8
   8   18   20
   9   1*    5
  10   11   11

K=  12, L= -13

   1   6*    7
   2   11    9
   3   6*    7
   4   13   14
   5    9    9
   6   8*    6
   7   13   12
   8   1*    1
   9   1*    8

K=  13, L= -13

   4   7*    3
   5   4*    5
   6   1*    3

K=   0, L= -12

   1   55   58
   2   51   54
   3   31   33
   4   47   47
   5   13   15
   6   60   58
   7   43   42
   8   42   43
   9   35   35
  10   1*    1
  11   53   53
  12   35   38
  13   14   14
  14   26   25
  15   13   10

K=   1, L= -12

   1   29   29
   2   47   51
   3   51   54
   4   25   26
   5   40   40
   6   11    8
   7   62   58
   8   47   46
   9   23   22
  10   61   61
  11   38   38
  12   24   23
  13   29   31
  14   1*    1
  15   13   15

K=   2, L= -12

   1   38   37
   2   41   43
   3   25   30
   4   40   42
   5   5*    1
   6   46   43
   7   36   34
   8   30   29
   9   40   41
  10   3*    1
  11   35   33
  12   34   36
  13   11   12
  14   20   22
  15   10   12

K=   3, L= -12
```

```
   H   FO   FC
   1   15   16
   2   34   38
   3   27   31
   4   14   16
   5   27   27
   6   24   23
   7   30   33
   8   39   39
   9   19   19
  10   25   24
  11   23   23
  12   13   13
  13   21   20
  14   5*    4
  15   7*   12

K=   4, L= -12

   1   45   46
   2   12   11
   3   36   39
   4   27   30
   5   13   14
   6   28   26
   7   32   34
   8   23   24
   9   33   34
  10    8    6
  11   17   18
  12   14   14
  13   5*    3
  14   14   15
  15   1*    4

K=   5, L= -12

   1   1*    1
   2   33   33
   3   31   32
   4   3*    1
   5   55   55
   6   21   21
   7   26   26
   8   23   24
   9   3*    4
  10   15   20
  11    7    6
  12   5*    6
  13   15   13
  14   14    2
  15    9    9

K=   6, L= -12

   1   10   10
   2   6*    5
   3   10    8
   4   33   34
   5    9    9
   6   18   16
   7   7*    3
   8   6*    5
   9    8    8
  10   6*    7
  11   4*    5
  12   1*    5
  13   4*    2
  14   1*    2

K=   7, L= -12

   1   7*    8
   2   5*    2
   3   1*    1
   4   14   14
   5   5*    0
   6   6*    7
   7    9   10
   8   1*    0
   9   7*    9
  10   4*    0
  11   1*    2
  12   4*    2
  13   8*    5
  14   4*    1

K=   8, L= -12

   1   5*    8
   2   13   13
   3   10   10
   4   11   14
   5   1*    1
   6   6*    1
   7   6*    5
   8   15   14
   9   7*    7
  10   4*    4
  11   5*    5
  12   4*    5
  13   6*    3

K=   9, L= -12

   1   5*    4
   2   20   20
   3   21   22
   4   11   11
   5   12   14
   6   16   15
   7   13   12
   8   11   10
   9   10    4
  10    9    7
  11   14    7
  11   8*    7
  12   11    8
  13   8*    8

K=  10, L= -12

   1   20   19
   2   15   15
   3   21   21
   4   18   17
   5   1*    3
   6   15   14
   7   17   16
   8   7*    7
   9   11   14
  10   7*    6
  11   13    9
  12   18   17

K=  11, L= -12

   1   1*    3
   2   25   24
   3   20   20
   4   16   16
   5   21   23
   6    9   11
   7   12   12
   8   17   20
   9   1*    1
  10   14   12
  11   17   15

K=  12, L= -12

   1   22   19
   2   14   13
   3   19   17
   4   25   24
   5   7*    0
   6   23   24
   7   20   20
```

```
   H   FO   FC
   8   10    9
   9   17   17
  10   1*    2

K=  13, L= -12

   1   1*    1
   2   21   21
   3   13   14
   4   10   10
   5   21   21
   6   4*    9
   7   19   18
   8   21   22

K=   1, L= -11

   1    9    7
   2   16   15
   3   22   22
   4   28   28
   5   35   33
   6   5*    1
   7   16   16
   8   1*    2
   9   1*    5
  10    8    7
  11    7    4
  12   10    5
  13   5*    3
  14   1*    2
  15   1*    5

K=   2, L= -11

   1   46   47
   2   16   17
   3   33   35
   4   38   40
   5   18   17
   6   42   40
   7    9    6
   8   1*    2
   9   19   19
  10    9    8
  11   14   14
  12   6*    5
  13   10   11
  14   12   12
  15   6*    5

K=   3, L= -11

   1   11   10
   2   31   33
   3   40   42
   4   46   49
   5   67   68
   6   10   10
   7   12   13
   8   36   35
   9   6*    5
  10   27   28
  11    7    5
  12   13   13
  13   19   18
  14    5    5
  15   10   10

K=   4, L= -11

   1   44   43
   2   3*    1
   3   28   28
   4   56   55
   5   18   16
   6   28   29
   7   44   45
   8   25   26
   9   46   47
  10    7    6
  11   20   20
  12   12   11
  13   16   14
  14   21   22
  15   1*    0

K=   5, L= -11

   1   38   36
   2   47   45
   3    8    4
   4   36   37
   5   51   51
   6   12   13
   7   55   55
   8   52   53
   9   26   25
  10   40   39
  11   5*    1
  12   14   14
  13   24   23
  14   8*    6
  15   18   18

K=   6, L= -11

   1   41   38
   2   1*    2
   3   54   57
   4   48   50
   5   38   38
   6   69   66
   7   1*    3
   8   45   45
   9   51   52
  10   12   12
  11   25   27
  12   13   12
  13   18   18
  14   24   25

K=   7, L= -11

   1   15   14
   2   32   31
   3   20   21
   4   52   54
   5   55   56
   6   22   21
   7   51   50
   8   37   39
   9   25   24
  10   39   40
  11    8    7
  12   24   22
  13   17   19
  14   7*    6

K=   8, L= -11

   1   26   25
   2    7    2
   3   28   28
   4   25   26
   5   30   31
   6   39   38
   7    5    8
   8   32   34
   9   37   38
  10   1*    1
  11   27   26
  12   15   14
  13   14   12
  14   20   21

K=   9, L= -11
```

```
   H   FO   FC
   1   1*    1
   2   21   18
   3   3*    3
   4   29   29
   5   37   37
   6   7*    9
   7   35   34
   8   20   21
   9   17   13
  10   32   31
  11    9    9
  12   17   16
  13   17   17

K=  10, L= -11

   1   25   25
   2   4*    5
   3   16   15
   4   13   14
   5   10   12
   6   28   27
   7   7*    9
   8   20   21
   9   19   22
  10   1*    3
  11   20   21
  12   7*    8

K=  11, L= -11

   1   1*    2
   2   15   16
   3   1*    4
   4   15   17
   5   17   18
   6   1*    0
   7   20   20
   8   5*    8
   9   8*    7
  10   17   16
  11   6*    1

K=  12, L= -11

   1   18   19
   2   1*    2
   3   13   13
   4   5*    5
   5   4*    4
   6   17   14
   7   4*    3
   8   11   10
   9    8    6
  10   1*    5

K=  13, L= -11

   1   6*    0
   2   13   11
   3   1*    1
   4   1*    1
   5   7*    5
   6   10    6
   7   1*    7
   8   6*    1
   9   4*    3

K=  14, L= -11

   2   1*    3
   3   1*    2
   4   6*    4
   5   6*    4
   6   1*    1
   7   1*    0

K=   0, L= -10

   1   66   65
   2   52   54
   3   91   92
   4   34   33
   5   74   73
   6   97   92
   7   25   23
   8   62   61
   9   12   10
  10   21   21
  11   71   72
  12   12   11
  13   22   24
  14   23   24
  15    9    5

K=   1, L= -10

   1   48   48
   2   66   71
   3   27   30
   4   78   79
   5   84   79
   6   65   60
   7  105  101
   8    8    5
   9   32   32
  10   56   56
  11    7    5
  12   34   37
  13   17   15
  14   12   12
  15   21   21

K=   2, L= -10

   1   58   57
   2   28   30
   3   74   80
   4   36   37
   5   45   41
   6   77   74
   7   13   12
   8   39   29
   9   45   45
  10   37   37
  11   52   54
  12   1*    5
  13   23   24
  14   21   21
  15   1*    4

K=   3, L= -10

   1   47   48
   2   62   69
   3   15   16
   4   34   37
   5   44   42
   6   5*    4
   7   57   56
   8   37   38
   9   38   38
  10   41   41
  11   12   11
  12   34   35
  13    9   12
  14   4*    6
  15   19   19

K=   4, L= -10

   1   41   40
   2   23   23
   3   32   35
   4   24   24
   5    8    8
```

```
   H   FO   FC
   6   46   45
   7   1*    1
   8   52   52
   9    8    9
  10   23   22
  11   23   23
  12   1*    4
  13   13   15
  14   14   15
  15   1*    3

K=   5, L= -10

   1   22   21
   2   68   65
   3    9    9
   4   24   23
   5   15   13
   6   12   11
   7    8    8
   8   11   12
   9    9    9
  10    8    6
  11   12   13
  12   14   15
  13   1*    5
  14   5*    7
  15   7*    5

K=   6, L= -10

   1   14   14
   2   21   20
   3   23   23
   4   23   24
   5   15   16
   6   10   10
   7   5*    3
   8   1*    1
   9   3*    2
  10   3*    3
  11   10    6
  12   6*    3
  13   10    8
  14   1*    2

K=   7, L= -10

   1   1*    2
   2    9    8
   3   25   25
   4   5*    1
   5    9   11
   6   13   13
   7   1*    2
   8   4*    3
   9   6*    3
  10   7*    7
  11   1*    5
  12   4*    1
  13   1*    3
  14   7*    4

K=   8, L= -10

   1   10    9
   2   15   12
   3   5*    8
   4   6*    2
   5    9   11
   6   16   12
   7    9   10
   8   10   13
   9   7*    5
  10   1*    2
  11    9    9
  12   4*    5
  13   1*    1
  14   6*    5

K=   9, L= -10

   1   14   15
   2   33   33
   3   3*    5
   4    8    8
   5   22   23
   6   1*    7
   7   17   16
   8   5*    2
   9   1*    3
  10   11   14
  11   8*    6
  12   11   12
  13   6*    7

K=  10, L= -10

   1   26   27
   2   1*    5
   3   18   17
   4   18   18
   5   6*    4
   6   28   30
   7   10    9
   8   13   12
   9    5   11
  10   7*    7
  11   17   18
  12   1*    4

K=  11, L= -10

   1   16   17
   2   31   30
   3    8    8
   4   18   17
   5   30   30
   6   5*    3
   7   20   22
   8    8    5
   9   8*   10
  10   19   17
  11   1*    3
  12   20   20

K=  12, L= -10

   1   27   29
   2   1*    6
   3   32   32
   4   15   14
   5   12   14
   6   20   22
   7   4*    1
   8   14   16
   9   10    9
  10   12   13
  11   24   23

K=  13, L= -10

   1   18   19
   2   26   27
   3   4*    6
   4   22   20
   5   21   20
   6   6*    8
   7   26   27
   8   8*    6
   9   16   15

K=  14, L= -10

   1   17   18
   2   11   11
   3   24   25
```

```
   H   FO   FC
   4   10   11
   5   15   12
   6   18   20
   7   1*    1
   8   18   16

K=   1, L=  -9

   1   13   13
   2    6    1
   3   1*    2
   4   17   17
   5   15   12
   6    7    6
   7   19   19
   8   35   35
   9   18   18
  10   4*    6
  11   12   15
  12   12   12
  13   1*    2
  14   1*    4
  15   1*    4

K=   2, L=  -9

   1   24   24
   2   28   30
   3   27   31
   4   1*    2
   5   23   23
   6   23   22
   7   27   25
   8    6    6
   9   20   20
  10   11   10
  11   19   21
  12   7*    6
  13   23   24
  14   7*    7
  15   1*    5

K=   3, L=  -9

   1   5*    4
   2   56   61
   3   4*    3
   4   42   44
   5   3*    1
   6   21   21
   7   32   30
   8   10    8
   9   56   56
  10   34   33
  11    9    8
  12   24   25
  13   1*    1
  14   13   16
  15   8*    6

K=   4, L=  -9

   1   60   59
   2    7    6
   3   64   68
   4   3*    1
   5   54   55
   6   36   35
   7   13   13
   8   83   83
   9   1*    3
  10   42   42
  11   35   33
  12   10   11
  13   29   30
  14    9    8
  15    9    7

