

DITHIOLATO COMPLEXES OF INDIUM(III)

by

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B. Sc., University of Hong Kong, 1965

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This is to certify that the thesis entitled  
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by Mr. M. K. Yang in partial fulfillment of the  
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meets the standards of the Department of Chemistry,  
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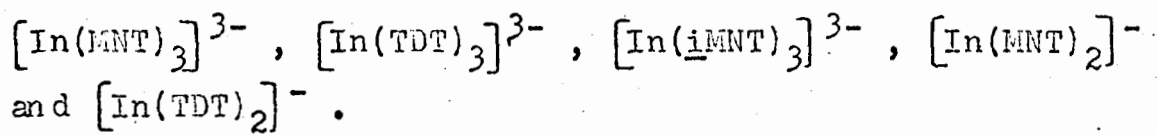
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## CHAPTER I

### I N T R O D U C T I O N

Although the general chemistry of indium is well established <sup>1</sup>, there has only recently been a detailed interest in its coordination chemistry. Complexes of indium(III) perchlorate <sup>2</sup>, halides <sup>3</sup>, pseudo-halides <sup>4,5</sup>, and nitrate <sup>6</sup>, and adducts of these with neutral monodentate or bidentate ligands have received attention <sup>7</sup>. The present studies have been concerned with an investigation of complex formation between indium(III) and certain unsaturated bidentate sulphur-donor ligands such as maleonitriledithiolate (MNT), 1,1-dicyanoethylene-2,2-dithiolate (1MNT), and toluene-3,4-dithiolate (TDT), and adducts of these complexes with some neutral and anionic ligands. Several complexes, with apparent coordination numbers of four, five, or six have been prepared, and their composition, chemical, and physical properties investigated; the oxidation states of indium in the complexes and the half-wave potentials were found using polarographic techniques. Polarography was also used to find stability constants, especially in the

anionic complexes:



CHAPTER IIII.. (A) GENERAL CHEMISTRY OF INDIUM

Indium was discovered by Reich and Richter in 1863 during a study of the mineral Sphaterite, and the element owes its name to the prominent indigo blue line in its emission spectrum.

Indium (atomic number,  $Z=49$ ) belongs to group IIIB in the periodic table, and atomic weight is 114.81; the electronic configuration of the element is  $\text{Kr } 4d^{10} 5s^2 5p^1$  (ionization potential  $I_1= 5.79\text{ev. } I_2=18.79\text{ev. } I_3=27.9\text{ev.}$ ) Metallic indium is usually prepared either by reduction of the oxide with hydrogen, or by electro-deposition. The physical properties of the element are similar to cadmium and tin. It is a silvery-white, lustrous metal; indium is one of the softest elements and can be easily cut with a knife. Although its melting point is comparatively low (156.4 C), the boiling point is high (about 2700 C). The chemistry of indium is generally similar to that of the related group IIIB elements aluminium, gallium and thallium. However, the amphoteric character of the hydroxide of indium is considerably less pronounced than those of gallium and



aluminium, and indium sulphide,  $\text{In}_2\text{S}_3$ , in contrast to the gallium and aluminium sulphide, is stable in the presence of water.

Indium forms compounds in the +1, +2, and +3 formal oxidation states. The trivalent state is more stable than the lower valency states whose compounds readily disproportionate into In(III) compounds and free metal in the presence of water. In general, however, the monovalent compounds of indium are somewhat more stable than those of gallium. The existence of indium(II) species is, however, rather doubtful. Although compounds of the correct stoichiometry have been isolated, these are diamagnetic, and not paramagnetic as would be expected for indium(II) compounds. It has been suggested<sup>8,9</sup> that these compounds are in fact mixed valence species of indium(I) and indium(III) and do not involve truly bivalent indium. Recently, however, evidence has been presented<sup>10</sup> for the existence of short-lived In(II) species in a matrix of frozen aqueous sulphuric acid after irradiation of indium(III) sulphate with  $\gamma$ -ray radiation at 77°K. The evidence for the existence of short-lived indium(II) species will be further discussed later in this thesis.

## II. (B) COMPOUNDS OF INDIUM IN THE TRIVALENT STATE

A very large number of the simple compounds of indium(III) were prepared and identified following the discovery of the element.

All four indium(III) halides are known. Anhydrous indium(III) fluoride,  $\text{InF}_3$ , is prepared by heating  $\text{In}_2\text{O}_3$  in hydrogen fluoride <sup>11,12</sup>, and is involatile and extremely insoluble in water. Anhydrous indium(III) chloride,  $\text{InCl}_3$ , and bromide,  $\text{InBr}_3$ , can be prepared by heating indium metal in chlorine or bromine gas. The iodide can be prepared by heating stoichiometric amounts of indium metal and iodine in an evacuated sealed tube. These halides are sufficiently volatile to be sublimed under vacuum. Solutions of indium(III) chloride and bromide are prepared directly by dissolving indium metal in hydrochloric or hydrobromic acid. Possible complexing pseudohalide ions include cyanide, thiocyanate, cyanate, and azide; however only indium(III) cyanide and thiocyanate have been prepared. Indium(III) cyanide was reported by Meyer <sup>12</sup> and by Wyrouboff <sup>13</sup> a long time ago. The compound was obtained by adding an aqueous solution of potassium cyanide to an aqueous solution of an indium(III) salt; it was described as an insoluble precipitate, but

soluble in excess of potassium cyanide. However, the compound was found to be unstable in water producing hydrocyanic acid, which has cast considerable doubts upon these reports.

Recently indium(III) cyanide was reinvestigated and prepared in solid state by a number of methods, one being the reaction of indium metal or indium hydroxide with HCN gas at  $350^{\circ}\text{C}$  <sup>13</sup>. At the same time the preparation of indium(III) thiocyanate,  $\text{In}(\text{SCN})_3$  has been reported. There are two methods for the preparation. The first involved reacting one mole of anhydrous indium(III) chloride with three moles of sodium thiocyanate in ethanol <sup>14</sup>, the second, the reaction of indium(III) sulphate in aqueous solution with the equivalent quantity of barium thiocyanate, followed by a slow removal of the water in vacuo <sup>15</sup>.

Anhydrous and hydrated indium(III) nitrate are both known. Anhydrous indium(III) nitrate can be prepared by the reaction of anhydrous indium trichloride with dinitrogen pentoxide <sup>16</sup>; the hydrate of this compound is obtained by dissolving indium metal in concentrated nitric acid, followed by evaporation and crystallization of the solution to give  $\text{In}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ .

Indium(III) sulphide,  $\text{In}_2\text{S}_3$ , which is yellow or brick brown in colour and very stable in water, is precipitated when hydrogen sulphide is passed into an aqueous solution containing a weak acid such as acetic acid.

The formal oxidation states indium(II) and (I) have been stabilised in compounds such as halides, sulphide, and oxide. The most important simple compounds of indium(III), (II) and (I) are summarized in the table II-1.

Table II-1

Summary of the Simple Compounds of Indium

<u>Oxidation State</u> <u>III</u>		<u>Oxidation State</u> <u>II</u>		<u>Oxidation State</u> <u>I</u>	
InF <sub>3</sub>	colourless	InF <sub>2</sub>	colourless	-	
InCl <sub>3</sub>	colourless	InCl <sub>2</sub>	colourless	InCl	lemon yellow
InBr <sub>3</sub>	colourless	InBr <sub>2</sub>	almost colourless	InBr	carmine
InI <sub>3</sub>	yellowish	InI <sub>2</sub>	almost colourless	InI	carmine
In <sub>2</sub> O <sub>3</sub>	yellowish			In <sub>2</sub> O	black
In <sub>2</sub> S <sub>3</sub>	yellow or brick red	InS	wine red	In <sub>2</sub> S	brown black
In(SCN) <sub>3</sub>	colourless				
In(CN) <sub>3</sub>	colourless				
In(NO <sub>3</sub> ) <sub>3</sub>	colourless				

## II. (C) THE COORDINATION CHEMISTRY OF INDIUM(III)

Studies of the coordination chemistry of indium(III) have shown that coordination numbers of three, four, five and six are possible, of which six appears predominant. Indium(III) complex compounds can obviously be classified as neutral, anionic or cationic species, all of which have been examined. The physical properties studied include electrolytical conductance, infrared and Raman spectra, thermogravimetric measurements. X-ray crystallographic studies have also been carried out on a small number of compounds.

### (a) Neutral Complexes of Indium(III)

In general, six types of neutral complexes have been reported, namely:  $\text{InX}_3\text{L}_3$ ,  $\text{InX}_3\text{L}_{2.5}$ ,  $\text{InX}_3\text{L}_2$ ,  $\text{InX}_3\text{L}_{1.5}$ ,  $\text{InX}_3\text{L}$  (where X is a halide or pseudohalide, and L is a donor (ligand)), plus chelate compounds. The properties of these neutral complexes have been examined either by infrared spectroscopy, or by electrical conductivity measurements in non-aqueous solvents such as nitromethane, nitrobenzene or acetonitrile.

$\text{InX}_3\text{L}_3$ : Complexes of  $\text{InX}_3\text{L}_3$  where L is a monodentate ligand are well known. Since both infrared spectra and conductivity measurements have suggested a neutral species<sup>17,18,19</sup> the coordination number is believed to be six. Indium(III) chloride complexes are known with the ligands urea, thiourea, pyridine, pyridine-N-oxide, 4-cyano-pyridine, and dimethyl sulphoxide; indium(III) bromide with pyridine, urea, dimethyl sulphoxide, and indium(III) iodide complex with pyridine only; and indium(III) thiocyanate with urea, thiourea, pyridine, triphenylphosphine and 4-picoline<sup>14</sup>.