K=   5, L=  -9

   1   49   47
   2   71   68
   3   13   12
   4   63   62
   5   24   22
   6   27   25
   7   77   76
   8   12    9
   9   56   55
  10   23   23
  11   11   11
  12   31   33
  13   1*    3
  14   16   17
  15   6*   10

K=   6, L=  -9

   1   38   36
   2   29   27
   3   70   72
   4   32   34
   5   41   39
   6   28   28
   7   19   18
   8   68   69
   9   22   23
  10   27   28
  11   29   30
  12   1*    1
  13   26   26
  14   1*    7

K=   7, L=  -9

   1   55   54
   2   64   63
   3   25   26
   4   96  100
   5   13   13
   6   44   45
   7   59   57
   8   1*    1
   9   43   43
  10   20   19
  11   6*    6
  12   28   29
  13    9    1
  14   13   15

K=   8, L=  -9

   1   20   23
   2   28   27
   3   50   51
   4   1*    2
   5   64   66
   6   48   48
   7   29   28
   8   61   61
   9   13   14
  10   23   22
  11   32   30
  12   4*    2
  13   21   23
  14   8*   10

K=   9, L=  -9

   1   37   36
   2   28   27
   3   23   24
   4   53   53
   5   32   34
   6   34   33
   7   49   50
   8   7*    2
```

```
   H    FO    FC

K=    9, L=   -9

   9    37    35
  10    26    25
  11     1*    5
  12    15    17
  13     6*    3

K=   10, L=   -9

   1    15    16
   2    14    14
   3    26    28
   4     7*    1
   5    43    43
   6    26    26
   7    14    14
   8    26    29
   9     5*    6
  10    19    20
  11    19    19
  12     6*    4

K=   11, L=   -9

   1    15    18
   2     6*    9
   3    13    13
   4    21    22
   5     1*    1
   6    17    16
   7    16    16
   8     1*    1
   9    21    22
  10    16    16
  11    11     8
  12     7*    6

K=   12, L=   -9

   1     8*   10
   2     6*    9
   3     4*    3
   4     1*    1
   5     9     9
   6     6*    6
   7     5*    6
   8     4*    4
   9     6*    3
  10     6*   10
  11     4*    2

K=   13, L=   -9

   1     9     7
   2     4*    1
   3     1*    4
   4     4*    2
   5     5*    4
   6     5    11
   7     6*    0
   8     7*    4
   9     1*    4
  10     4*    3

K=   14, L=   -9

   1     1*    6
   2     7*    1
   3     7*    3
   4     7*    5
   5     1*    1
   6     4*    3
   7     1*    2
   8     8     2

K=   15, L=   -9

   1     8*    5
   2     1*    2
   3    10     8
   4     7*    7
   5     1*    2
   6     1*    1

K=    0, L=   -8

   1    51    51
   2    92    97
   2    55    97
   3    71    70
   4    25    23
   4    25    23
   5   135   138
   6    57    55
   7    35    34
   8    74    75
   9    12    11
  10    30    31
  11    20    20
  12    10     9
  13    35    40
  14     7*   10
  15    27    26

K=    1, L=   -8

   1   113   115
   2    23    24
   3    67    84
   4   175   172
   5    43    63
   6    57    56
   7    55    52
   8     4*    2
   9    56    56
  10    14    14
  11    34    33
  12    24    27
  13     4*    1
  14    31    31
  15     4*    7

K=    2, L=   -8

   1     5*    5
   2   108   106
   4    23    21
   5   119   116
   6    34    33
   7    54    52
   8    63    63
   9    20    20
  10    74    77
  11    10    11
  12    23    25
  13    27    27
  14     6*    5
  15    18    18

K=    3, L=   -8

   1    53    54
   2    15    19
   3    37    46
   4    51    89
   5     2*    1
   6    31    33
   7    61    58
   8     5*    1
   9    56    55
  10     3*    4
  11    43    43
  12    22    21
  13     5*    8
  14    16    18
  15     6*    8

   H    FO    FC

K=    4, L=   -8

   1     3*    1
   2    46    44
   3    35    39
   4    16    15
   5    45    53
   6     9     5
   7    47    45
   8    40    38
   9     4*    4
  10    33    33
  11    20    20
  12    13    13
  13    20    20
  14     4*    4
  15     6*    8

K=    5, L=   -8

   1    18    18
   2    23    21
   3    13    14
   4     7     6
   5     9     8
   6    27    26
   7    23    24
   8     6     5
   9    19    18
  10     7     2
  11    19    19
  12    16    14
  13     1*    0
  14    11    11
  15     1*    4

K=    6, L=   -8

   1    10    12
   2     5*    5
   3     1*    1
   4    14    14
   5     7     6
   6    13    12
   7    15    13
   8    11    11
   9     9     8
  10     7     5
  11    14    13
  12     4*    3
  13     6*    8
  14     1*    3

K=    7, L=   -8

   1    18    17
   2     4*    0
   3     5*    3
   4     8     6
   5     4*    0
   6    11     5
   7    10     8
   8    28    28
   9     9     7
  10     7     1
  11     3*    2
  12     1*    4
  13     1*    3
  14     1*    0

K=    8, L=   -8

   1    17    18
   2    10    10
   3    17    16
   4     8     7
   5    27    26
   6    20    20
   7     6*    9
   8    11    10
   9    11    14
  10    11     8
  11     1*    4
  12     1*    0
  13     7*    4
  14     1*    5

K=    9, L=   -8

   1    26    28
   2     1*    3
   3     1*    3
   4    25    27
   5     4*    1
   6    40    38
   7     9    11
   8     1*    4
   9    16    15
  10     5*    2
  11    11    12
  12     5     6
  13     6*    4

K=   10, L=   -8

   1     6*    2
   2    21    21
   3    14    13
   4     6*    1
   5    40    39
   6     7     8
   7    34    33
   8    23    23
   9     6*    1
  10    25    26
  11     8*    7
  12     1*    4
  13    18    16

K=   11, L=   -8

   1    27    27
   2     7     6
   3    14    13
   4    37    39
   5     3*    0
   6    30    32
   7    14    13
   8     6*    7
   9    28    27
  10     8*    5
  11    16    16
  12    12    12

K=   12, L=   -8

   1     6*    4
   2    25    24
   3    19    18
   4    10     8
   5    29    25
   6     1*    4
   7    16    15
   8    27    25
   9     1*    2
  10    24    24
  11     9     7

K=   13, L=   -8

   1    26    26
   2    11    10
   3    18    19
   4    28    29
   5     1*    4
   6    27    23

   H    FO    FC

   7    16    15
   8     4*    5
   9    21    20
  10     7*    7

K=   14, L=   -8

   1     4*    3
   1     1*    2
   2    21    23
   3    18    21
   5    22    24
   6    11    10
   7    17    15
   8    16    17
   9     6*    0

K=   15, L=   -8

   1    23    23
   2    13    13
   3    15    18
   4    19    21
   5     1*    2
   6    19    18
   7    15    15

K=    1, L=   -7

   1     9     7
   2    54    51
   3    13     5
   4    23    23
   5     6     4
   6    35    37
   7    11    10
   8    36    36
   9     7     7
  10     9     5
  11     9     8
  12    18    19
  13     6*    3
  14     7*    5
  15     4*    4

K=    2, L=   -7

   2    47    48
   4    23    24
   6    11    11
   7    57    59
   8    15    19
   9    15    14
  10    43    44
  11    21    20
  12    12    12
  13    15    14
  14     7*    2
  15    11    11

K=    3, L=   -7

   1    46    45
   2     1*    3
   3    90    89
   4    10     6
   5    22    23
   6    87    88
   7    14    13
   8    66    65
   9    43    44
  10    10     5
  11    36    35
  12     6*    5
  13     7*    9
  14    11    12
  15     8*    7

K=    4, L=   -7

   1     9     9
   2    58    96
   4    61    60
   5    57    57
   6     9     5
   7    89    86
   8    22    21
   9    34    34
  10    48    48
  11    23    24
  12    31    30
  13    10     5
  14     1*    2
  15    10    10

K=    5, L=   -7

   1   117   114
   2    46    45
   3    66    69
   4    36    35
   5    17    16
   6    55    52
   7    20    20
   8    47    47
   9    39    40
  10    13    13
  11    46    48
  12    16    15
  13    16    17
  14    13    14
  15     4*    4

K=    6, L=   -7

   1    10    10
   2    55    88
   3    37    37
   4    46    44
   5    70    69
   6    21    19
   7    79    76
   8    36    35
   9    17    16
  10    56    55
  11    20    21
  12    24    27
  13    20    21
  14     4*    0

K=    7, L=   -7

   1   113   112
   2    51    48
   3    58    58
   4    51    50
   5     6*    5
   6    53    50
   7    28    27
   8    31    30
   9    35    36
  10     2*    1
  11    36    37
  12    17    17
  13    15    14
  14    17    15

K=    8, L=   -7

   1     7     7
   2    73    68
   3    37    37
   4    26    26
   5    62    61
   6     8    10
   7    57    57
   8    20    20

   H    FO    FC

   9    23    22
  10    32    24
  11    13    15
  12    18    20
  13    18    16
  14     4*    1

K=    9, L=   -7

   1    76    75
   2    22    22
   3    49    50
   4    51    50
   5     4*    9
   6    54    55
   7    16    14
   8    40    41
   9    21    21
  10    10     5
  11    20    20
  12     9     8
  13    10    11

K=   10, L=   -7

   1     6*    9
   2    50    48
   3    28    28
   4    30    30
   5    31    30
   6     3*    1
   7    21    21
   8    25    22
   9    17    17
  10    28    28
  11     8*    5
  12     9*   13

K=   11, L=   -7

   1    21    19
   2     9     5
   3    21    23
   4    27    27
   5    14    14
   6    18    16
   7    15    13
   8     5     5
   9    24    25
  10     7*    0
  11    11    10
  12     8*    5

K=   12, L=   -7

   1    12    10
   2     6*    8
   3    10     9
   4    11    11
   5    15    15
   6     1*    3
   7     5     8
   8     9    10
   9     5*    6
  10    12    13
  11     6*    4

K=   13, L=   -7

   1     4*    1
   2     5*    2
   3     5*    2
   4     1*    4
   5    17    17
   6     8     8
   7     4*    0
   8     1*    4
   9     4*    6
  10     1*    2

K=   14, L=   -7

   1     1*    4
   2     5*   10
   3     5*    2
   4     5*    3
   5     1*    2
   6     6*    6
   7     1*    1
   8     4*    3
   9     1*    5

K=   15, L=   -7

   1     1*    8
   2     1*    0
   3     9     5
   4     1*    2
   5     1*    5
   6     6*    5
   7     7*    3

K=   16, L=   -7

   2    14    13
   3     1*    1
   4     1*    3

K=    0, L=   -6

   1    45    45
   2    85    86
   2    86    86
   3   106   104
   4    59    58
   4   102    58
   5   117   119
   6    14    12
   7    86    85
   8    55    54
   9    70    70
  10    31    29
  11     6*    6
  12    45    49
  13    34    35
  14    20    22
  15    18    19

K=    1, L=   -6

   1    71    72
   2     3*    2
   3   148   145
   4    74    72
   5    48    51
   6    54    60
   7    25    24
   8    90    90
   9    53    51
  10    30    30
  11    26    27
  12     5     8
  13    30    31
  14    19    21
  15     6*    7

K=    2, L=   -6

   2   106   103
   4   157   155
   6    26    26
   7    82    81
   8    41    35
   9    47    48
  10    33    33
  11    15    14
  12    29    29

   H    FO    FC

  13    17    16
  14    12    11
  15    13    12

K=    3, L=   -6

   1    66    66
   2     3*    4
   3   123   119
   4    71    70
   5    80    77
   6    65    66
   7    21    20
   8    50    49
   9    23    23
  10    17    19
  11    33    33
  12    16    14
  13    24    26
  14     9     9
  15     7*    4

K=    4, L=   -6

   2    39    39
   4    50    88
   6    47    45
   7    78    73
   8    44    43
   9    18    18
  10    30    30
  11     7*    8
  12    20    22
  13    11    11
  14    11    11
  15    10     7

K=    5, L=   -6

   1    27    26
   2    53    52
   3    62    61
   4    29    29
   5    47    44
   6    62    61
   7     6     8
   8    19    18
   9    15    16
  10    14    13
  11    20    22
  12     6*    5
  13     4*    7
  14     9    10

K=    6, L=   -6

   1    15    15
   2     7     5
   3    15    15
   4    22    21
   5    26    27
   6     1*    9
   7    40    39
   8    23    24
   9     9     9
  10    19    17
  11     1*    0
  12     5*    3
  13     5*    1
  14     1*    1

K=    7, L=   -6

   1    10     9
   2    20    19
   3     7     7
   4     6     4
   5     9     6
   6    10    10
   7    12     8
   8     1*    1
   9     3*    1
  10     8     5
  11     1*    2
  12     9     5
  13     7*    3
  14     1*    1