$\text{In}_3\text{L}_{2.5}$ : Only one compound has been obtained in this type; indium trichloride dissolves in N,N'-dimethyl-acetamide (dma) to give  $\text{InCl}_3(\text{dma})_{2.5}$ . Conductivity measurement shows that the compound is neutral, but the structure of this compound is still doubtful.

$\text{InX}_3\text{L}_2$ : This type of complex where L is again a monodentate ligand and X is a halide, may be either a five-coordinate monomer or a polymeric species. The compounds found include  $\text{InCl}_3(\text{Ph}_3\text{PO})_2$ ,  $\text{InCl}_3(\text{Me}_3\text{NO})_2$ ,

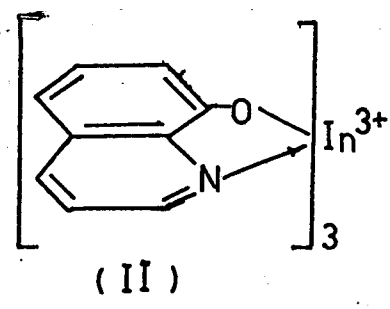
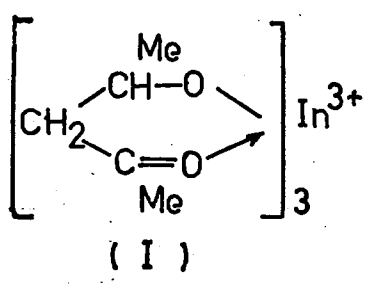
$\text{InBr}_3(\text{Ph}_3\text{P})_2$ ,  $\text{InBr}_3(\text{Ph}_3\text{PO})_2$ ,  $\text{InBr}_3(\text{Ph}_3\text{P})_2$ ,  $\text{InI}_3(\text{dmsO})_2$ ,  
 $\text{InI}_3(\text{Ph}_3\text{PO})_2$  and  $\text{InI}_3(\text{Ph}_3\text{P})_2$ <sup>18,20,21</sup>.

$\text{InX}_3\text{L}_{1.5}$ : Indium(III) halide and pseudohalide complexes with bidentate ligands (L=2,2'-bipyridyl and o-phenanthroline X=Cl, Br, I, NCS, NCO) have been obtained.<sup>14,15,17,18,22</sup>

The structure of these compounds is currently being studied by detailed infrared and other methods.

$\text{InX}_3\text{L}$ : The only known complexes of this type, where L is a monodentate ligand, are  $\text{InI}_3 \cdot \text{Ph}_3\text{P}$  (which is a monomer in the solid state from x-ray studies),  $\text{InI}_3 \cdot \text{bisphenylphosphinoctane}$  and  $\text{InBr}_3 \cdot \text{bisphenylphosphinoctane}$ . The coordination number of these complexes should be four<sup>18</sup>. Indium(III) halides (chloride, bromide and iodide) and ammonia also yield complexes with a 1:1 ratio of halide : ammonia<sup>23</sup>.

Chelate Complexes: Of the neutral indium(III) chelate ring complexes, the best known are those involving acetylacetonone (I) and 8-hydroxyquinoline (II).



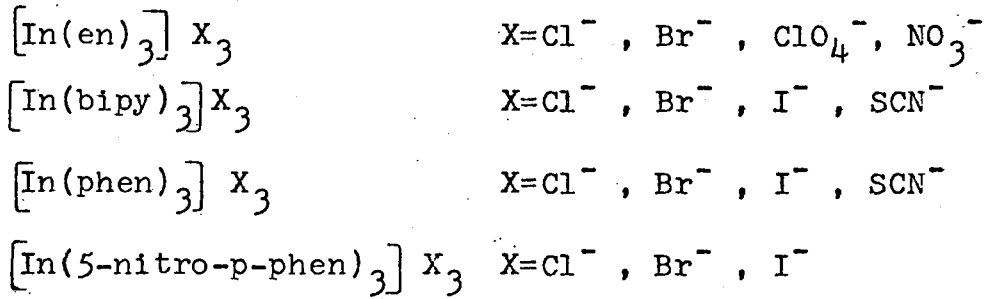


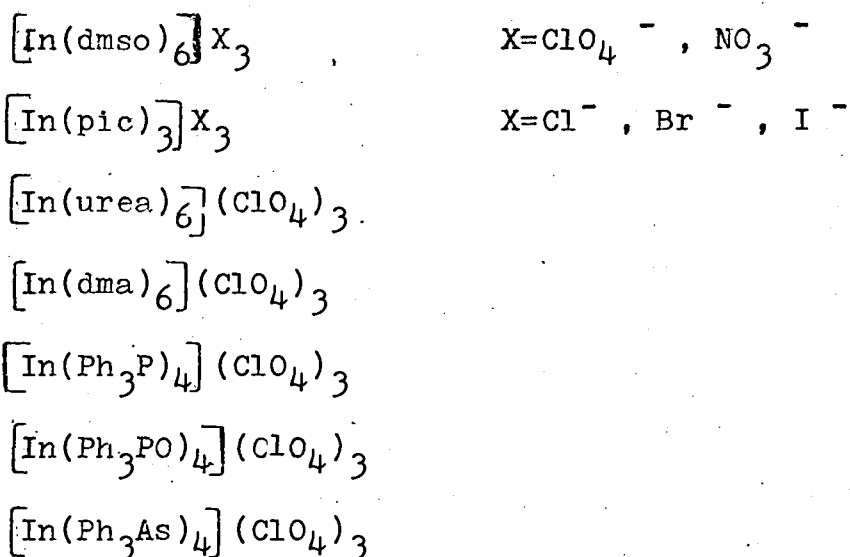
They presumably are six coordinates, with pseudo-octahedral structures. A number of other chelating ligands, such as salicylaldehyde and  $\beta$ -diketone, trifluoroacetylacetone derivatives, also form neutral In(III) chelate complexes.

(b) Cationic Complexes of Indium(III)

During studies of indium(III) species using an ionic volume measurement technique, Celeda and Tuck found evidence for the existence of  $[\text{In}(\text{H}_2\text{O})_6]^{3+}$  in dilute aqueous perchlorate acid solution<sup>24</sup>. The solid crystal obtained from the corresponding solution is

$[\text{In}(\text{H}_2\text{O})_6] \cdot (\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$  in which the perchlorate anion was shown to be non-ligating by infrared spectroscopic methods. This compound has been used as the starting material for the preparation of various indium(III) cationic complexes<sup>6</sup>. The following cationic complexes have been obtained: 2,5,6,18.





(c) Anionic Complexes of Indium(III)

A number of indium(III) anionic complexes are known with the ligands sulphate<sup>25,26</sup>, oxalate<sup>27</sup>, halides<sup>26</sup>, plus adducts of these species with neutral donors<sup>3,6</sup>. The coordination number of these complexes is four, five, or six, with six being the most common.

There are early reports of indium(III) sulphate complexes such as  $[\text{Et}_2\text{NH}_2][\text{In}(\text{SO}_4)_2]$  with various amounts of water, and the oxalate  $M_3[\text{In}(\text{C}_2\text{O}_4)_2] \cdot n\text{H}_2\text{O}$  where  $M=\text{NH}_4^+$ ,  $n=2$ ,  $M=\text{Na}^+$ ,  $n=3$ ,  $M=\text{K}^+$ ,  $n=4$ . No trioxalate compounds  $M_3[\text{In}(\text{C}_2\text{O}_4)_3]$  could be prepared. It is believed that all these compounds involve six coordinate indium(III).

The anionic complexes of indium(III) halides were

first reported by Ekeley and Potratz <sup>26</sup>; in later works these halide complexes have been formulated as anionic complexes  $\text{InX}_4^-$ ,  $\text{InX}_5^{2-}$ ,  $\text{InX}_6^{3-}$ , and  $\text{InX}_7^{4-}$  <sup>8</sup>. The anionic species  $\text{InX}_4^-$  has been assigned a tetrahedral anionic structure by vibrational spectra <sup>28,29,30</sup> and this has recently been confirmed by x-ray crystallography <sup>31</sup>.

Brown, Einstein and Tuck <sup>32</sup> have studied the five coordinate chloride compound,  $(\text{Et}_4\text{N})_2\text{InCl}_5$  by x-ray crystallography; the anion  $\text{InCl}_5^{2-}$  has a tetragonal pyramidal structure as shown in Figure II-1. Five coordinate anionic complexes have been found to be important in the work described in this thesis.