K=    8, L=   -6

   1     1*    1
   2     1*    1
   3    22    22
   4    28    27
   5     6     5
   6     1*    5
   7    12    11
   8    34    33
   9    17    16
  10     8*    9
  11     6*    3
  12     4*    7
  13     6*    5

K=    9, L=   -6

   1     7     6
   2     7     8
   3    41    40
   4    21    21
   5    28    27
   6    20    21
   7    13    12
   8    17    17
   9     6*    3
  10     5*    7
  11    10     7
  12    11    11
  13     8*    9

K=   10, L=   -6

   1    23    24
   2    20    19
   3     3*    1
   4    51    51
   5    20    21
   6    15    15
   7    47    45
   8    16    15
   9    19    20
  10     7*    8
  11     6*    5
  12    10     7

K=   11, L=   -6

   1    16    18
   2    15    16
   3    56    57
   4    19    19
   5    32    30
   6    26    26
   7    17    17
   8    33    32
   9    21    22
  10    11    11
  11     6*   13
  12     4*    3

K=   12, L=   -6

   1    19    19
   2    36    35
   3     3*    3
   4    46    47
   5    26    26

   H    FO    FC

   6    16    15
   7    28    30
   8    22    22
   9    16    18
  10    18    19
  11     1*    1

K=   13, L=   -6

   1    16    15
   2    12    11
   3    32    36
   4    19    18
   5    23    24
   6    27    27
   7     1*    4
   8    21    24
   9    20    20
  10     8     4

K=   14, L=   -6

   1    12    15
   2    23    23
   3     1*    4
   4    24    25
   5    19    20
   6     9     6
   7    23    24
   8     8*    9
   9    10    12

K=   15, L=   -6

   1    18    18
   2     1*    4
   3    17    18
   4    12    12
   5    11    11
   6    23    21
   7     4*    2

K=   16, L=   -6

   1     1*    6
   2    15    17
   3     8*    2
   4    11    14
   5    16    15

K=    1, L=   -5

   1     5*    8
   2    78    76
   3    44    44
   4    61    57
   5    42    43
   6    28    27
   7    27    27
   8    20    21
   9    20    21
  10     8     8
  11    12    10
  12     4*    0
  13    11     9
  14     7*    2
  15     1*    4

K=    2, L=   -5

   2    59    57
   4    58    58
   6    30    31
   7    55    55
   8    21    20
   9    26    27
  10    21    20
  11    24    24
  12     7*    6
  13     8     8
  14    10     8
  15     7*   11

K=    3, L=   -5

   1    38    38
   2   104   101
   3   110   109
   4    48    48
   5    61    62
   6    40    41
   7     8     9
   8    38    37
   9    36    37
  10    27    27
  11    21    21
  12     6*    5
  13     5*    5
  14    15    14
  15     7*    6

K=    4, L=   -5

   2   106   101
   4   116   114
   6    70    72
   7    42    40
   8    14    13
   9    34    33
  10    35    35
  11    13    13
  12    21    21
  13     9     7
  14     9    10

K=    5, L=   -5

   1   109   107
   2    83    82
   3    80    78
   4    40    42
   5    93    93
   6    75    80
   7    32    31
   8    26    27
   9    20    21
  10    44    44
  11    38    40
  12     1*    4
  13    21    22
  14    16    14

K=    6, L=   -5

   1   118   123
   2    48    50
   3    15    15
   4    68    66
   5    59    59
   6    74    72
   7    54    52
   8     4*    4
   9    52    50
  10    52    51
  11    22    21
  12    22    23
  13     7*   10
  14    16    15

K=    7, L=   -5

   1    69    68
   2    24    25
   3    54    51
   4    35    33
   5    71    69
   6    58    57
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```
   H   FO   FC
   7   21   19
   8   42   42
   9    4*   9
  10   52   52
  11   28   31
  12    5*   7
  13   18   19
  14   14   16

K=   8, L=  -5

   1   52   50
   2   35   71
   3    1*   3
   4   53   51
   5   34   33
   6   50   50
   7   45   45
   8    9    6
   9   49   50
  10   31   31
  11   12   13
  12   21   22
  13    1*   8

K=   9, L=  -5

   1   51   50
   2   25   23
   3   50   50
   4   16   16
   5   37   37
   6   27   25
   7   25   24
   8   31   30
   9    8    5
  10   20   20
  11   22   23
  12    1*   2
  13   17   16

K=  10, L=  -5

   1   43   45
   2   48   46
   3    5    9
   4   36   36
   5    5*   7
   6   20   20
   7   32   30
   8    1*   4
   9   31   29
  10   12   12
  11    1*   9
  12   13   14

K=  11, L=  -5

   1   27   26
   2   16   16
   3   41   42
   4    1*   0
   5   21   21
   6   15   15
   7    5    8
   8   25   25
   9    8    9
  10   14   15
  11   15   14
  12    4*   3

K=  12, L=  -5

   1    5    8
   2   24   24
   3    1*   0
   4   24   23
   5   10   10
   6    6*   6
   7   14   15
   8    1*   0
   9    1*   8
  10    7*   7
  11    4*   1

K=  13, L=  -5

   1    7    1
   2    7*   1
   3   10   10
   4    1*   4
   5    4*   2
   6   11   10
   7    4*   4
   8    8*  10
   9    1*   6
  10    7*   1

K=  14, L=  -5

   1    4*   1
   2    1*   3
   3    4*   3
   4    1*   5
   5    1*   1
   6    4*   5
   7    6*   6
   8    1*   2
   9    4*   1

K=  15, L=  -5

   1    1*   4
   2    7*   7
   3    6*   2
   4    7*   5
   5    1*   2
   6    4*   3
   7    6*   4

K=  16, L=  -5

   1   13   11
   2    1*   7
   3    1*   3
   4    5    6
   5   12   11

K=   0, L=  -4

   1   36   35
   2  116  113
   2  115  113
   3  128  133
   4   79   80
   4   80   80
   5   16   16
   6  141  142
   7  105  112
   8   56   57
   9   68   69
  10   32   32
  11   35   35
  12   37   40
  13   17   16
  14   14   13
  15    9    7

K=   1, L=  -4

   1   77   74
   2  104  102
   3   83   81
   4   76   75
   5   79   80
   6   51   53
   7  112  111

   H   FO   FC
   8   96   97
   9    1*   1
  10   35   36
  11   37   36
  12   21   23
  13   29   27
  14    4*   6
  15   11   10

K=   2, L=  -4

   2   60   59
   4   59  102
   6   71   72
   7   55   94
   8   30   32
   9   55   56
  10   29   29
  11   18   19
  12   27   29
  13    1*   1
  14   16   13
  15   10   10

K=   3, L=  -4

   1  101   55
   2   65   66
   3  113  111
   4   66   62
   5   84   85
   6   34   35
   7   44   46
   8   58   58
   9    3*   0
  10   27   27
  11   30   30
  12   15   16
  13   23   23
  14    1*   1

K=   4, L=  -4

   2   37   37
   4   83   82
   6   56   54
   7   47   41
   8   19   18
   9   25   24
  10   19   18
  11    9    9
  12   21   20
  13    8    5
  14   10   11

K=   5, L=  -4

   1   35   33
   2   28   28
   3   27   28
   4   30   30
   5   32   32
   6   41   42
   7   13   13
   8   22   22
   9    1*   2
  10   18   19
  11    3*   5
  12   11    9
  13    8*   8
  14    6*   2

K=   6, L=  -4

   2   13   12
   4   65   64
   5   22   22
   6   16   15
   7   21   20
   8    8    7
   9   19   18
  10    5*   6
  11    5*   8
  12    6*   3
  13    1*   0
  14    1*   3

K=   7, L=  -4

   1   17   17
   2   16   14
   3   29   27
   4   17   17
   5   10    9
   6   12   12
   7   10   11
   8    1*   2
   9    6*   6
  10    1*   2
  11   11   10
  12    1*   3
  13    1*   1

K=   8, L=  -4

   1   10    7
   2   23   21
   3   35   35
   4   13   12
   5   12   10
   6   12   11
   7   31   28
   8   21   21
   9   15   13
  10    3*   4
  11    1*   2
  12   10    6
  13    6*   4

K=   9, L=  -4

   1   34   35
   2   23   23
   3   31   30
   4   13   12
   5   11   12
   6   30   30
   7   17   16
   8   17   18
   9    3*   2
  10    8    7
  11   12   13
  12    8*   6
  13    9    7

K=  10, L=  -4

   1   33   33
   2   37   36
   3   33   34
   4   42   42
   5   14   14
   6   21   22
   7   36   35
   8   11   11
   9    9   12
  10   14   13
  11    1*   4
  12   11   13

K=  11, L=  -4

   1   18   20
   2   44   43
   3   46   47
   4   13    5
   5   22   23

   H   FO   FC
   6   26   26
   7   22   22
   8   25   28
   9    1*   3
  10   11    5
  11   11   11

K=  12, L=  -4

   1   36   36
   2   36   37
   3   35   37
   4   34   36
   5    1*   3
   6   25   27
   7   26   25
   8    9    5
   9   15   19
  10   11   11
  11    9*  12

K=  13, L=  -4

   1   20   19
   2   33   32
   3   34   37
   4   11   10
   5   32   31
   6   12   14
   7   18   20
   8   24   24
   9    1*   4
  10   14   14

K=  14, L=  -4

   1   30   32
   2   12   14
   3   14   15
   4   30   29
   5    8    9
   6   22   22
   7   21   24
   8   12   10
   9   20   19

K=  15, L=  -4

   1    4*   2
   2   16   16
   3   16   15
   4    1*   7
   5   26   24
   6    9    9
   7   15   15

K=  16, L=  -4

   1   15   15
   2    7*   6
   3   14   13
   4   18   19
   5    1*   0

K=   1, L=  -3

   1   24   23
   2   26   25
   3   34   33
   4    3*   2
   5    2*   1
   6    5*   6
   7   11   11
   8    9   11
   9    1*   2
  10    4*   4
  11    6*   3
  12    8    7
  13    5*   4
  14    1*   3

K=   2, L=  -3

   2  120  119
   4  103  103
   6   37   36
   7   15   17
   8   16   15
   9   18   19
  10   23   22
  11   21   19
  12   11   11
  13    6*   3
  14   11   10

K=   3, L=  -3

   1   27   26
   2   44   43
   3  145  143
   4   18   19
   5   88   86
   6   11    7
   7   17   16
   8   53   53
   9   23   22
  10   30   30
  11    1*   3
  12    5    5
  13   19   20
  13   13   20
  14    1*   1

K=   4, L=  -3

   2   41   42
   4  122  122
   6   21   22
   7   28   28
   8    4*   2
   9   43   43
  10   14   13
  11   21   21
  12   22   23
  13    8*   7
  14   18   18

K=   5, L=  -3

   1   31   31
   2  123  120
   3   96   96
   4   52   54
   5   85   88
   6    4*   3
   7   33   32
   8   39   37
   9   30   30
  10   46   45
  11   12   12
  12   15   14
  13   28   26
  14    4*   7

K=   6, L=  -3

   2   17   16
   4  126  126
   5   29   31
   6   84   79
   7   55   53
   8   34   34
   9   55   54
  10   10    5
  11   23   23
  12   16   15
  13    7*   8

   H   FO   FC

K=   7, L=  -3

   1   54   54
   2   76   75
   3   75   74
   4   55   55
   5   81   80
   6    6    7
   7   38   37
   8   44   43
   9   34   35
  10   44   44
  11   11    8
  12   11   12
  13   20   20

K=   8, L=  -3

   1   69   66
   2    7    7
   3   81   78
   4   75   74
   5   38   37
   6   81   81
   7   39   37
   8   26   24
   9   47   46
  10    1*   3
  11   22   21
  12   10   13
  13    9    7

K=   9, L=  -3

   1   31   30
   2   76   75
   3   40   39
   4   37   37
   5   64   64
   6    3*   1
   7   39   38
   8   33   33
   9   14   12
  10   30   32
  11    9   10
  12   16   15

K=  10, L=  -3

   1   54   54
   2    5*   5
   3   37   37
   4   31   32
   5   16   15
   6   41   40
   7   20   19
   8   14   16
   9   14   15
  10    1*   3
  11   17   15
  12   12   12

K=  11, L=  -3

   1    5*   7
   2   36   35
   3   18   18
   4   20   19
   5   22   23
   6    6*   4
   7   25   25
   8    5*  10
   9    1*   3
  10   14   14
  11    4*   3

K=  12, L=  -3

   1   38   39
   2   22   21
   3   23   24
   4   12   11
   5    8    6
   6   14   14
   7    1*   4
   8    4*   6
   9    8*   6
  10    1*   0

K=  13, L=  -3

   1    1*   4
   2   12   14
   3    7*   3
   4    7*   6
   5    1*   7
   6    9    8
   7   13   11
   8    1*   2
   9    1*   4
  10    4*   1

K=  14, L=  -3

   1    1*   2
   2    1*   1
   3    5*   0
   4    7*   6
   5   10   11
   6    4*   1
   7    1*   2
   8    1*   3

K=  15, L=  -3

   1   10   10
   2    4*   1
   3    8*   7
   4    4*   5
   5   10   11
   6    9    1
   7    1*   5

K=  16, L=  -3

   1   10   11
   2    1*   3
   3    6*   7
   4   13   12
   5    1*   3

K=  17, L=  -3

   1    4*   4

K=   0, L=  -2

   1  248  239
   2   33   30
   2   33   30
   3  184  154
   4  102  104
   4  101  104
   5   42   44
   6  166  167
   7   13   10
   8   62   61
   9   44   45
  10    5*   8
  11   46   46
  12    1*   1
  13    9   11
  14   12   12

K=   1, L=  -2

   H   FO   FC
   1   93   87
   2  129  125
   3   40   40
   4   60   63
   5  135  135
   6   57   57
   7  116  126
   8   35   36
   9   20   21
  10   59   63
  11    3*   1
  12   24   25
  13   11   12
  14    4*   2

K=   2, L=  -2

   2  105  101
   4   86   89
   6  111  114
   7   19   18
   8   45   46
   9   53   52
  10    3*   4
  11   37   35
  12    1*   3
  13   11   10
  14   18   17

K=   3, L=  -2

   1    4    6
   2  114  117
   3    3*   4
   4   86   93
   5   63   64
   6   26   26
   7   57   55
   8   15   15
   9   28   28
  10   49   48
  11    1*   2
  12   25   24
  14    1*   4

K=   4, L=  -2

   2   11   10
   4   25   24
   6   42   43
   7   13   12
   8   42   41
   9   37   37
  10    1*   5
  11   21   20
  12    5*   2
  13   13   12
  14    6*   7

K=   5, L=  -2

   1   55   58
   2   52   50
   3   28   28
   4   23   23
   5   28   27
   6   10    8
   7   22   21
   8    1*   6
   9   28   28
  10   12   12
  11    3*   4
  12    5*  12
  13    1*   8

K=   6, L=  -2

   2   49   49
   4   15   13
   5   17   16
   6    1*   4
   7    6    1
   8   28   29
   9    7    6
  10   11   12
  11    1*   1
  12    1*   1
  13    1*   2

K=   7, L=  -2

   1    6    5
   2   32   33
   3   11   12
   4   13   12
   5   24   24
   6    1*   0
   7    3*   3
   8    5*   5
   9    6*   4
  10    6*   3
  11    1*   2
  12    1*   2
  13    4*   2

K=   8, L=  -2

   1   20   22
   2   10   11
   3   21   20
   4   20   19
   5    1*   2
   6   28   28
   7    7    6
   8   13   12
   9   13   14
  10    5*   4
  11    5*   6
  12    8*   5

K=   9, L=  -2

   1    5*   6
   2   42   40
   3   13   12
   4    3*   1
   5   32   32
   6    5*   3
   7   17   16
   8    3*   3
   9    6*   5
  10   21   22
  11    7*   6
  12    7*   8

K=  10, L=  -2

   1   63   65
   2   29   28
   3   12   12
   4   13   13
   5    9    8
   6   37   38
   7   14   12
   8   21   19
   9   18   19
  10    1*   1
  11   13   16

K=  11, L=  -2

   1   14   15
   2   28   28
   3   13   11
   4    9    9
   5   33   33
   6   14   14

   H   FO   FC      PAGE  4
   7   31   30
   8    1*   2
   9    8    9
  10   19   19
  11    1*   1

K=  12, L=  -2

   1   49   51
   2   15   14
   3   32   32
   4   19   19
   5   14   14
   6   30   30
   7    1*   2
   8   16   15
   9   16   18
  10    6*   4

K=  13, L=  -2

   1    8*   7
   2   42   43
   3    1*   3
   4   24   25
   5   23   24
   6   13   13
   7   27   27
   8    9*  11
   9   15   11

K=  14, L=  -2

   1   37   38
   2    5*   5
   3   30   32
   4   23   23
   5   16   17
   6   24   27
   7    6*   1
   8   20   20

K=  15, L=  -2

   1   13   11
   2   21   21
   3    1*   2
   4   23   21
   5   16   17
   6    7*   4
   7   20   20

K=  16, L=  -2

   1   13   13
   2    1*   5
   3   20   22
   4   10    9
   5    9    8

K=  17, L=  -2

   1   10    5
   2   11   12

K=   1, L=  -1

   1   78   72
   2    9   13
   3   17   18
   4   19   19
   5   14   13
   6   12   12
   7   50   51
   8    1*   2
   9   19   18
  10    3*   4
  11    3*   2
  12   11   10
  13    4*   1
  14    1*   1

K=   2, L=  -1

   2   32   30
   4   26   27
   6   50   53
   7    5*   6
   8   25   35
   9   15   13
  10   18   17
  11   15   15
  12    4*   2
  13   12   11
  14    1*   2

K=   3, L=  -1

   1    5    5
   2   82   81
   3   52   50
   4   65   63
   5   13   12
   6   39   39
   7   61   62
   8    3*   1
   9   35   36
  10   15   13
  11    1*   1
  12   22   23
  13    5*   5

K=   4, L=  -1

   2    9    8
   4   17   16
   6   54   58
   7   10    9
   8   58   59
   9    7    6
  10   14   15
  11   28   29
  12    7*   2
  13   21   20

K=   5, L=  -1

   1   31   31
   2  123  122
   3   31   32
   4  113  114
   5   27   26
   6   31   32
   7   80   79
   8    6*   2
   9   37   37
  10   22   21
  11    6*   3
  12   29   30
  13    4*   3

K=   6, L=  -1

   2   84   85
   4   18   18
   5   71   68
   6   60   61
   7    3*   2
   8   61   62
   9    8    9
  10   13   12
  11   22   21
  12    4*   3
  13   20   19

K=   7, L=  -1
```

```
  H   FO   FC

K=  7, L=  -1

  1   65   64
  2  114  114
  3   1*    4
  4  115  114
  5   40   40
  6   18   18
  7   74   73
  8   13   11
  9   34   35
 10   15   16
 11   5*    5
 12   22   23

K=  8, L=  -1

  1   47   48
  2   72   73
  3  121  118
  4   18   19
  5   47   46
  6   62   67
  7   3*    5
  8   38   38
  9   10   12
 10   15   17
 11   18   19
 12   7*    3

K=  9, L=  -1

  1   83   82
  2   66   63
  3   25   24
  4   45   43
  5   39   38
  6   23   23
  7   47   46
  8    7    7
  9   21   21
 10   14   14
 11    9    7
 12   19   16

K= 10, L=  -1

  1   22   23
  2   15   14
  3   46   46
  4   27   28
  5   40   40
  6   36   39
  7   1*    3
  8   15   15
  9   5*    5
 10   10   10
 11   18   16

K= 11, L=  -1

  1   28   26
  2   42   41
  3   4*    2
  4   40   42
  5   13   14
  6   22   22
  7   19   19
  8    9    4
  9   13   12
 10   8*   11

K= 12, L=  -1

  1   26   25
  2   18   18
  3   12   13
  4   6*    4
  5   16   16
  6    9   10
  7    5    7
  8   7*    5
  9   1*    4
 10   11   11

K= 13, L=  -1

  1   8*   11
  2   10   11
  3   3*    3
  4   1*    1
  5   1*    4
  6   11   13
  7   4*    1
  8   1*    1
  9   1*    3

K= 14, L=  -1

  1   5*    3
  2   1*    4
  3   12   11
  4   1*    3
  5   1*    1
  6   4*    4
  7   7*    6
  8   6*    2

K= 15, L=  -1

  1   1*    4
  2   14   13
  3   5*    2
  4   10   13
  5   1*    1
  6   4*    0
  7   6*    7

K= 16, L=  -1

  1    5    7
  2   1*    2
  3   15   15
  4   4*    1
  5   1*    4

K= 17, L=  -1

  1   1*    5
  2   10   10

K=  0, L=   0

  1   87   81
  2  147  152
  3  119  124
  4   29   30
  5  107  110
  6   39   40
  7   25   23
  8   57   59
  9   10   10
 10   53   52
 11   11   12
 12   6*    5
 13   18   18

K=  1, L=   0

  1  209  138
  2   78   79
  3   16   16
  4  157  162
  5   44   46
  6   72   74
  7   37   37
  8   4*    2

  H   FO   FC

  9   64   66
 10   17   17
 11   21   21
 12   18   17
 13   4*    6

K=  2, L=   0

  0  153  136
  1  150  146
  2   29   30
  3  119  119
  4   55   53
  5   88   93
  6   19   19
  7   19   19
  8   41   41
  9   15   16
 10   42   42
 11   15   14
 12   5*    5
 13   20   20

K=  3, L=   0

  1  136  132
  2   61   61
  3   12   12
  4  108  108
  5    6    1
  6   57   58
  7   33   33
  8   20   20
  9   50   51
 10   18   17
 11   16   16
 12   15   16
 13   1*    3

K=  4, L=   0

  0   42   41
  1   11   10
  2   58   57
  3   91   89
  4   1*    2
  5   81   81
  6   13   13
  7   39   39
  8   42   42
  9   12   10
 10   21   20
 11   11   10
 12   5*    7
 13   12   13

K=  5, L=   0

  1   52   49
  2   19   18
  3   34   35
  4   23   24
  5    7    6
  6   36   38
  7   14   12
  8   13   11
  9   29   29
 10   10   11
 11   5*    5
 12   10   12
 13   1*    2

K=  6, L=   0

  0   11    9
  1    8    9
  2   35   35
  3   14   14
  4   45   49
  5   23   22
  6   5*    4
  6   5*    4
  7   19   18
  8   18   19
  9   1*    4
 10   1*    2
 11   1*    3
 12   1*    3

K=  7, L=   0

  1   25   24
  2    8    7
  3   26   27
  4   22   21
  5   4*    2
  6   6*    6
  7   18   18
  8    5   11
  9   1*    2
 10   6*    2
 11   1*    3
 12   6*    1

K=  8, L=   0

  0   43   43
  1   13   15
  2   17   15
  3   54   53
  4   1*    1
  5   42   41
  6   18   20
  7   6*    2
  8   5*   10
  9    9    6
 10    8   10
 11   6*    3
 12   6*    0

K=  9, L=   0

  1   57   57
  2   3*    2
  3   5*    1
  4   16   16
  5    7    2
  6   17   15
  7   6*    7
  8   1*    2
  9   27   26
 10    9    6
 11    9    9

K= 10, L=   0

  0   48   46
  1   10    9
  2   26   25
  3   1*    4
  4   10    8
  5   38   37
  6   10   14
  7    8   10
  8   22   22
  9   6*    8
 10   16   15
 11   7*    5

K= 11, L=   0

  1   37   37
  2   14   14
  3   1*    3
  4   50   49
  5   3*    1
  6   32   32

  H   FO   FC

  7   16   15
  8   1*    4
  9   24   26
 10   8*    8

K= 12, L=   0

  0   62   63
  1   16   15
  2   23   23
  3   30   31
  4    9    8
  5   43   42
  6   16   13
  7   11   12
  8   22   23
  9   6*    3

K= 13, L=   0

  1   35   36
  2   18   19
  3   15   15
  4   36   35
  5   4*    5
  6   27   27
  7   15   16
  8    5    4
  9   20   19

K= 14, L=   0

  0   45   45
  1   20   18
  2   21   22
  3   27   25
  4   7*    2
  5   23   24
  6   11    9
  7   10   11
  8   12   14

K= 15, L=   0

  1   23   24
  2   15   18
  3   11   12
  4   23   22
  5    9    7
  6   15   13

K= 16, L=   0

  0   17   18
  1   13   13
  2   14   14
  3   19   21
  4   6*    1
  5   8*   10

K= 17, L=   0

  1   16   16
  2   11   12

K=  1, L=   1

  0   80   73
  1   72   71
  2  168  172
  3   30   31
  4   2*    3
  5    5    6
  6   35   37
  7   30   29
  8   14   15
  9   6*    6
 10    8    7
 11   1*    4
 12   5*    2
 13   6*    1

K=  2, L=   1

  0   85   85
  1   27   27
  2  208  213
  3   35   33
  4   62   62
  5   45   50
  6   20   21
  7   26   25
  8    8    9
  9   1*    2
 10   21   22
 11    8    8
 12    5    7
 13    5    3

K=  3, L=   1

  0   38   36
  1   31   31
  2    7    5
  3  137  138
  4   42   43
  5   3*    2
  6   92   93
  7   46   47
  8   13   14
  9   25   26
 10   16   18
 11   18   17
 12   1*    6
 13   1*    4