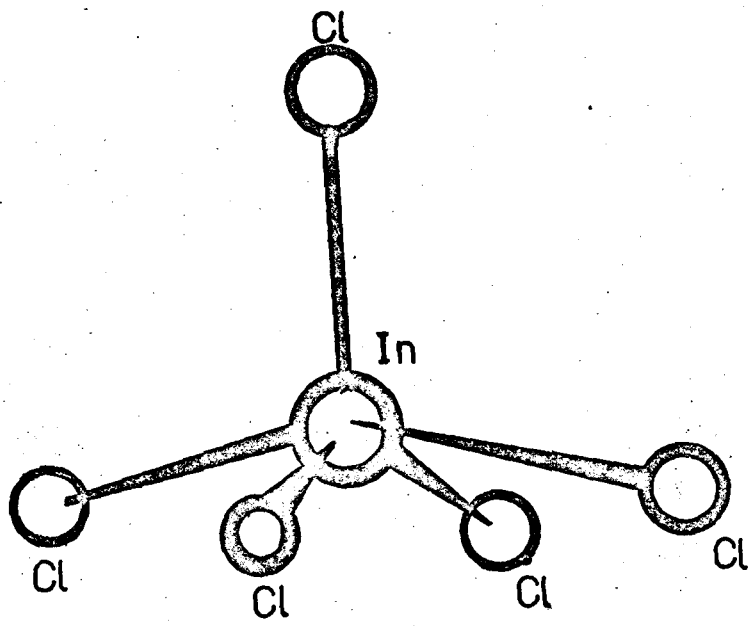
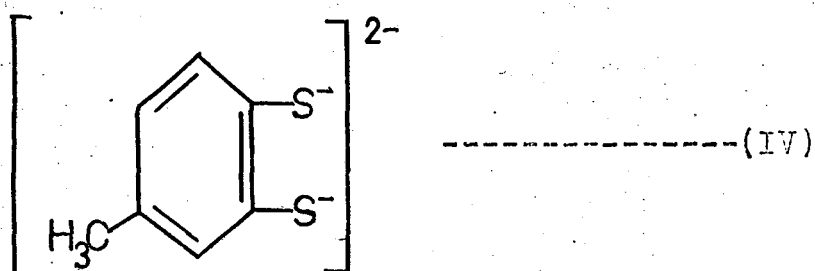
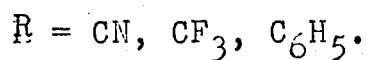
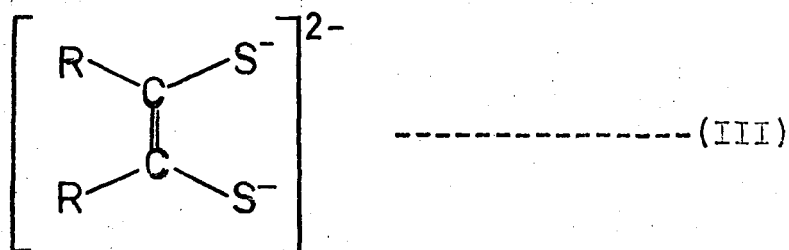


Fig. II-1 Geometry of  $\text{InCl}_5^{2-}$

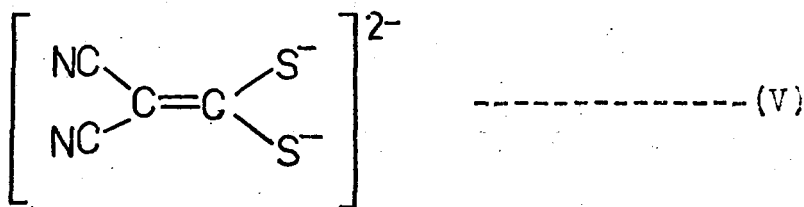
## II(D) THE COORDINATION CHEMISTRY OF UNSATURATED SULPHUR

### DONOR LIGANDS

In recent years, many paper have been published on the coordination behavior of unsaturated bidentate sulphur donor ligands such as (III), (IV) and (V).

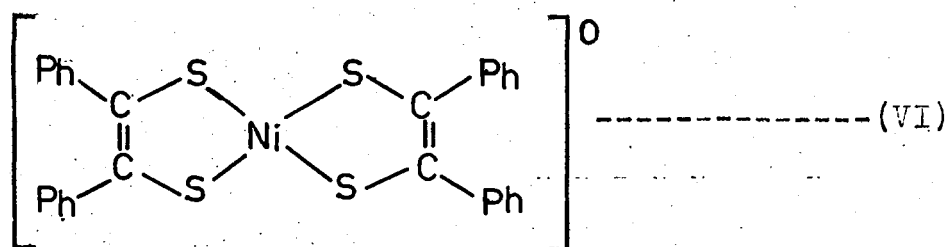


toluene-3,4-dithiolate (TDT)

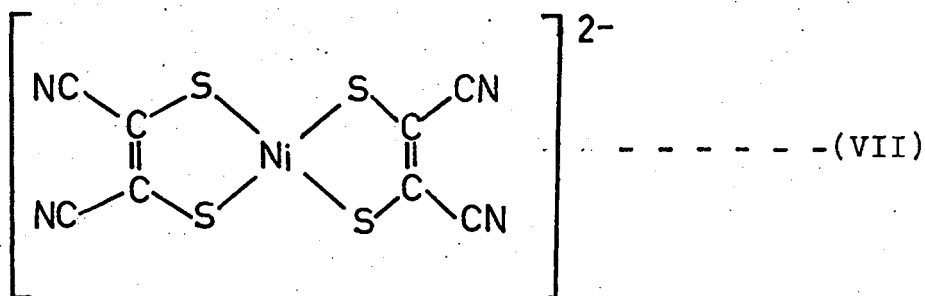


1,1'-dicyanoethylene-2,2'-dithiolate  
(iMNT)

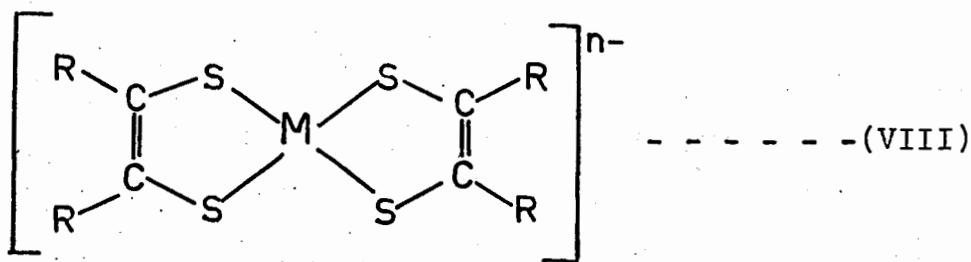
The first report appears to be that of Schrauzer and Mayweg<sup>33</sup> who obtained the neutral complex (VI) by the reaction of nickel sulphide with diphenylacetylene, or by the reaction of nickel carbonyl, sulphur, and diphenylacetylene.



At the same time, H.B. Gray et al.<sup>34,35,36</sup> reported a number of maleonitriledithiolate (MNT) complexes with the divalent metal ions  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Co}^{2+}$ , as in (VII)



Obviously, the comparison of the oxidation states in (VI) and (VII) reveals a difference of two electrons, associated either with the central metal or on the chelate rings, depending apparently on the substituents (CN or  $C_6H_5$  groups). The compounds (VI) and (VII) are quite stable, which raises the possibility that (VI) species might be reducible to mono or dinegative anions, whereas the (VII) species might be oxidizable to a monoanion or neutral complex. Later, Davison et al.<sup>37,38</sup> synthesized complexes of the type (VIII) in different oxidation states, and studied these polarographically and spectroscopically.



$R = CN, CF_3, C_6H_5$ ;  $M = Ni^{2+}, Cu^{2+}, Co^{2+}, Pd^{2+}, Pt^{2+}$ ;  $n = 0, 1, 2$ .

The polarographic study of the complexes (VIII) has given information on the oxidation states, half-wave potentials and stabilities of such square planar complexes<sup>40</sup> (See table II-3).

Table II-3

Half-wave Potentials of Planar Complexes in Non-Aqueous

Solution

<u>Couples</u>		<u>Solvent</u>	<u>E<sub>1</sub> (volts)</u>
Co(MNT) <sub>2</sub> <sup>2-</sup>	⇌ Co(MNT) <sub>2</sub> <sup>-</sup> + e	CH <sub>3</sub> CN	+0.050 (a)
Pt(MNT) <sub>2</sub> <sup>2-</sup>	⇌ Pt(MNT) <sub>2</sub> <sup>-</sup> + e	CH <sub>3</sub> CN	+0.210 (a)
Ni(MNT) <sub>2</sub> <sup>2-</sup>	⇌ Ni(MNT) <sub>2</sub> <sup>-</sup> + e	CH <sub>3</sub> CN	+0.226 (a)
Cu(MNT) <sub>2</sub> <sup>2-</sup>	⇌ Cu(MNT) <sub>2</sub> <sup>-</sup> + e	CH <sub>3</sub> CN	+0.330 (a)
Pd(MNT) <sub>2</sub> <sup>2-</sup>	⇌ Pd(MNT) <sub>2</sub> <sup>-</sup> + e	CH <sub>3</sub> CN	+0.440 (a)
Fe(TDT) <sub>2</sub> <sup>-</sup>	+e ⇌ Fe(TDT) <sub>2</sub> <sup>2-</sup>	DMF	-1.46 (b)
Co(TDT) <sub>2</sub> <sup>-</sup>	+e ⇌ Co(TDT) <sub>2</sub> <sup>2-</sup>	DMF	-1.41 (b)
Ni(TDT) <sub>2</sub> <sup>-</sup>	+e ⇌ Ni(TDT) <sub>2</sub> <sup>2-</sup>	DMF	-1.068 (b)
Cu(TDT) <sub>2</sub> <sup>-</sup>	+e ⇌ Cu(TDT) <sub>2</sub> <sup>2-</sup>	DMF	-1.145 (b)
Au(TDT) <sup>-</sup>	+e ⇌ Au(TDT) <sub>2</sub> <sup>2-</sup>	DMF	-1.95 (b)

(a) Measured at room temperature relative to an aqueous calomel electrode saturated with NaCl; rotatin platinum indicator electrode <sup>39</sup>.

(b) Measured at room temperature relative to a Ag/AgClO<sub>4</sub> electrode; dropping mercury electrode ( H.B. Gray et al. unpublished work <sup>40</sup>.)



A number of comments can be made about these results. Firstly, for complexes for a given ligand with metals in the same oxidation state, the order of half-wave potentials gives the order of stability of the complexes. This stability order is  $\text{Cu} > \text{Ni} > \text{Co}$  in the dianionic  $\text{MNT}^{2-}$  series, and  $\text{Ni} > \text{Cu} > \text{Co} > \text{Fe}$  in the dianionic  $\text{TDT}^{2-}$  series. Proceeding down the periodic table in the nickel group, the stability order is  $\text{Ni} < \text{Pd} < \text{Pt}$  in both the  $\text{MNT}^{2-}$  and  $\text{TDT}^{2-}$  series. Secondly, the half-wave potential indicates the ease of electron transfer and hence the ease of forming different oxidation states in solution. From this information, it is possible to select reducing agents for synthetic work on these complexes.