K=  4, L=   1

  0   37   37
  1    8    5
  2  102  107
  3   69   67
  4   34   36
  5   74   77
  6   44   43
  7   64   64
  8   27   28
  9   1*    1
 10   21   21
 11   17   15
 12   18   17
 13   4*    7

K=  5, L=   1

  0    5    3
  1  113  112
  2   13   14
  3  105  104
  4   63   64
  5   6*    5
  6  102  100
  7   30   30
  8   28   29
  9   21   21
 10   14   14
 11   24   22
 12   8*   11

K=  6, L=   1

  0   75   76
  1    5    8
  2  143  142
  3   45   47
  4   18   17
  5   78   79

  H   FO   FC

  6   13   12
  7   65   66
  8   27   27
  9   7*    6
 10   18   22
 11    9    9
 12   20   17

K=  7, L=   1

  0   3*    3
  1  123  121
  2   41   40
  3   83   80
  4   55   54
  5   12   13
  6   50   52
  7   25   25
  8   21   19
  9   24   24
 10    9    6
 11   26   25
 12   14   12

K=  8, L=   1

  0  104  101
  1   16   17
  2   90   87
  3   34   33
  4   20   19
  5   37   37
  6   22   21
  7   40   39
  8   26   27
  9   7*    5
 10   22   22
 11   1*    5

K=  9, L=   1

  0    8    5
  1   66   65
  2   24   24
  3   33   32
  4   36   36
  5   14   14
  6   50   51
  7   24   25
  8   16   17
  9   20   21
 10   4*    0
 11   16   16

K= 10, L=   1

  0   56   57
  1   22   22
  2   36   35
  3   42   43
  4   19   19
  5   36   36
  6   1*    2
  7   17   16
  8   17   16
  9   5*    8
 10   18   17

K= 11, L=   1

  0   20   20
  1   19   19
  2   5*    3
  3   26   26
  4   27   29
  5   24   22
  6   24   24
  7   11   11
  8   5*    7
  9   17   13
 10   4*    1

K= 12, L=   1

  0   20   19
  1   13   15
  2   14   15
  3   15   15
  4   11    9
  5   16   17
  6   4*    5
  7   1*    7
  8   1*    6
  9   8*    6

K= 13, L=   1

  0   6*    5
  1   5*    2
  2   1*    2
  3   1*    5
  4   11   12
  5   11   10
  6   1*    5
  7   7*    7
  8   4*    1

K= 14, L=   1

  0   4*    5
  1   13   14
  2   5*    7
  3   4*    5
  4   8*    3
  5   7*    0
  6   1*    4
  7   6*    3

K= 15, L=   1

  0   4*    3
  1   6*    7
  2   4*    0
  3   4*    4
  4   1*    1
  5   1*    5
  6   4*    6

K= 16, L=   1

  0    9    9
  1   5*    6
  2   11   12
  3   7*    6
  4   4*    1

K= 17, L=   1

  0   1*    2
  1   10   11

K=  0, L=   2

  0  160  167
  1   66   70
  2   16   16
  3   38   39
  4   90   93
  5   33   34
  6    8    7
  7   34   34
  8   11   11
  9   50   50
 10   23   23
 11   7*    8
 12   18   20

  H   FO   FC

K=  1, L=   2

  0  140  138
  1  156  164
  2   27   26
  3  142  147
  4   35   36
  5   44   48
  6   40   41
  7   25   26
  8   56   56
  9   40   40
 10   14   11
 11   20   19
 12   14   13

K=  2, L=   2

  0   97   97
  1   76   76
  2  152  157
  3  111  112
  4  103  105
  5   58   58
  6   4*    2
  7   44   45
  8   29   28
  9   39   39
 10   28   28
 11   1*    3
 12   19   18

K=  3, L=   2

  0  176  175
  1   42   44
  2   57   55
  3   80   82
  4   96   97
  5   47   50
  6   52   53
  7   20   20
  8   44   44
  9   16   14
 10   7*    6
 11   15   14
 12   7*   11

K=  4, L=   2

  0   40   40
  1   98   97
  2   97   97
  3   39   38
  4   34   33
  5   51   53
  6   4*    4
  7   45   44
  8   15   16
  9   14   14
 10   8*   11
 11   5*    3
 12   10   10

K=  5, L=   2

  0   85   82
  1   67   66
  2   18   17
  3   64   62
  4   29   29
  5    9    9
  6   41   41
  7   4*    2
  8   6*    4
  9   11   13
 10   1*    3
 11   12   10
 12   4*    3

K=  6, L=   2

  0   23   23
  1   52   52
  2   56   55
  3   13   14
  4   31   30
  5   10    9
  6   3*    4
  7   3*    1
  8    5    8
  9   1*    3
 10   6*    8
 11   6*    1
 12   7*    3

K=  7, L=   2

  0    7    7
  1   32   32
  2   27   27
  3    6    7
  4   5*    3
  5   13   14
  6   5*    5
  7    8    6
  8   1*    1
  9   1*    3
 10   1*    1
 11   1*    1

K=  8, L=   2

  0    6    6
  1   24   23
  2   17   17
  3   14   14
  4   30   28
  5   21   23
  6   1*    3
  7   1*    2
  8   17   16
  9   6*    6
 10   1*    1
 11   7*    4

K=  9, L=   2

  0   51   51
  1   16   16
  2   18   18
  3   32   32
  4   21   20
  5   11   11
  6   14   14
  7   20   20
  8   16   16
  9   5*    8
 10   8*    5

K= 10, L=   2

  0   25   25
  1   23   23
  2   54   52
  3   27   27
  4   41   39
  5   26   27
  6   6*    7
  7   20   21
  8   17   16
  9   13   13
 10   11    8

K= 11, L=   2

  0   47   46

  H   FO   FC

  1   44   45
  2   4*    6
  3   57   57
  4   26   25
  5   23   21
  6   18   18
  7   16   16
  8   18   19
  9   13   12

K= 12, L=   2

  0   18   18
  1   12   11
  2   38   37
  3   22   23
  4   33   34
  5   27   28
  6   1*    4
  7   15   15
  8   7*    8
  9   14   13

K= 13, L=   2

  0   40   41
  1   31   31
  2   3*    3
  3   36   35
  4   20   20
  5   11   11
  6   21   22
  7   4*    6
  8   16   14

K= 14, L=   2

  0   28   30
  1   12   14
  2   29   29
  3   13   13
  4   15   17
  5   19   19
  6   1*    0
  7   11   14

K= 15, L=   2

  0   16   16
  1   25   26
  2   1*    4
  3   21   20
  4   17   15
  5   7*    8

K= 16, L=   2

  0   19   20
  1   4*    3
  2   22   22
  3   1*    4
  4   6*    9

K= 17, L=   2

  0   10    9

K=  0, L=   3

  0   0*    0

K=  1, L=   3

  0   17   17
  1   17   19
  2   23   23
  3   26   27
  4   48   50
  5   10    9
  6   15   14
  7    8    5
  8    7    4
  9    8   10
 10   1*    2
 11   8*    6
 12   1*    1

K=  2, L=   3

  0  107  105
  1   65   67
  2   50   52
  3   38   37
  4   5*    6
  5   30   30
  6    8    8
  7   1*    4
  8   13   11
  9   10   10
 10   17   16
 11   7*    7
 12   1*    3

K=  3, L=   3

  0   95   98
  1   85   85
  2   72   73
  3  121  124
  4   44   46
  5   52   55
  6   30   31
  7   1*    3
  8   12   12
  9   29   28
 10   13   14
 11    9    8
 12   1*    3

K=  4, L=   3

  0  156  153
  1  102  101
  2   64   64
  3   67   68
  4   71   71
  5   66   68
  6   45   45
  7   39   39
  8   12   11
  9   22   23
 10   18   17
 11   10    9
 12   12    9

K=  5, L=   3

  0  146  148
  1   65   67
  2   64   64
  3   33   33
  4   61   60
  5   57   57
  6   62   63
  7   22   21
  8   25   25
  9   19   19
 10   13   13
 11   14   12

K=  6, L=   3

  0   47   48
  1   67   68
  2   62   62
  3    7    7
  4   45   45
```

```
  H   FO   FC

  5   35   37
  6   54   54
  7   34   34
  8   14   13
  9   15   16
 10   24   21
 11    9*  10

K=   7, L=   3

  0   74   73
  1   67   69
  2   36   34
  3   44   43
  4   14   15
  5   50   50
  6   33   34
  7    8*   1
  8   34   33
  9   26   26
 10   16   17
 11   19   17

K=   8, L=   3

  0   62   62
  1   46   46
  2   40   40
  3   11   11
  4   54   53
  5   25   25
  6   36   36
  7   36   37
  8   12   11
  9   20   21
 10   18   17

K=   9, L=   3

  0   46   46
  1   33   34
  2   31   31
  3   56   56
  4    9   10
  5   45   45
  6   28   30
  7   17   16
  8   26   25
  9   13   13
 10   11   10

K=  10, L=   3

  0   40   40
  1   19   18
  2   31   31
  3    7    7
  4   34   35
  5   11   12
  6   14   15
  7   26   26
  8    8*   4
  9   18   17

K=  11, L=   3

  0    5    8
  1    9   10
  2   12   12
  3   37   37
  4    7*   6
  5   16   16
  6   14   15
  7    5*   1
  8   14   14
  9    1*   5

K=  12, L=   3

  0    8    7
  1    1*   5
  2   17   17
  3    3*   2
  4    6*   8
  5    1*   4
  6    6*   3
  7   11   12
  8    4*   1

K=  13, L=   3

  0   19   19
  1    5*   3
  2    5*   4
  3   14   14
  4    1*   1
  5    4*   0
  6    7*   9
  7    1*   4

K=  14, L=   3

  0    1*   0
  1    5*   2
  2   13   15
  3    1*   2
  4    4*   4
  5    9    6
  6    4*   3

K=  15, L=   3

  0    7*   6
  1    4*   2
  2    7*   6
  3    1*   1
  4    5    7
  5    1*   6

K=  16, L=   3

  0   11   11
  1   10   10
  2    1*   7
  3    1*   0

K=   0, L=   4

  0    5    5
  1   87   95
  2  105  112
  3   77   80
  4   39   88
  5   22   21
  6   33   34
  7   46   48
  8   22   23
  9   26   27
 10   26   25
 11    5*   8

K=   1, L=   4

  0   23   25
  1   27   28
  2  126  129
  3  106  110
  4   28   28
  5   65   67
  6   72   73
  7   26   26
  8   40   38
  9    6*   7
 10   12   12
 11   19   18

K=   2, L=   4

  H   FO   FC

  0    9    8
  1  103  106
  2  108  110
  3   83   85
  4   65   68
  5   22   22
  6   38   39
  7   45   45
  8   15   16
  9   28   28
 10   13   13
 11   12   12

K=   3, L=   4

  0  153  156
  1   59   58
  2   84   86
  3   78   80
  4    6    9
  5   57   59
  6   38   38
  7   16   18
  8   25   24
  9    6*   7
 10    9   10
 11   14   13

K=   4, L=   4

  0   24   22
  1   76   76
  2   43   43
  3    5*   1
  4   40   39
  5   40   40
  6   34   35
  7   32   33
  8   12   12
  9    6*   8
 10    5*   4
 11    6*   5

K=   5, L=   4

  0   77   79
  1   77   76
  2    6    6
  3   38   38
  4    9    8
  5    4*   1
  6   19   19
  7    1*   2
  8    5*   5
  9    1*   3
 10   14   13
 11    4*   7

K=   6, L=   4

  0   25   24
  1   26   26
  2   22   21
  3    5*   5
  4   18   18
  5    4*   7
  6    6*   8
  7    1*   1
  8    9    9
  9   11    9
 10    1*   2
 11    4*   4

K=   7, L=   4

  0   28   29
  1    6    2
  2    3*   4
  3    6    3
  4   18   16
  5   12   13
  6   16   16
  7    1*   0
  8    5*   2
  9    1*   1
 10    4*   3

K=   8, L=   4

  0    9   10
  1   13   13
  2   20   20
  3   13   16
  4    7    3
  5    8    7
  6    3*   3
  7   21   22
  8    4*   0
  9    1*   0
 10    1*   2

K=   9, L=   4

  0   30   31
  1   47   48
  2   26   25
  3   35   34
  4    6*   3
  5    9   10
  6   18   19
  7    9    7
  8    1*   7
  9    1*   2

K=  10, L=   4

  0    6*   3
  1   32   32
  2   42   42
  3   21   22
  4   22   22
  5   12   13
  6   12   12
  7   16   16
  8    1*   6
  9    1*   4

K=  11, L=   4

  0   47   47
  1   31   32
  2   33   32
  3   38   38
  4    6*   1
  5   14   13
  6   17   18
  7    8    8
  8    7*  11