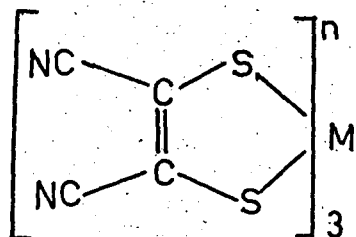
However, the problem of meaningfully assigning the oxidation states of the central metals in these complexes is still a very subtle one.<sup>41</sup>

The crystal structure of the compounds  $[(\text{CH}_3)_4\text{N}]_2[\text{Ni}(\text{MNT})_2]$ ,  $[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Co}(\text{MNT})_2]$  and  $[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{Cu}(\text{MNT})_2]$  etc., have shown the existence of stable square planar structures, with the metal atom in the same plane as the sulphur atoms. Bond lengths and angles have also been measured by x-ray methods

the cations occupy positions above and below the plane.

Until the recent studies, the square planar geometry was believed to be restricted to the diamagnetic,  $d^8$  complexes of Ni(II), Cu(III), Pd(II), Pt(II), Rh(I), Ir(I), and Au(III), except for a few paramagnetic ( $S = \frac{1}{2}$ ), square-planar Co(II) and Cu(II) complexes.

Complexes of coordination number six with unsaturated bidentate sulphur-donor ligands of the general structure (IX) and (X) have been reported <sup>42</sup>.

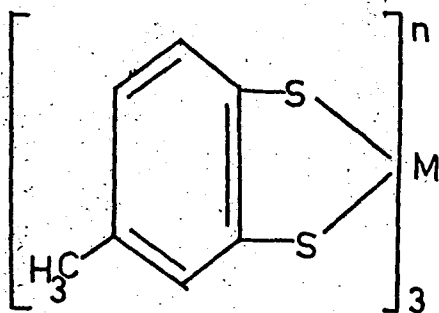


----- (IX)

R=CN; n=-2, -3.

R=CF<sub>3</sub>, Ph ; n=0, -1, -2.

M=V, Cr, Mo, W, Re, Fe, Ru, Os, and Co.



----- (X)

n= 0, -1, -2.

In fact, the first of the ligands mentioned in (VIII) introduced was toluene-3,4-dithiolate (TDT) (X), originally used by Clark in 1936 for the colorimetric determination of tin<sup>43,44</sup>. Since that time, TDT has been used as a qualitative test for such metals as Mo, W, and Re, but there had been no further study of the complex compounds until recently. The first actual isolation of a complex of this stoichiometry was by Gilbert and Sandell who made  $\text{Mo}(\text{TDT})_3$ <sup>45</sup>.

The six-coordinate complexes are extremely interesting, because x-ray crystallographic and spectroscopic measurements strongly indicate that (VII) and (VIII) have perfect, or nearly perfect, trigonal prismatic coordination instead of the more usual pseudo octahedral structure<sup>46,47,48</sup>.

X-ray structural investigation of the 6-coordinate  $\text{Re}(\text{S}_2\text{C}_2\text{Ph}_2)_3$  complex has shown that rhenium is surrounded by the six sulphur atoms in a nearly perfect trigonal-prismatic coordination. The sides of the prism are square. A perspective drawing of the coordination geometry is shown in Figure II-2.

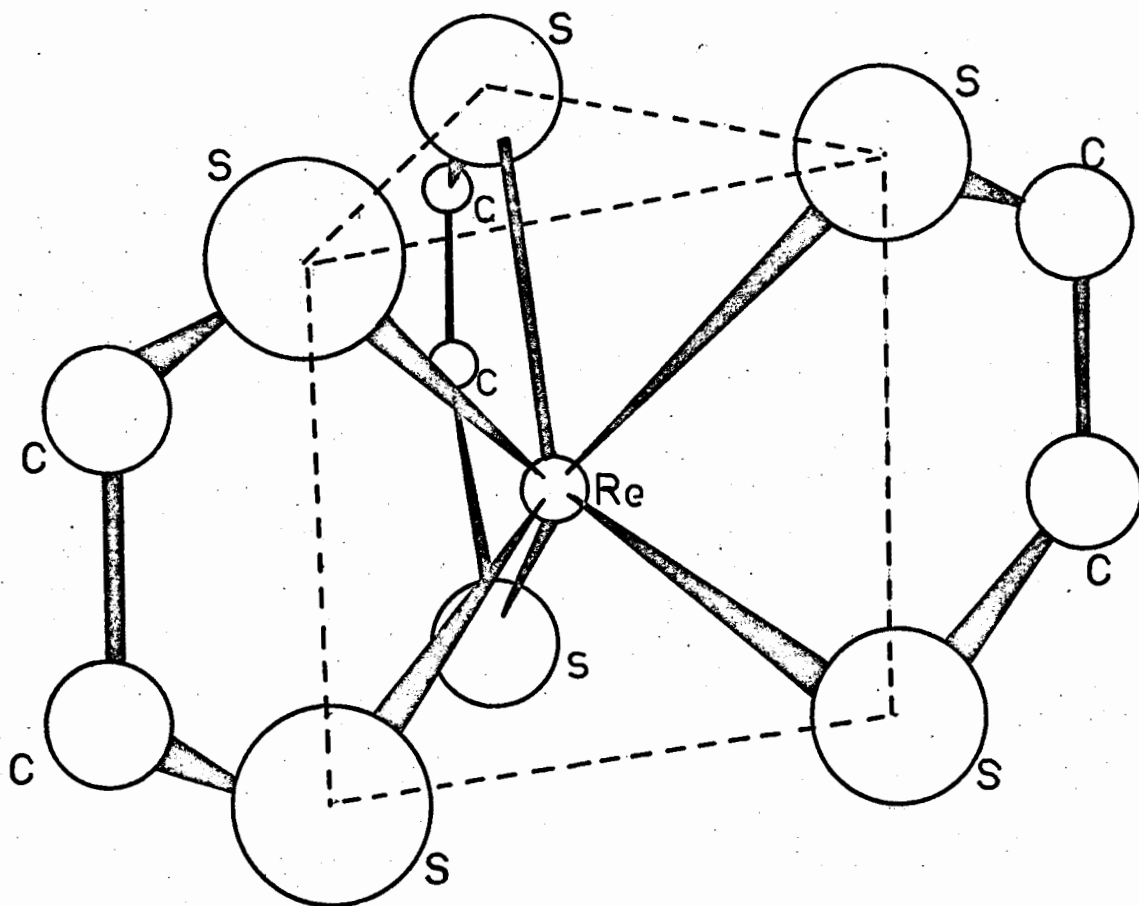
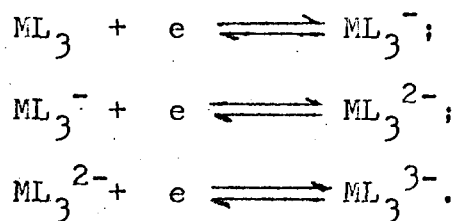


Fig. II-2 Coordination in the  $\text{Re}(\text{S}_2\text{C}_2\text{Ph}_2)_3$  complex.

The polarographic behavior of the trigonal-prismatic complexes as in the MNT and TDT series shows that a series of reversible one electron transfers occur:



These results indicate at least the transient existence of reduced or oxidized species which probably also possess the trigonal-prismatic geometry. Until very recently, little information<sup>46</sup> was available about the structures of neutral and monoanionic species  $(\text{VS}_6\text{C}_6\text{Ph}_6)$  and  $(\text{VS}_6\text{C}_6\text{Ph}_6)^{1-}$  which are also probably trigonal-prismatic. However, a recent structure of  $[\text{Me}_4\text{N}]_2[\text{VS}_6\text{C}_6(\text{CN})_6]$  has revealed<sup>47</sup> that this dianion adopts a geometry intermediate between the trigonally distorted octahedral and trigonal-prismatic arrangements. Certain of the reduced forms have already been isolated with ligands MNT and TDT.<sup>49, 50, 51, 52</sup>

## CHAPTER III

### III. (A) PHYSICAL MEASUREMENTS

#### (a) Infrared Spectra

Infrared spectra were measured with Unicam SP200, Perkin-Elmer 475 and Beckman IR-12 spectrophotometers, with ranges of 5000-650, 4000-300, and 400-200  $\text{cm}^{-1}$ , respectively. Spectra were obtained with Nujol mulls using sodium chloride and/or cesium iodide windows, or potassium bromide pellets.

#### (b) Ultraviolet Spectra

Ultraviolet spectra were taken on a Unicam SP800 Spectrophotometer with a range of 200  $\text{m}\mu$  - 450  $\text{m}\mu$ , generally using a 1 cm. quartz cell. Spectro-quality acetonitrile and methanol were used as solvents.

#### (c) Melting Point Measurements

Melting point measurements were carried out using Fisher-John or Gallenkamp melting point apparatus.

#### (d) Conductivity Measurements

Conductivity measurements were carried out with  $10^{-3}\text{M}$  solutions in acetonitrile at room temperature, using

conductivity meter type C.D.M. 2d (Radiometer Ltd. Copenhagen). A commercial platinum black electrode was used; the cell constant was 0.1. The solvent, acetonitrile (Fisher Certified grade), was purified by shaking with a cold saturated aqueous solution of potassium hydroxide, followed by preliminary drying over anhydrous sodium carbonate and finally two distillations at  $81.0 \pm 0.5$  from phosphorus pentoxide<sup>53</sup>.

(e) Nuclear Magnetic Resonance Spectra (NMR)

Nuclear magnetic resonance spectra were taken on a Varian A-56/60 Spectrophotometer; the coupling constant (J) is given in cps, and the resonance frequencies as values based on tetramethylsilane as the internal standard. The solvent used was dimethyl sulphoxide- d<sub>6</sub> (purity 99.5%) or dimethyl sulphoxide.

(f) Microanalyses

Microanalyses were done by Alfred Bernhardt, Max Planck Institut für Kohlenforschung, Mulheim (Kuhr), West Germany.

(g) Chemicals and Solvents

Chemicals and solvents were of reagent grade and were used without purification unless otherwise specified.

III. (B) ANALYTICAL TECHNIQUES

Indium was determined either by a gravimetric method, weighing  $\text{In}_2\text{O}_3$ , or by volumetric titration with ethylenediamine-tetra-acetic-acid (E.D.T.A.) using pyridine-2-azo-4-resorcinol as an indicator.<sup>54,55.</sup>

The general procedure of the gravimetric method was to weigh duplicate amounts of a complex into a porcelain crucible; the compounds were decomposed with conc. nitric acid, and dried on a steam-bath, and the temperature gradually increased until volatile matter was expelled. The crucibles were ignited at 1100C in a muffle furnace and the non-hygroscopic  $\text{In}_2\text{O}_3$  weighed in the open crucible.

The general procedure in the volumetric work was to weigh out duplicate quantities into 150 ml flasks, after which the compounds were decomposed with conc. nitric acid for two hours on a steam-bath; the solution was then diluted and made slightly alkaline with 3N ammonium hydroxide as indicated by the precipitation of white indium(III) hydroxide. The contents were warmed and the precipitate dissolved by adding sodium potassium tartrate. Excess ammonium hydroxide was boiled off and the pH of the solution adjusted to 8-10 by adding 0.01M solution of borax. Finally the solution



was titrated at 80°C (heating is necessary to accelerate the reaction) against a standard 0.01M solution of E.D.T.A., using two drops of indicator. (Concentration of the indicator = 0.1%). The end point is indicated by a colour change from orange-red to yellow.

### III. (C) PREPARATION OF MALEONITRILEDITHIOLATE COMPLEX COMPOUNDS

#### (a) Preparation of Sodium Maleonitriledithiolate, Na<sub>2</sub>MNT

NaS-C-CN was prepared according to the method of Bahr  
 $\parallel$   
 NaS-C-CN

and Schleitzer.<sup>56</sup> 4.9 g of anhydrous sodium cyanide powder was partially dissolved in 30 ml of N,N'-dimethyl formamide and 7.8 g of CS<sub>2</sub> added dropwise with stirring for 30 minutes. The solution was then diluted to 100 ml with iso-BuOH, and gradually warmed, after which the hot solution was filtered to remove unreacted NaCN. The filtrate was cooled, and the red-brown prismatic crystals of NaC<sub>2</sub>NS<sub>2</sub>·3Me<sub>2</sub>NCHO which separated were washed twice with a small amount of CCl<sub>4</sub> (yield = 20-23 g). The crystals were allowed to stand for five to six days under 100 ml CHCl<sub>3</sub>, during which time a yellow solid precipitated; this was washed with CHCl<sub>3</sub> and Et<sub>2</sub>O, and dissolved in the minimum amount of boiling MeOH in a Soxhlet extraction apparatus. The concentrated solution was cooled to -20 C and ether was added. The lemon

yellow cis- $\text{Na}_2\text{MNT}$  was precipitated. This hygroscopic salt was dried and stored over calcium chloride in a vacuum dessicator prior to use.

Table III-1. The I.R. Spectra of Na<sub>2</sub>MNT

<u>Billig et al</u> <sup>36</sup>	<u>Adams and Cornell</u> <sup>57</sup>	<u>Present Work</u>
(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )
2210	2190s	2200s
1450	-	1450s
1430	1424s	1438s
1151	1152m-s	1155m-s
1110	1112s	1115s
1050	1055m	1055m
1010	1017m	1015m
1000	-	-
-	862s	860s
-	522s	535m
-	384m	384w
-	234sh	-
-	215s	215s
-	185m	-
-	165sh	-
-	146w	-

The material obtained had an I.R. spectra in good agreement with those in the literature. (See Table III-1).

(b) Indium trichloride trihydrate.

$\text{InCl}_3 \cdot 3\text{H}_2\text{O}$  was prepared by dissolving 5.0 g of indium metal (Fisher standard 99.9% pure) in concentrated hydrochloric acid, followed by removal of excess HCl and  $\text{H}_2\text{O}$  on steam-bath. After being dried at 110 C in an oven overnight, approximately 11.45 g of  $\text{InCl}_3 \cdot 3\text{H}_2\text{O}$  was obtained.

(c)  $(\text{C}_2\text{H}_5)_4\text{N} [\text{In}(\text{MNT})_2]$ : tetraethylammonium bis(maleonitriledithiolate) indate(III).

A solution of 6.7 g of  $\text{Na}_2\text{MNT}$  in 20 ml of 1:2 aqueous methanol solution was warmed on a steam-bath, the temperature of the solution being about 65-70°C. A solution of 4.5 g of  $\text{InCl}_3 \cdot 3\text{H}_2\text{O}$  in 20 ml of 1:2 aqueous methanol was added to the warm  $\text{Na}_2\text{MNT}$  solution with stirring. The colour of the solution changed as the  $\text{In}^{3+}$  was added; the solution was then filtered and to the filtrate was added 20 ml of 4 g of  $(\text{C}_2\text{H}_5)_4\text{NBr}$  in aqueous methanol solution. After cooling in an ice bath, yellow crystals formed, and were separated on a Buchner funnel. The yellow crystals were very soluble in acetone, so that sodium chloride and bromide were easily removed. Water was added to the acetone solution, for recrystallization of  $(\text{C}_2\text{H}_5)_4\text{N} [\text{In}(\text{MNT})_2]$

which was dried at 60-65°C in vacuo for about four hours; yield 2.8 g of yellow needle crystals.

M.P. = 238 - 240

Analytical data:

	C	H	N	In
Calc.	36.52	3.80	13.32	21.90
Found	36.61	3.95	13.40	21.81

(d) Preparation of  $[(Et_4N)]_3 [In(MNT)_3]$  : tetraethylammonium tris(maleonitriledithiolate) indate(III).

2.3 g of  $In^{3+}$  in 20 ml of aqueous methanol solution was added to a warm solution of 5.8 g of  $Na_2MNT$  in 20 ml of 1:1 aqueous methanol at 60°C with stirring during about 20 minutes (approximate In:MNT (mole ratio) = 1:3.5) The solution was filtered. A solution of 5.6 g of  $(Et)_4NBr$  in 15 ml 1:1 aqueous methanol solution was added to the filtrate at 60°C. After cooling, fine yellow crystals were produced, and these were recrystallized from hot acetone/water solution (1:2); the lemon yellow needle crystals were separated, washed with ether and dried in vacuo at 60-65°C about four hours.

M.P. = 168 - 170

Analytical data:

	C	H	N	In
Calc.	46.75	6.54	13.01	12.75
Found	46.87	6.66	13.06	12.77

(e) Preparation of  $\text{Et}_4\text{N}[\text{In}(\text{MNT})_2 \cdot \text{o-phen}]$ : tetraethyl-  
ammonium bis(maleonitriledithiolate)1,10-phenanthroline  
indate(III).

A solution of 0.5 g of 1,10-phenanthroline (Fisher Certified Reagent) in 15 ml methanol was added dropwise to a solution of 1.5 g  $\text{Et}_4\text{N}[\text{In}(\text{MNT})_2]$  in 25 ml methanol at  $50^\circ\text{C}$  with stirring. As the 1,10-phenanthroline was added, the colour of the solution distinctly changed from brownish-yellow to yellow, and after a few minutes fine lemon-yellow crystals were obtained. These were recrystallized from hot methanol-acetone solution, and dried at  $60-65^\circ\text{C}$  in vacuo for about four hours; yield 1.1g of lemon yellow lustrous plate-like crystals.

M.P. = 249-250

Analytical data:

	C	H	N	In
Calc.	47.66	4.01	13.88	16.26
Found	47.93	3.89	13.82	16.26
	47.77	4.05	13.82	

(f) Preparation of  $\text{Et}_4\text{N}[\text{In}(\text{MNT})_2 \cdot \text{bipy}]$ : tetraethyl-  
ammonium bis(maleonitriledithiolate)2,2'-bipyridyl  
indate(III).

The method of preparation was carried out as above, using Fisher Certified Reagent 2,2'-bipyridyl. The shape of the lustrous lemon-yellow crystals was needle-like.

M.P. = 241 - 243

Analytical data:

	C	H	N	In
Calc.	45.81	4.14	14.38	16.88
Found	46.03	3.93	14.44	17.03
	45.99	4.11	14.23	

(g) Preparation of  $\text{Et}_4\text{N}[\text{In}(\text{MNT})_2\text{en}]$ : tetraethyl ammonium bis(maleonitriledithiolate)ethylenediamine indate(III).

A solution of 0.13 g of ethylenediamine (Fisher Certified Reagent) in 20 ml ethanol was neutralized using acetic acid to pH = 7-8 and then added dropwise with stirring to a solution of 1.00 g  $\text{Et}_4\text{N}[\text{In}(\text{MNT})_2]$  in 40 ml methanol at 55°C. After a few minutes, small yellowish crystals appeared and were recrystallized from acetone-ethanol solution and then dried at 60°C in vacuo for about four hours. The final product was brownish-yellow.