K=  12, L=   4

  0   13   13
  1   28   28
  2   43   44
  3   13   14
  4   24   24
  5    6*  11
  6   12   10
  7   13   14

K=  13, L=   4

  0   24   24
  1    9   11
  2   17   18
  3   24   25

  H   FO   FC

  4    8    5
  5   19   19
  6   20   20
  7    9    8

K=  14, L=   4

  0    4*   0
  1   30   31
  2   16   15
  3    1*   6
  4   17   17
  5    7*   7

K=  15, L=   4

  0   23   27
  1   13   11
  2   22   22
  3   17   18
  4    6*   6

K=  16, L=   4

  0    1*   0
  1   14   17
  2    5   11

K=   0, L=   5

  0    1*   0

K=   1, L=   5

  0   44   46
  1   15   17
  2    5    2
  3   43   45
  4    6    0
  5   16   17
  6   10    8
  7    7    7
  8   13   14
  9    1*   0
 10    5    2
 11    6*   4

K=   2, L=   5

  0   16   16
  1    9    8
  2   54   54
  3    7    7
  4   38   38
  5    7    5
  6    8    6
  7    3*   1
  8    8    8
  9   16   17
 10    1*   1
 11    6*   6

K=   3, L=   5

  0  106  106
  1   11   10
  2   32   32
  3   50   50
  4   25   19
  5   15   14
  6    7    7
  7    9   11
  8   31   31
  9    4*   3
 10   12   13
 11    1*   1

K=   4, L=   5

  0   19   19
  1   68   68
  2   23   23
  3   17   16
  4   55   56
  5   31   31
  6   27   27
  7   12   13
  8   19   18
  9   26   25
 10    4*   5

K=   5, L=   5

  0  114  118
  1    7    6
  2   25   28
  3   60   58
  4   17   15
  5   52   54
  6    3*   3
  7   23   24
  8   27   26
  9    8    8
 10   14   13

K=   6, L=   5

  0   34   36
  1   60   62
  2   33   33
  3   43   43
  4   51   51
  5   13   13
  6   32   33
  7   36   35
  8    8*  11
  9   30   31
 10    8*   0

K=   7, L=   5

  0   98   99
  1    3*   6
  2   57   55
  3   68   68
  4   34   33
  5   48   49
  6   10    9
  7   15   16
  8   34   33
  9    4*   8
 10   19   17

K=   8, L=   5

  0   32   32
  1   55   56
  2   16   16
  3   49   48
  4   54   55
  5   16   15
  6   31   34
  7   16   16
  8    9*   9
  9   20   20

K=   9, L=   5

  0   55   56
  1    8    8
  2   55   56
  3   39   38
  4   17   17
  5   31   32
  6    1*   5
  7   19   19
  8   15   15

  H   FO   FC

  9    1*   1

K=  10, L=   5

  0   14   14
  1   39   41
  1   35   41
  2   14   14
  3   26   27
  4   33   32
  5    1*   1
  6   20   20
  7    9   11
  8   14   11

K=  11, L=   5

  0   27   26
  1    1*   4
  2   32   33
  3   16   17
  4    6*   3
  5    9   12
  6    4*   8
  7   11   11
  8   13   11

K=  12, L=   5

  0   10    8
  1   14   14
  2   13   13
  3    5*   6
  4    1*   4
  5    8*   6
  6    9*  10
  7    1*   3

K=  13, L=   5

  0    9   11
  1    7*   7
  2    6*   6
  3    1*   0
  4    5*   4
  5    7*   3
  6    1*   2

K=  14, L=   5

  0   12   10
  1    9    8
  2    5*   3
  3    1*   4
  4    7*  11
  5    1*   1

K=  15, L=   5

  0   10    8
  1    1*   9
  2    1*   1
  3    8*   7

K=  16, L=   5

  0    1*   5
  1    8*  11

K=   0, L=   6

  0   73   74
  1  123  125
  2   18   19
  3   59   60
  4   73   72
  5   21   21
  6   65   66
  7    8    7
  8   14   13
  9   19   20
 10    6*   2

K=   1, L=   6

  0   94   56
  1   74   77
  2  142  148
  3   47   47
  4   37   38
  5   80   80
  6    1*   1
  7   32   33
  8   13   13
  9    4*   1
 10   21   20

K=   2, L=   6

  0   56   56
  1  119  124
  2   20   20
  3   67   66
  4   35   36
  5   13   13
  6   55   55
  7    6*   9
  8   15   15
  9   17   20
 10    1*   4

K=   3, L=   6

  0   72   73
  1   33   33
  2   52   53
  3    3*   6
  4   20   20
  5   43   42
  6    6*   4
  7   17   18
  8   10    8
  9   11    8
 10   13   13

K=   4, L=   6

  0   24   23
  1   45   45
  2    1*   3
  3   32   32
  4   25   25
  5   23   23
  6   33   34
  7    1*   0
  8   13   10
  9   11   11
 10    6*   0

K=   5, L=   6

  0   60   60
  1   16   16
  2   15   15
  3    6    7
  4   23   23
  5   18   19
  6    3*   1
  7   18   17
  8    5*   6
  9   11   11
 10    9*  10

K=   6, L=   6

  0    8*  10
  1    6*   7

  H   FO   FC

  2    5*   4
  3   11   11
  4    5*   1
  5   14   14
  6    6*   1
  7    8    7
  8    8    8
  9    8*   6

K=   7, L=   6

  0   30   31
  1   14   13
  2   14   13
  3    1*   3
  4    9   10
  5   13   11
  6    8   12
  7    8    3
  8    5*   0
  9    9    0

K=   8, L=   6

  0    7    4
  1   32   32
  2    1*   5
  3    9    7
  4   10   10
  5    5*   0
  6   10    9
  7    1*   2
  8    4*   1
  9    8*   5

K=   9, L=   6

  0   35   35
  1   11   10
  2   23   24
  3    9*   1
  4    1*   2
  5   21   21
  6    5*   5
  7   11    7
  8    1*   1

K=  10, L=   6

  0    1*   4
  1   32   34
  2    6*   9
  3   14   15
  4   13   14
  5    5*   6
  6   22   22
  7    7*   4
  8    6*   3

K=  11, L=   6

  0   30   31
  1   18   17
  2   21   23
  3    5*   4
  4    5*   8
  5   17   18
  6    4*   5
  7   14   13

K=  12, L=   6

  0   13   13
  1   29   29
  2    6*   6
  3   18   19
  4   13   13
  5   10    8
  6   20   21

K=  13, L=   6

  0   18   21
  1   13   11
  2   29   30
  3   11   12
  4   16   15
  5   20   22

K=  14, L=   6

  0   14   17
  1   20   21
  2    4*   0
  3   14   14
  4   14   13

K=  15, L=   6

  0   16   16
  1   10   11
  2   22   22

K=  16, L=   6

  0   12   12

K=   0, L=   7

  0   12    0

K=   1, L=   7

  0    4*   1
  1   11   11
  2   21   23
  3    6*   6
  4   24   25
  5    9    9
  6   13   13
  7   12   11
  8    5**  0
  9    1*   2
 10    1*   1

K=   2, L=   7

  0   20   21
  1   25   25
  2    5*   1
  3   36   35
  4    7    9
  5   16   17
  6   15   13
  7    5*   6
  8   18   18
  9   10    5
 10    6*   2

K=   3, L=   7

  0   11   12
  1   21   20
  2   49   49
  3   12   12
  4   36   35
  5   11   10
  6    5*   1
  7   31   30
  8    1*   4
  9   10   10

K=   4, L=   7

  0   42   45
  1   39   40
  2    9*   9

  H   FO   FC

  3   57   58
  4    7    2
  5   17   18
  6   23   23
  7    1*   2
  8   28   26
  9    7*   7

K=   5, L=   7

  0   32   33
  1   18   18
  2   68   67
  3    6*   4
  4   45   43
  5   21   20
  6    1*   2
  7   28   27
  8    5*   3
  9   12   12

K=   6, L=   7

  0   72   71
  1   50   49
  2   21   20
  3   71   72
  4   15   16
  5   19   19
  5   18   19
  6   31   33
  7    5*   0
  8   28   27
  9    4*   6

K=   7, L=   7

  0   60   61
  1   21   21
  2   77   77
  3   11   11
  4   40   41
  5   19   19
  6    3*   3
  7   24   24
  8    1*   2

K=   8, L=   7

  0   43   43
  1   55   56
  2    7    5
  3   59   58
  4   22   20
  5   14   14
  6   20   21
  7    5*   1
  8   16   14

K=   9, L=   7

  0   33   32
  1   30   29
  2   44   45
  3   10   11
  4   15   17
  5   16   18
  6    4*   7
  7   17   15

K=  10, L=   7

  0   47   47
  1   29   30
  2   10   11
  3   21   21
  4   12   12
  5    7*   9
  6   12   12
  7    4*   3

K=  11, L=   7

  0   16   15
  1   15   15
  2   17   18
  3    1*   2
  4    8*   9
  5   13   11
  6    4*   6

K=  12, L=   7

  0    9   10
  1   13   14
  2    1*   5
  3    7*   6
  4    1*   3
  5    8*   8

K=  13, L=   7

  0    8    8
  1    7*   6
  2    4*   2
  3    8*   1
  4   11    6

K=  14, L=   7

  0    4*   3
  1    1*   6
  2    1*   6
  3    1*   6

K=  15, L=   7

  0    1*   2
  1    1*   0

K=   0, L=   8

  0  112  120
  1   46   46
  2   20   20
  3   55   95
  4   16   16
  5   55   54
  6   12   11
  7    8*   9
  8   19   18
  9    7*   6

K=   1, L=   8

  0   34   35
  1   73   74
  2   51   50
  3    8    6
  4   48   49
  5    8    7
  6   30   29
  7   20   19
  8    8*   5
  9   19   16

K=   2, L=   8

  0   84   84
  1   20   20
  2   26   29
  3   44   44
  4    3*   3
  5   40   39
  6   20   19
  7    4*   4
  8   22   21
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                                                                  PAGE  7

   H   FO    FC
K=   2, L=   8

   9   10     5

K=   3, L=   8

   0    5     9
   1   42    42
   2   29    29
   3    3*    2
   4   41    40
   5   12    11
   6   16    15
   7   15    17
   8    5*    3
   9   15    16

K=   4, L=   8

   0   38    37
   1    7     3
   2   36    36
   3   31    31
   4    8     7
   5   33    33
   6   16    16
   7    1*    3
   8   15    12
   9    6*    6

K=   5, L=   8

   0    1*    1
   1   26    27
   2   12    12
   3   17    17
   4   25    24
   5    1*    4
   6   12    14
   7    7*    8
   8    8*    6

K=   6, L=   8

   0    5*    4
   1    6     2
   2   18    17
   3   16    16
   4    6*    7
   5   10    11
   6   11    11
   7    1*    2
   8    6*    6

K=   7, L=   8

   0    9     9
   1    1*    0
   2   13    15
   3   13    12
   4    6*    1
   5    1*    1
   6    1*    1
   7    4*    4
   8    4*    0

K=   8, L=   8

   0   10     9
   1    1*    2
   2    1*    1
   3    7*    9
   4    4*    2
   5   12    12
   6    7*    1

   H   FO    FC
   7    4*    2

K=   9, L=   8

   0   11    12
   1   16    15
   2   15    13
   3    5*    2
   4   21    21
   5    5*    0
   6   10    10
   7    4*    1

K=  10, L=   8

   0   26    27
   1    9    10
   2   14    15
   3   16    17
   4    1*    3
   5   19    22
   6   10     7

K=  11, L=   8

   0    6*    5
   1   28    27
   2    8     8
   3    1*    0
   4   21    20
   5    7*    5

K=  12, L=   8

   0   30    31
   1    4*    6
   2   20    19
   3   20    21
   4    1*    0
   5   19    18

K=  13, L=   8

   0    1*    1
   1   22    24
   2   19    18
   3    7*    6
   4   18    19

K=  14, L=   8

   0   21    24
   1    9*   11
   2    7*    9

K=  15, L=   8

   0    1*    3

K=   0, L=   9

   0    9*    0

K=   1, L=   9

   1   41    41
   2   10    10
   3   16    17
   4   10    11
   5    6*    1
   6   11    10
   7    1*    0
   8    1*    0

K=   2, L=   9

   H   FO    FC

   0   30    29
   1   20    19
   2   39    35
   3   15    15
   4    1*    2
   5   19    20
   6   14    13
   7   10    10
   8    1*    3

K=   3, L=   9

   0   24    23
   1   62    62
   2   24    26
   3   28    26
   4   26    25
   5   15    13
   6   18    18
   7   14    12
   8    6*    4

K=   4, L=   9

   0   66    67
   1    6     5
   2   59    59
   3   27    27
   4    8     7
   5   27    26
   6   17    16
   7   16    13
   8   12    10