M.P. = 181 - 184

Analytical data:

	C	H	N	In
Calc.	36.95	4.78	16.75	19.62
Found	37.02	4.87	16.78	19.42

(h) Preparation of  $(\text{Et}_4\text{N})_2[\text{In}(\text{MNT})_2 \cdot \text{oxine hydroxyquinoline}]$ : tetraethylammonium 8-hydroxyquinolate bis(maleonitriledithiolate) indate(III).

A solution of 2 g of  $\text{Et}_4[\text{In}(\text{MNT})_2]$  in 50 ml methanol was neutralized with tetraethylammonium hydroxide (10% in water; Eastman Organic Chemicals) and a solution of 0.6 g of 8-hydroxyquinoline in 15 ml acetone added dropwise to the neutralized solution with stirring at a temperature of about  $45^\circ\text{C}$ . The pH of the solution was adjusted to 6-7 using tetraethylammonium hydroxide before addition of 8-hydroxyquinoline; 25 ml water was then added to the solution. After overnight standing, a yellow compound precipitated, and was dried at room temperature in vacuo for about six hours.

M.P. = 115-117

Analytical data:

	In
Calc.	14.40
Found	14.30

(i) Preparation of  $\text{Et}_4\text{N}[\text{In}(\text{MNT})_2(\text{dma})_2]$ : tetraethylammonium bis(maleonitriledithiolate) bis(dimethylacetamide) indate(III).

2.00 g of  $\text{Et}_4\text{N}[\text{In}(\text{MNT})_2]$  was dissolved in excess N,N'-dimethylacetamide (dma: Fisher Certified Reagent),



and the solution heated to 55° and stirred for about one hour. The solution was then kept for one or two days at room temperature, during which time yellowish rectangular crystals appeared; these were air dried at room temperature for about two hours. The compound decomposed under vacuo. M.P. = decomposed at 60°, the compound turning yellow.

Analytical data:

	C	H	N	In
Calc.	40.20	5.44	13.99	16.40
Found	40.09	5.52	13.35	16.15

The compound has lower carbon, nitrogen, and indium and higher hydrogen contents than the theoretical values, which indicates that it might contain moisture. These results may also be indicative of the low stability of the compound.

### III. (D) PREPARATION OF THE LIGAND 1,1'-DICYANOETHYLENE-2,2'-DITHIOLATE, AND ITS COMPLEX COMPOUNDS

(a) Preparation of Sodium 1,1'-dicyanoethylene-2,2'-dithiolate (iMNT).

$$\begin{array}{c} \text{NC} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{NC} \end{array} = \begin{array}{c} \text{SNa} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{SNa} \end{array}$$
 was prepared according to the published method.<sup>58</sup> 4 g of sodium metal was dissolved in 50 ml of methanol and the solution made up to 52.5 ml to give a solution of sodium methoxide. To 30 ml NaOMe solution at

10 was added 6.6 g of malononitrile; after cooling to 5° in an ice bath, 3 ml carbon disulphide was added dropwise with stirring, followed by 15 ml NaOMe and 0.75 ml CS<sub>2</sub>, was finally added, the reaction mixture kept below 10°C in an ice bath yielding a yellow precipitate. The pale yellow sodium salt obtained was used without further purification. The I.R. and U.V. spectra ( Table III-2, III-3) were taken to confirm that the material prepared was identical with that described in the literature.

Table III-2. Infrared Spectra of  $\text{Na}_2(\text{iMNT})$

(a)	(b)
<u>Published data (cm<sup>-1</sup>)</u> 52,59	<u>This work (cm<sup>-1</sup>)</u>
3500	3490
3300	3250
2180	2180
	2110
1630	1620
1370	1375
1220	1239
950	950
880	880
-	660
-	620
-	510
-	481
-	318
-	280

(a) Infrared spectrum was measured with a Perkin-Elmer model 42 spectrophotometer using KBr disk.

(b) Infrared spectrum was measured with a Perkin-Elmer model 475 grating infrared spectrophotometer using KBr disk technique.

Table III-3. Ultraviolet Spectra of Na<sub>2</sub>(1MNT)

(a) Published data ( <u>max cm<sup>-1</sup></u> )	(b) This work ( <u>max cm<sup>-1</sup></u> )
29100	29100
31400	31400
38600	38600
39600	39600
49500	47500

- (a) Electronic spectrum was measured on a Cary Model 14 recording spectrophotometer in acetonitrile solution.
- (b) U.V. spectrum was measured on a Unicam SP 800 recording spectrophotometer in acetonitrile.

(b) Preparation of  $[(n-C_4H_9)_4N]_2 [In(iMNT)_2X]$ :  
tetrabutylammonium halo bis(1,1-dicyanoethylene-2,2'-  
dithiolate) indate(III).

A solution of 1.6 g of In(III) (as  $InCl_3 \cdot 3H_2O$ ) in 16 ml of methanol was added dropwise with stirring to a solution of 6 g of  $Na_2(iMNT)$  in 30 ml of methanol. the pH after addition of In(III) solution was approximately 4. The pale yellow solution was filtered and sodium chloride easily removed. The filtrate was added to a stirred solution containing an equimolar quantity of  $(n-C_4H_9)_4NX$  (X=Cl, Br or I) at  $45-50^\circ$ . After a few minutes, sodium halide precipitated and was filtered off. The filtrate was kept overnight at room temperature, and the pale yellow crystals which formed were collected and washed with water and water-methanol solution (1:1) and recrystallized from methanol, yielding triclinic crystals of  $(n-C_4H_9)_4N_2 [In(iMNT)_2X]$  which were then dried in vacuo at 50 for about four hours.

M.P. (X=Cl) = 164-165

(X=Br) = 136-138

(X=I) = 130-131

Analytical data:

	C	H	N	Br	In
Calc.	50.04	7.55	8.75	8.32	11.95
Found	50.59	7.56	8.78	8.42	11.98

In the chloride and iodide compounds, the indium percentages were

X = Cl

Calc. 12.52

Found 12.44, 12.48

X = I

Calc. 11.41

Found 11.52, 11.69

(c) Preparation of  $[(n-C_4H_9)_4N]_3 [In(\underline{i}MNT)_3]$ : tetra-butylammonium tris(1,1'-dicyanoethylene-2,2'-dithiolate) indate(III).

1.6 g of In(III) (as  $InCl_3 \cdot 3H_2O$ ) in 23 ml of methanol was added to a stirred solution of 9 g of  $Na_2(\underline{i}MNT)$  in 30 ml of methanol at temperature of 50 (molar ratio In(III):  $Na_2(\underline{i}MNT) = 1:3$ ). The yellow solution was filtered and sodium chloride removed. A solution of 10 g of  $Bu_4NBr$  in 20 ml of methanol was added to the filtrate with stirring at 45°, when a white precipitate of NaBr appeared and was filtered off. Yellow crystals of the complex were obtained after standing overnight. Recrystallization from hot methanol-acetone solution gave yellow hexagonal crystals, which were washed with water and water-methanol and dried in vacuo at 50°.

M.P. = 165 - 166

Analytical data:

	C	H	N	In
Calc.	57.07	8.62	9.98	9.09
Found	57.29	8.41	9.83	9.06

(d) Preparation of  $(n\text{-Bu}_4\text{N})[\text{In}(\text{iMNT})_2\text{phen}]$ :  
tetrabutylammonium bis(1,1'-dicyano-2,2'-dithiolate)  
1,10-phenanthroline indate(III).

A solution of 0.5 g of 1,10-phenanthroline in 15 ml of methanol was added dropwise to a solution of 2.4 g of  $(n\text{-Bu}_4\text{N})_2 \text{In}(\text{iMNT})_2\text{Br}$  in 50 ml of methanol at 45°C with stirring; after a few minutes a yellowish precipitate was obtained. Recrystallization from a methanol-acetone solution (1:1) gave yellowish orthorhombic crystals, which were filtered, washed with cold water:methanol (1:2) and dried in vacuo at 60-65°.

M.P. = 274-276

Analytical data:

	C	H	N	In
Calc.	52.61	5.88	11.93	13.99
Found	52.79	5.71	11.97	14.07

(e) Preparation of  $n\text{-Bu}_4\text{N}[\text{In}(\text{iMNT})_2\text{bipy}]$ : tetra-butylammonium bis(1,1'-dicyanoethylene-2,2'-dithiolate)-2,2'-bipyridyl indate(III).

The preparation of the compound was carried out as above. The crystals were orthorhombic, like those of 1,10-phenanthroline compound.

M.P. = 241 - 243

Percentage In: Calc. 14.60 Found 14.44.

III. (E) PREPARATION OF TOLUENE-3,4-DITHIOLATE COMPLEX COMPOUNDS

(a) The ligand, toluene-3,4-dithiol (TDT), was procured from Matheson, Coleman and Bell Co. (Melting point 28-30 ).

(b) Preparation of  $\text{Et}_4\text{N}[\text{In}(\text{TDT})_2]$ : tetraethyl-ammonium bis(toluene-3,4-dithiolate) indate(III).

Toluene-3,4-dithiol (TDT) in 50 ml of ethanol was added dropwise to a solution of 4.3 g of  $\text{InCl}_3 \cdot 3\text{H}_2\text{O}$  in 200 ml of ethanol at 55-60°. The solution was stirred and neutralized with 3% NaOH in ethanol to adjust the pH to about 3-4. The white precipitate of sodium chloride was filtered off and 3.5 g of  $(\text{C}_2\text{H}_5)_4\text{NBr}$  in 15 ml of ethanol added to the filtrate. After cooling, the pale yellow crystals were filtered off and washed with distilled



water until no bromide ion could be identified in the washings. The product was recrystallized from hot ethanol and dried in vacuo at 60°.