K=   5, L=   9

   0    4*    1
   1   64    65
   2   19    21
   3   28    28
   4   27    26
   5   16    18
   6   18    20
   7    5     6
   8    1*    7

K=   6, L=   9

   0   56    55
   1   18    18
   2   48    48
   3   26    26
   4    3*    1
   5   26    27
   6   12    11
   7   17    16

K=   7, L=   9

   0   13    13
   1   47    47
   2   23    25
   3   25    24
   4   25    25
   5    1*    4
   6   19    18
   7    4*    5

K=   8, L=   9

   0   48    49
   1   18    17
   2   35    37
   3   23    23

   H   FO    FC

   4   10     7
   5   19    21
   6    9     7

K=   9, L=   9

   0    6*    0
   1   28    28
   2   13    12
   3    9     5
   4   16    17
   5    4*    1
   6   14    15

K=  10, L=   9

   0   31    30
   1    1*    1
   2   16    14
   3   17    12
   4    5*    4
   5   15    15

K=  11, L=   9

   0    9     7
   1   17    18
   2    8     5
   3   10    12
   4   10    11
   5    6*    2

K=  12, L=   9

   0   10    12
   1    6*    2
   2    8*    8
   3    7*    8
   4    6*    6

K=  13, L=   9

   0    5*    9
   1    4*    4
   2    6*    1
   3    4*    4

K=  14, L=   9

   0    1*    1
   1    7*    7

K=   0, L=  10

   0   47    48
   1    3*    3
   2   33    32
   3   19    20
   4   36    35
   5   19    19
   6    1*    1
   7   20    19
   8   14    13

K=   1, L=  10

   0   22    23
   1   37    38
   2   16    15
   3   40    40
   4   19    18
   5   18    19
   6   22    22
   7   13    11

   H   FC    FC
K=   2, L=  10

   0   32    31
   1    1*    4
   2   42    41
   3   24    23
   4   29    28
   5   20    20
   6    5*    2
   7   17    17

K=   3, L=  10

   0   33    33
   1   28    26
   2   10    10
   3   28    26
   4   18    17
   5    9     9
   6   15    15
   7    9    10

K=   4, L=  10

   0   33    32
   1   23    24
   2   42    41
   3   15    17
   4    1*   10
   5   15    15
   6    7*    4
   7   10     9

K=   5, L=  10

   0   13    11
   1   33    32
   2   10     9
   3   12    13
   4   11    11
   5    7*    3
   6   12    10
   7    1*    0

K=   6, L=  10

   0   12    12
   1    3*    1
   2   20    19
   3   13    13
   4    4*    2
   5    7*    7
   6    5*    1
   7    1*    2

K=   7, L=  10

   0    1*    3
   1   12    13
   2    7*    1
   3    5*    4
   4    1*    3
   5    4*    2
   6    1*    1

K=   8, L=  10

   0    1*    4
   1    6*    5
   2   11    10
   3   10     9
   4    9    11
   5    7*    1
   6    6*    2

   H   FO    FC
K=   9, L=  10

   0   15    16
   1    9     9
   2    5*    6
   3   15    15
   4    7*    6
   5    1*    5

K=  10, L=  10

   0    9    11
   1    7*    5
   2   22    20
   3   17    17

K=  11, L=  10

   0   14    14
   1   19    19
   2   12    11
   3    9*   12
   4   11    11

K=  12, L=  10

   0   20    20
   1    4*    0
   2   19    20
   3   11    10

K=  13, L=  10

   0   10    10
   1   20    21

K=  14, L=  10

   0   16    19

K=   0, L=  11

   0    1*    0

K=   1, L=  11

   0   23    23
   1    9     9
   2    1*    0
   3    1*    5
   4    6*    6
   5    1*    3
   6    5*    3
   7    1*    1

K=   2, L=  11

   0   38    37
   1    9     9
   2   21    20
   3   10     9
   4    5*    8
   5   12    13
   6    1*    4
   7    1*    3

K=   3, L=  11

   0   23    25
   1   36    35
   2    1*    0
   3   16    18
   4   15    17
   5   13    11
   6    8*   10
```

```
   H    FO    FC

K=    4, L=   11

   0    44    43
   1    30    28
   2    22    21
   3    12    10
   4    15    14
   5    17    16
   6     1*    4

K=    5, L=   11

   0    45    45
   1    33    35
   2    15    13
   3    17    16
   4    17    18
   5    10    11
   6    13    14

K=    6, L=   11

   0    22    23
   1    30    30
   2    32    31
   3     5*    4
   4    24    22
   5    17    20
   6     1*    7

K=    7, L=   11

   0    32    33
   1    24    24
   2     5    10
   3    25    23
   4     7*   10
   5    14    16

K=    8, L=   11

   0    13    12
   1    23    24
   2    20    20
   3     1*    1
   4    22    21
   5    17    16

K=    9, L=   11

   0    20    21
   1    18    17
   2     7*    7
   3    18    19
   4     7*    9

K=   10, L=   11

   0    11    11
   1    12    12
   2    18    17
   3     1*    1

K=   11, L=   11

   0    12    13
   1    11    11
   2     1*    4
   3    13    15

K=   12, L=   11

   0     5*    7
   1     6*    4

   H    FO    FC

   2    13    10

K=   13, L=   11

   0     6*    7

K=    0, L=   12

   0     3*    6
   1    36    35
   2    37    35
   3    11     5
   4    26    24
   5    15    13
   6     8*   10

K=    1, L=   12

   0    38    37
   1    24    23
   2    29    28
   3    33    31
   4     1*    1
   5    16    16
   6    16    16

K=    2, L=   12

   0    17    16
   1    30    29
   2    40    39
   3    12    11
   4    20    18
   5     9     8
   6    10     9

K=    3, L=   12

   0    31    31
   1    28    28
   2    15    15
   3    26    23
   4     5*    3
   5    11     5
   6    11    10

K=    4, L=   12

   0     6*   10
   1    24    26
   2    18    17
   3     1*    1
   4     4*    7
   5     7*    6

K=    5, L=   12

   0    13    13
   1    13    13
   2     1*    5
   3    10     7
   4     4*    0
   5     6*    5

K=    6, L=   12

   0    10     8
   1     5*    0
   2     4*    6
   3     4*    4
   4     1*    4
   5     1*    2

K=    7, L=   12

   H    FO    FC

   0     3*    0
   1     9     6
   2     6*    6
   3     4*    5
   4     4*    2

K=    8, L=   12

   0     1*    0
   1     7*    7
   2    12    11
   3     6*    3
   4     8*    3

K=    9, L=   12

   0     5*    7
   1    13    12
   2     1*    3
   3     1*    6

K=   10, L=   12

   0     9     5
   1     8*    8
   2    15    14

K=   11, L=   12

   0     9    11
   1    12    15

K=   12, L=   12

   0    11    12

K=    0, L=   13

   0     5*    0

K=    1, L=   13

   0    10    10
   1    10    11
   2     6*    3
   3     7*    3
   4     1*    0
   5     9     4

K=    2, L=   13

   0     1*    1
   1     1*    4
   2     1*    3
   3     5*    2
   4     5*    5
   5     6*    1

K=    3, L=   13

   0    13    15
   1     8     8
   2     5    10
   3    14    13
   4     8*    8
   5     8*   10

K=    4, L=   13

   0     1*    1
   1    20    19
   2    10    10
   3     8*    9

   H    FO    FC

   4    17    16

K=    5, L=   13

   0    27    30
   1     5*    1
   2    16    14
   3    16    17
   4     4*    7

K=    6, L=   13

   0    13    14
   1    28    28
   2    18    15
   3    12    13
   4    15    17

K=    7, L=   13

   0    26    27
   1     5*    1
   2    15    15
   3    18    17

K=    8, L=   13

   0    13    12
   1    23    24
   2    14    14
   3     7*    8

K=    9, L=   13

   0    22    24
   1     7*    5
   2    13    13

K=   10, L=   13

   0     1*    0
   1    14    14

K=   11, L=   13

   0    13    13

K=    0, L=   14

   0    22    20
   1    32    31
   2     4*    2
   3     1*    6
   4    17    17

K=    1, L=   14

   0    32    32
   1     4*    5
   2    27    26
   3    16    14
   4     6*    3

K=    2, L=   14

   0     3*    4
   1    35    35
   2     7*    7
   3    16    16
   4    13    10

K=    3, L=   14

   0    30    32

   H    FO    FC

   1     1*    4
   2    20    20
   3     1*    8
   4     9     7

K=    4, L=   14

   0     5     9
   1    15    13
   2     1*    1
   3     8*    7

K=    5, L=   14

   0     4*    4
   1     5*    1
   2     9     5
   3     6*    0

K=    6, L=   14

   0     5*    3
   1     1*    1
   2     4*    1
   3     6*    5

K=    7, L=   14

   0     9     8
   1     8*    4
   2     4*    1

K=    8, L=   14

   0     1*    3
   1    10     7
   2     1*    2

K=    9, L=   14

   0     8*    9
   1     1*    1

K=   10, L=   14

   0     6*    5

K=    0, L=   15

   0     1*    0

K=    1, L=   15

   0     7*    6
   1     8     5
   2     4*    2
   3    11     3

K=    2, L=   15

   0     5*    5
   1     5*    7
   2     4*    2
   3    10     8

K=    3, L=   15

   0     5*    3
   1    10     9
   2    17    17

K=    4, L=   15

   0    16    15

   H    FO    FC      PAGE   8

   1    14    14
   2     1*    2

K=    5, L=   15

   0    11    10
   1    10     6
   2    18    19

K=    6, L=   15

   0    14    15
   1    19    19

K=    7, L=   15

   0    17    16
   1     7*    3

K=    8, L=   15

   0    14    13

K=    0, L=   16

   0    19    18
   1     7*    7
   2     1*    2

K=    1, L=   16

   0     5*    9
   1    17    14
   2    11    12

K=    2, L=   16

   0    19    19
   1     7*    9

K=    3, L=   16

   0     8*    3
   1    10    11

K=    4, L=   16

   0    12    13
   1     1*    6

K=    5, L=   16

   0     4*    1
   1     7*    6

K=    6, L=   16

   0    10     6

K=    0, L=   17

   0     1*    0

K=    1, L=   17

   0     4*    0

K=    2, L=   17

   0    11    11

K=    3, L=   17

   0     6*    1
```

6.3 Results

(a) In(acac)bipyCl_2 Crystal Data

In(acac)bipyCl_2, M = 440.82, Monoclinic, $P2_1/c$, $a = 11.340(3)$, $b = 12.198(3)$, $c = 14.330(3)$ Å, $\beta = 120.25(2)^{\circ}$, $V = 1712$ Å^3, $\rho_o = 1.69(5)$ g.cm^{-3}(flotation), $\rho_c = 1.70$ g.cm^{-3}, $Z = 4$, $\mu(Mo - K_{\alpha}) = 16.80$ cm^{-1}, Mo-K_{α_1} = 0.70926 Å , T = 20°C.

(b) Description and Discussion of the Structure

Acetylacetonato-2,2'-bipyridyldichloroindium(III) is a molecular monomeric indium(III) complex where the indium atom is surrounded by two cis chlorine atoms,a bidentate bipyridyl and a bidentate acetylacetonato anion (figure 8). The $InCl_2O_2N_2$ group possesses a distorted octahedral configuration as can be expected for a complex having three different ligands. Table 49 lists the interatomic distances and angles along with the estimated standard deviations. Mean planes through appropriate groups of atoms are given in table 50.

In In(acac)bipyCl_2 all ligand pairs are cis located. As a consequence,one chlorine atom is trans located to O(2) of the acetylacetonato anion and the other is trans to N(1) of the bipyridyl group. The reasons why the chlorine atoms are cis are not clear at present,but probably either kinetic, mechanistic,packing force effects or requirements in the

TABLE 49

Interatomic distances (Å) and angles (deg)

(a) Interatomic Bonded Contacts

In	-Cl(1)	2.443(1)	In	-Cl(2)	2.394(1)
	- O(1)	2.124(3)		- O(2)	2.164(3)
	- N(1)	2.276(4)		- N(2)	2.299(4)
N(1)	- C(1)	1.335(6)	N(2)	- C(10)	1.327(6)
	- C(5)	1.337(5)		- C(6)	1.354(6)
C(1)	- C(2)	1.375(7)	C(10)	- C(9)	1.369(7)
C(2)	- C(3)	1.357(8)	C(9)	- C(8)	1.361(8)
C(3)	- C(4)	1.390(8)	C(8)	- C(7)	1.387(8)
C(4)	- C(5)	1.373(6)	C(7)	- C(6)	1.374(6)
C(5)	- C(6)	1.472(6)			
O(1)	- C(11)	1.266(5)	O(2)	- C(14)	1.258(5)
C(11)	- C(12)	1.488(7)	C(14)	- C(15)	1.490(7)
	- C(13)	1.392(7)		- C(13)	1.402(7)

Table 49 (continued)

(b) Interatomic angles (deg)

Cl(1)	-In	- Cl(2)	96.8(1)	N(1)	-In	- O(2)	81.4(1)
O(1)	-In	- O(2)	85.4(1)	N(2)	-In	-Cl(1)	92.3(1)
N(1)	-In	- N(2)	71.7(1)	Cl(2)	-In	- O(1)	100.4(1)
Cl(1)	-In	- O(1)	90.2(1)	N(2)	-In	- O(2)	90.1(1)
N(1)	-In	- O(1)	91.2(1)	N(2)	-In	-Cl(2)	96.2(1)
Cl(1)	-In	- N(1)	92.4(1)	O(2)	-In	-Cl(2)	90.2(1)
In	-N(1)-	C(1)	122.2(3)	In	-N(2)-	C(10)	124.3(3)
		- C(5)	118.0(3)			-C(6)	116.3(3)
C(1)	-N(1)-	C(5)	119.7(4)	C(6)	-N(2)-	C(10)	118.7(4)
N(1)	-C(1)-	C(2)	122.1(5)	N(2)	-C(10)-	C(9)	123.1(5)
C(1)	-C(2)-	C(3)	118.8(5)	C(10)	-C(9)	-C(8)	118.7(5)
C(2)	-C(3)-	C(4)	119.2(5)	C(9)	-C(8)	-C(7)	119.4(5)
C(3)	-C(4)-	C(5)	119.4(5)	C(8)	-C(7)	-C(6)	119.1(5)
C(4)	-C(5)-	C(6)	122.7(4)	C(7)	-C(6)	-C(5)	122.7(4)
In	-O(1)-	C(11)	128.1(3)	In	-O(2)	-C(14)	127.3(3)
O(1)	-C(11)-	C(12)	114.7(4)	O(2)	-C(14)-	C(15)	115.3(5)
		- C(13)	125.3(4)			-C(13)	125.4(4)
C(12)	-C(11)-	C(13)	120.1(4)	C(15)	-C(14)-	C(13)	119.4(4)

Table 49 (continued)

(c) Selected Intramolecular Non-bonded Contacts

In	- C(13)	3.430(5)			
	- C(5)	3.134(4)			
	- C(6)	3.143(4)			
Cl(1)	- Cl(2)	3.616(2)	N(1)	- O(2)	2.897(5)
	- N(1)	3.409(4)	Cl(2)	- O(2)	3.233(4)
	- N(2)	3.422(4)	O(1)	- O(2)	2.907(4)
	- O(1)	3.242(4)	N(2)	- O(2)	3.161(5)
Cl(2)	- N(2)	3.494(4)	N(1)	- O(1)	3.144(5)
	- O(1)	3.476(4)		- N(2)	2.739(6)

(d) Intermolecular Contacts Shorter than 4.0 Å

Cl(1)	-C(8)	3.80(4)(4)(a)	Cl(2)	- C(1)	3.35(5)(3)
	-C(9)	3.68(2)(3)		- C(2)	3.49(8)(3)
	-C(15)	3.77(6)(2)		- C(12)	3.99(1)(3)
				- C(14)	3.94(2)(1)
				- C(15)	3.89(1)(3)

(a) Figures in this column refer to the following symmetry transformations with respect to atoms in column one
(1) x, y, z; (2) x, $\frac{1}{2}$+y, $\frac{1}{2}$-z; (3) x, $\frac{1}{2}$-y, z-$\frac{1}{2}$;
(4) 1-x, y-$\frac{1}{2}$, $\frac{1}{2}$-z

TABLE 50

Mean planes as Ax + By + Cz + D = 0

Plane	Atomos in the plane and their deviations (Å)	A	B	C	D	χ^2
1	In (0.008) Cl(1) (-0.032) O(1) (-0.292) O(2) (-0.215) N(2) (-0.349)	0.1851	-0.7181	-0.6709	5.0880	23093.2
2	In (-0.003) Cl(1) (-0.011) Cl(2) (0.064) N(1) (0.395) O(2) (-0.127)	0.7676	0.5400	-0.3454	-0.5292	11500.6
3	In (-0.003) Cl(2) (0.045) N(1) (0.275) N(2) (-0.060)	-0.6810	0.4632	-0.5671	0.5157	5589.7

Table 50 (continued)

4	O(1) (-0.008)	O(2) (0.008)	C(11) (0.019)	0.1520	-0.7346	-0.6613	5.3111	48.2
	C(13) (0.002)	C(14) (-0.002)						
5	N(1) (-0.0012)	C(1) (-0.006)	C(2) (0.011)	-0.5455	0.3749	-0.7496	1.6806	7.1
	C(3) (-0.006)	C(4) (-0.004)	C(5) (0.005)					
6	N(2) (-0.006)	C(6) (0.012)	C(7) (-0.010)	-0.5276	0.5399	-0.6559	0.2296	15.06
	C(8) (-0.002)	C(9) (0.010)	C(10) (-0.001)					

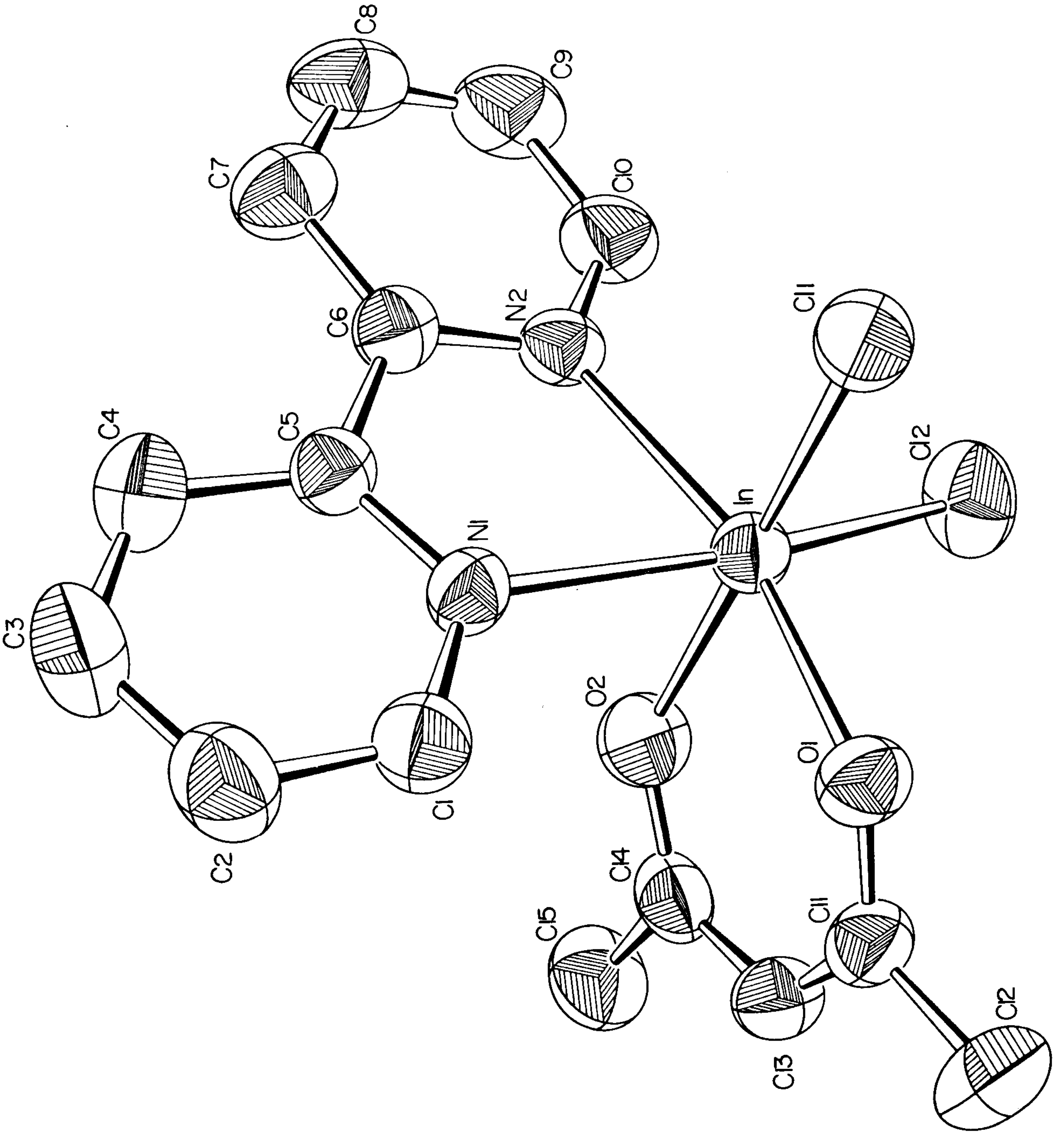

Figure 8. The molecular configuration of In(acac)bipyCl_2

bond lengths and angles needed to accomodate two bulky chelate ligands,are involved.

The observed indium-chlorine bond lengths are 2.443(1) and 2.394(1) Å for In-Cl(1) and In-Cl(2) respectively,in keeping with previously reported indium-chlorine bond distances in some halide complexes of indium(III).

Indium-chlorine bond lengths in In(acac)bipyCl_2 are larger than in $InCl_4^-$ [69](2.36(3) Å). In fact,the determined In-Cl bond distances resemble closer those found in pentacoordinate indium(III) species[71] than in the hexacoordinate complex[184]. Direct comparison however cannot be made since in $InCl_4^-$,$InCl_5^{2-}$ and $InCl_6^{3-}$ one is dealing with charged anionic species and all ligands are equivalent in contrast with the present neutral mixed ligands complex. The difference in In-Cl bond lengths is in agreement with the difference in trans power effect of the nitrogen and oxygen donor ligands; In-Cl(1) is longer than In-Cl(2) as result of being trans to O(2). Thermal motion corrections on the indium-chlorine bond lengths bring these bond distances closer to the $InCl_5^{2-}$ values (In-Cl(1) = 2.455(1) and In-Cl(2) = 2.414(1) for In(acac)bipyCl_2 and In-Cl_{apical}= 2.415(12) and In-Cl_{basal} = 2.456(7) for $InCl_5^{2-}$),but again direct comparison cannot be made as for the pentacoordinate indium(III) species no thermal motion corrections on the In-Cl bond distances were made.

Analysis for planarity of the bipyridyl rings showed that one of the heterocyclic rings is planar,whereas the other,that containing N(2) presents a large departure from planarity. The heterocyclic rings make an angle of 10.9° between each other.

Similarly the acetylacetonato group presents a large departure from statistical planarity. However this deviation can be explained in terms of the very small estimated standard deviations of the coordinate position of the atoms as calculated from the least square refinement compared with that one can calculate for the supposed chemically equivalent bonds.

Comparison of the determined indium-oxygen and indium-nitrogen bond lengths is rather difficult. At present there is no X-ray crystal structure determination reported on any indium-nitrogen donor ligand system,and very few on indium-oxygen donor systems.

The complexed bipyridyl presents bond lengths which are essentially those observed in the free ligand,although in the crystalline state the molecule has a trans configuration[185],whereas in the complex it is cis.

A detailed analysis of the indium-oxygen bond lengths is not possible,at least from the point of view of comparing with other indium(III) species. At present no crystal structure data on other acetylacetonato complexes of indium(III) are available and the most it can be said is that the indium-oxygen bond distances in In(acac)bipyCl_2 resemble closely those found in $InI_3(dmso)_2$[56] (2.15 and 2.20 Å).

In the acetylacetonato ligand the value of 1.397 Å (averaged value) for the C-C (bridge) bond length in In(acac)bipyCl_2 lies between a single bond (1.54 Å) and a double bond (1.33 Å) values and hence the ring in this ligand may be considered to involve delocalized π-bonding (or resonance) entirely comparable with other acetylacetonato complexes.

Analysis of the data reported in the literature shows that the angles within the chelate ring vary rather more than the C-O and C-C distances from one compound to another. The angles found in In(acac)bipyCl_2 are in the same general range as those in other complexes. Cotton and Wood[186] have suggested that the greater variability of the angles can be attributed to:

i) the need for some sort of adjustment in the chelate ring shape in order to allow for the various sizes of the metal atoms, and

ii) the fact that the angle deformation force constants are typically much smaller than those for bond stretching and compression.

The O-M-O angle can be assumed to be dependent on the size of the central atom. Thus, the O(1)-In-O(2) angle in

$In(acac)bipyCl_2$ is comparable with that found in $Zr(acac)_4$[187];both metals having comparable sizes. However, in $In(acac)bipyCl_2$ where other two ligands are present,one of which is producing a large distortion,simple relationships do not hold. Although indium is larger than platinum, the O-M-O in $Me_3Pt(acac)en$[188] is 85° and the M-O bond length is 2.16 Å .

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