M. P. = 205-207

analytical data:

	C	H	S	In
Calc.	47.74	5.85	23.15	20.75
Found.	47.74	6.14	23.86	20.92

(c) Preparation of  $\text{Et}_4\text{N}[\text{In}(\text{TDT})_2\text{phen}]$ : tetraethylammonium bis(toluene-3,4-dithiolate)-1,10-phenanthroline indate(III).

To a solution of 1.5g of  $\text{Et}_4\text{N}[\text{In}(\text{TDT})_2]$  in 60ml of acetonitrile, or tetrahydrofuran (THF) was added 0.37g. of 1,10-phenanthroline in 15ml of ethanol with stirring at temperature of 40°C. The colour of the solution changed distinctly from pale yellow to orange during the addition of 1,10-phenanthroline. After a few minutes standing at room temperature, both orange and yellow crystals precipitated and were subsequently recrystallized from hot acetonitrile-methanol (2:1) or tetrahydrofuran-methanol solutions. The crystals were separated by picking out the yellow precipitate in methanol; the crystals were dried at 60° for about four hours.

M. P. = 218-220° (orange)

= 276-278° (yellow)

## Analytical data (orange crystals)

	C	H	S	In
Calc.	55.65	5.50	17.45	15.65
Found.	55.65	5.55	17.33	15.45

(d) Preparation of  $\text{Et}_4\text{N} [\text{In}(\text{TDT})_2\text{dipy}]$  : tetraethyl-  
ammonium bis(toluene-3,4-dithiolate)-2,2-dipyridyle indate(III).

The preparative method was exactly like that for the phenanthroline complex, and yielded orange crystals mixed with very small amount of yellow material. It was not possible to obtain a pure sample of this latter substance.

M.P. = 158-159

## Analytical data:

	C	H	N	In
Calc.	54.19	5.64	5.92	16.18
Found.	54.14	5.61	5.95	16.21

CHAPTER IV

POLAROGRAPHY

IV. (A) PRINCIPLES OF METHOD

Polarography involves the electrolysis of a solution of electro-oxidizable or electro-reducible materials between a dropping mercury electrode and some reference electrode. The potential applied between these is varied and the consequent change in the flow of current are measured. The dropping mercury electrode (DME) is experimentally simple, consisting of a fine capillary attached to a reservoir containing mercury, which passes slowly down the capillary and emerges in the form of small drops. The commonest use of this electrode is as a cathode so that the processes studied are reduction processes. Very often the reduction studied are those of metal ions, when the metal itself forms an amalgam on the surface of the mercury drop. In polarography the situation is so arranged that the reducible ions arrive at the DME by natural diffusion alone and to make this possible, a "supporting electrolyte" (or background or "base" electrolyte) is added to the solution so that electrical migration has a negligible effect.

Polarography can be used for the identification of elements, measurement of concentration, or the determination

of oxidation states of reducible or oxidizable species such as metal ion, chelate complexes, inorganic acid radicals, and numerous organic compounds. Trace quantities of chemical impurities, and the amount of gases in solution, redox potentials, formation constants, coordination number, and kinetic parameters have also been determined. Substances can be studied in aqueous solution or in non-aqueous media, such as ethanol, methanol, acetonitrile, dimethylformamide, ammonia, and molten salts.

A simple treatment of polarographic theory will now be given.

Consider the electrode reaction as



Ox = Oxidisable species                      Red = Reducible species

The Ilkovic equation states that:

$$i_d = k n D^{\frac{1}{2}} C m^{\frac{2}{3}} t^{\frac{1}{6}} \quad \text{--- (II)}$$

Where  $i_d$  = limiting current in microamps ( $\mu\text{A}$ )

$k$  = a constant

$n$  = number of electrons transferred in reaction (I)

$D$  = Diffusion coefficient of the electro-active species

$C$  = Concentration of electro-active species in millimoles per liter.

$m$  = rate of flow of mercury from the dropping mercury electrode (DME) in mg per second

t = life time of one drop of mercury in seconds.

A second useful equation is the polarographic wave equation (III)

$$E_{dc} = E_{\frac{1}{2}} - \frac{RT}{nf} \cdot \ln \frac{i}{i_d - i} \text{ - - - - - (III)}$$

Which at 298 C gives

$$E_{dc} = E_{\frac{1}{2}} - \frac{0.0592}{\alpha n} \log \frac{i}{i_d - i} \text{ - - - - - (IV)}$$

Where  $E_{dc}$  = dropping electrode potential

$E_{\frac{1}{2}}$  = half-wave potential where  $i = \frac{i_d}{2}$

i = the current in microamps ( $\mu A$ )

F = 1 Faraday (96500 coulombs per equivalent)

$\alpha$  = reversibility

Graphs of equation (III) for various values of n are shown in figures IV-1 and IV-2. It is important to note that the polarographic wave equation for the reduction of a complex metal ion is the same as the equation for the reduction of a simple metal ion.

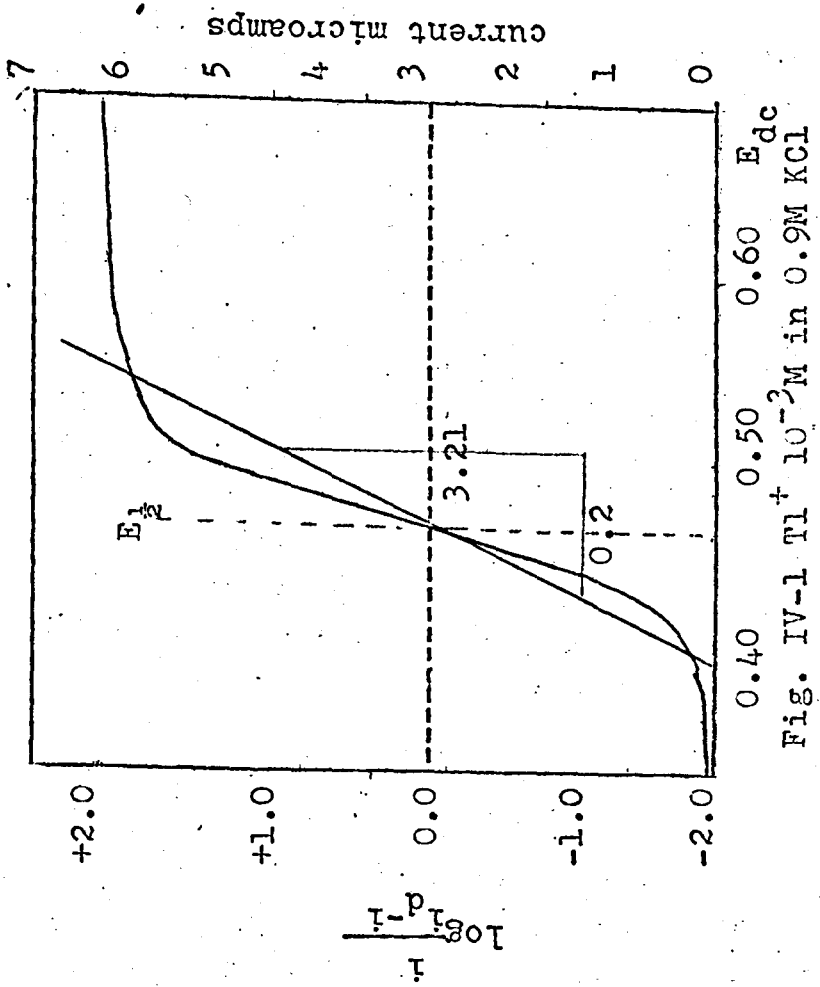


Fig. IV-1 Tl<sup>+</sup> 10<sup>-3</sup>M in 0.9M KCl

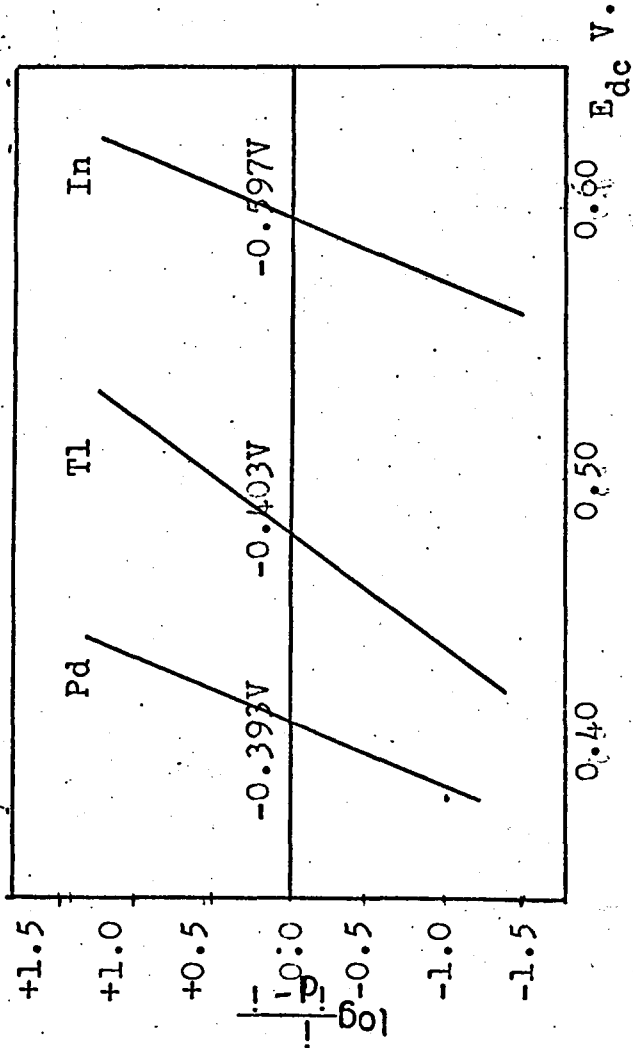


Fig. IV-2  $\log \frac{i}{i_d - i}$  vs  $E_{dc}$  for  $Tl^+$ ,  $Pd^{2+}$ ,  $In^{3+}$   
Three straight lines are obtained, the slope of  $Tl^+$ ,  $Pd^{2+}$ ,  $In^{3+}$  are 0.059, 0.033 and 0.020 respectively in agreement with  $n=1, 2,$  and  $3.$

Thermodynamic and polarographic reversibility are not necessarily synonymous. A thermodynamically irreversible electro-chemical process will always result in an irreversible polarographic process, but a reversible thermodynamic reaction may be reversible or irreversible polarographically. Reversibility in the present discussion therefore implies polarographic reversibility and not thermodynamic reversibility. In the irreversible case the potential no longer depends on the rate of diffusion of the electro-active substance, so that the rate determining step may depend on the electrochemical process, on adsorption at the dropping mercury electrode, on some chemical reaction preceding or following the electro-chemical process, or on some combination of these.

The simplest test for reversibility is the slope of the plot of  $\log \frac{i}{i_d - i}$  versus  $E_{dc}$  (equation (III) ), which gives the reversibility parameter  $\alpha$ . In fig. IV-2 the proofs of reversibility are in the values

$Tl^+$	Slope = 0.592	$n=1$	$\alpha=1$	(reversible)
$Pd^{2+}$	Slope = 0.033	$n=2$	$\alpha=0.88$	(irreversible)
$In^{3+}$	Slope = 0.020	$n=3$	$\alpha=1$	(reversible)



The half-wave potential of complex ions may depend on (a) the ligands present, and (b) the concentrations of the ligand (see table IV-I). For a given ligand, the half-wave potential shift depends on the ligand concentration, and this has been used to determine the coordination number of complex ions. Equation (V) has been derived for a mononuclear reversible reaction: -

$$\frac{d(E_{\frac{1}{2}})_c}{d \log C_x} = \frac{0.0592}{n} p \quad \text{--- (V)}$$

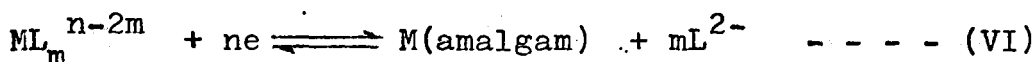
Where p = number of ligands per metal ion

$C_x$  = concentration of ligand.

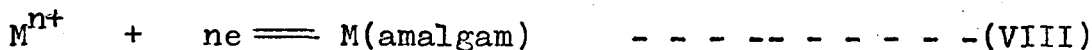
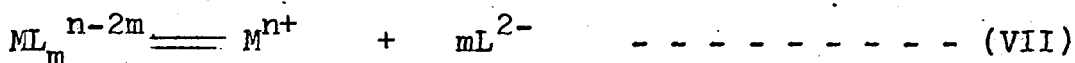
The value of p can be obtained directly from the slope of a plot of  $E_{\frac{1}{2}}$  against  $\log C_x$ .

The dissociation constant of a complex  $ML_m$  can be obtained in some cases from the half-wave potential of the complex ions, and the potential of the simple ion using equation (V).<sup>60,61,62.</sup>

For a complex ion of a metal which is reduced to the metallic state (i.e. amalgam) at the dropping mercury electrode, the reduction process may be represented by



When  $L^{2-}$  is a bidentate ligand, this reaction may be regarded as the sum of the partial reactions



$$K_d = \frac{M^{n+} L^{2- m}}{ML_m^{n-2m}} \quad \text{--- (IX)}$$

$K_d$  is the dissociation constant, related to  $\beta_1$  by

$$\beta_1 = \frac{1}{K_d} \frac{ML_m^{n-2m}}{M^{n+} L^{2- m}} \quad \text{--- (X)}$$

Where  $\beta_1$  is the overall formation constant for the complex  $ML_m^{n-2m}$ .

From equation (VI) it can be shown that

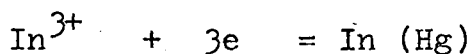
$$E(C)_{\frac{1}{2}} - E(S) = \frac{0.0592}{n} \log K_d - p \frac{0.0592}{2} \log C_x \quad \text{(at } 25^\circ\text{C)}$$

Where  $E(C)_{\frac{1}{2}}$  = half-wave potential of the complex ion

$E(S)$  = half-wave potential of the uncomplexed metal ion.

IV. (B) REVIEW OF POLAROGRAPHIC STUDIES OF INDIUM

The normal electrode potential of indium in aqueous solution has been determined by Hattox<sup>63</sup> and by Hakomori<sup>64</sup> who find  $E = -0.336V$  and  $-0.340V$  respectively, which potential is very close to that for cadmium. The original studies of reduction of trivalent indium ions, using polarographic method in solutions containing chloride or bromide ion were done by Heyrovsky<sup>65</sup>, Cozz<sup>66</sup>, Kolthoff<sup>62</sup> and Schufle<sup>67</sup>. Indium(III) is reduced at a dropping mercury cathode to metal in a single reversible step:



No evidence of reduction to divalent or monovalent states has been reported. The half-wave potential for indium(III) however depends on the presence of complex forming agents (ligands). (See table IV-1).

Table IV-1

The half-wave potential of In(III) at different concentrations of ligands.

<u>Salt</u>	<u>Concentration (M)</u>	<u><math>E_{\frac{1}{2}}</math> (a)</u>
KCl	0.1	0.56
KCl	1	0.636
KCl	$6 \times 10^{-5}$	0.504
KCl	0.185	0.578
KCl	0.51	0.596
KCl	1.0	0.612
KBr	0.1	0.512
KBr	0.16	0.546
KBr	0.20	0.579
ethylenediamine	1.0	1.07
ethylenediamine	1.0	1.07
ethylenediamine	2.0	1.30

(a) The potential is relative to a normal calomel electrode; it was suggested that the shifts in the half-wave potential are due to the formation of indium complex ions  $\text{InL}_x^{3-x}$  in solution.

#### IV. (C) EXPERIMENTAL

A Metrohm Polarocord E261R rapid polarograph and a Metrohm iR Compensator E446 (for obtaining error-free polarograms from low conductivity solutions) were used to obtain the polarograms. A dropping mercury electrode with the drop controller on the polarography stand served as the working electrode (Metrohm EA '53). The reference electrode was a Ag/AgCl electrode (EA 420 Metrohm) in 0.1M  $\text{Et}_4\text{NClO}_4$  acetonitrile solution, inserted into the sample solution. The rate of leakage of  $\text{ClO}_4^-$  through the porous tip of the reference electrode was negligible during a polarographic measurement. A constant temperature water bath maintained at  $25 \pm 0.1^\circ\text{C}$  was used throughout this work to thermostat the electrode compartment.

The supporting electrolyte,  $\text{Et}_4\text{NClO}_4$ , was prepared by the following procedure. A hot 1M aqueous solution of tetraethylammonium bromide was added slowly with stirring to an equivalent amount of hot 0.1M aqueous solution of sodium perchlorate. After cooling in an ice bath the precipitate was filtered off on a Buchner funnel and washed with ice-cold water until the wash-liquid was free from bromide. The salt was recrystallized from water and dried in vacuo at  $60^\circ$  for about five hours.

The solvent, acetonitrile, was purified by the method used for conductivity studies.<sup>53</sup>

De-aeration: the electrolysis solution could be deaerated completely in about 15 minutes by bubbling purified nitrogen through it. Nitrogen was purified by the method described by Meites and Meites.<sup>61</sup>

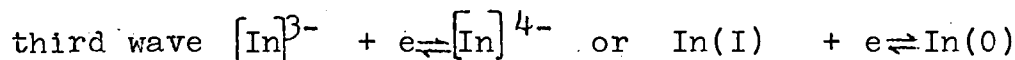
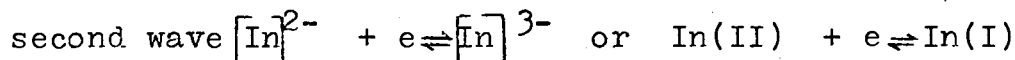
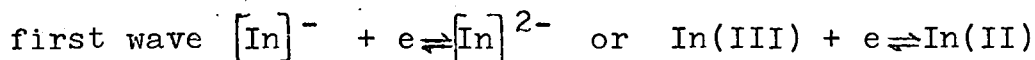
Due to the high vapor pressure of acetonitrile (Ca 80mm at 20°), it was necessary to presaturate the nitrogen with acetonitrile vapour, by passing the nitrogen through a train of wash bottles containing acetonitrile at room temperature.

#### IV. (D) RESULTS AND DISCUSSION

The object of the polarographic work was to study the reduction or oxidation, the relative stability and coordination number of the complexes whose preparation was described in Chapter III.

##### (a) The study of half-wave potentials and reversibility.

Three polarographic reduction waves of these complexes in acetonitrile solution with tetraethylammonium perchlorate as a supporting electrolyte showed in almost every case a series of reversible or irreversible one electron transfer reactions:



This behaviour is in sharp contrast to the usual aqueous) phase polarographic reduction



and represents reduction to In(I) and In(0) complexes, and the first identification of an In(II) complex.

Usually the height of each reduction wave should be approximately equal in polarograms. However, three reduction waves were observed. The second wave was generally 10-20% lower than the first, and the third wave usually had an abnormally high large hump, which might be due to an

In(0) complex combining with an intermediate. Vlcek<sup>69</sup> has suggested that such humps result from reoxidation of intermediate products. (Fig. IV-1 solid line). In order to observe this phenomenon properly, a high resolution a.c. polarograph was carried out. (Fig. IV-3 broken line).

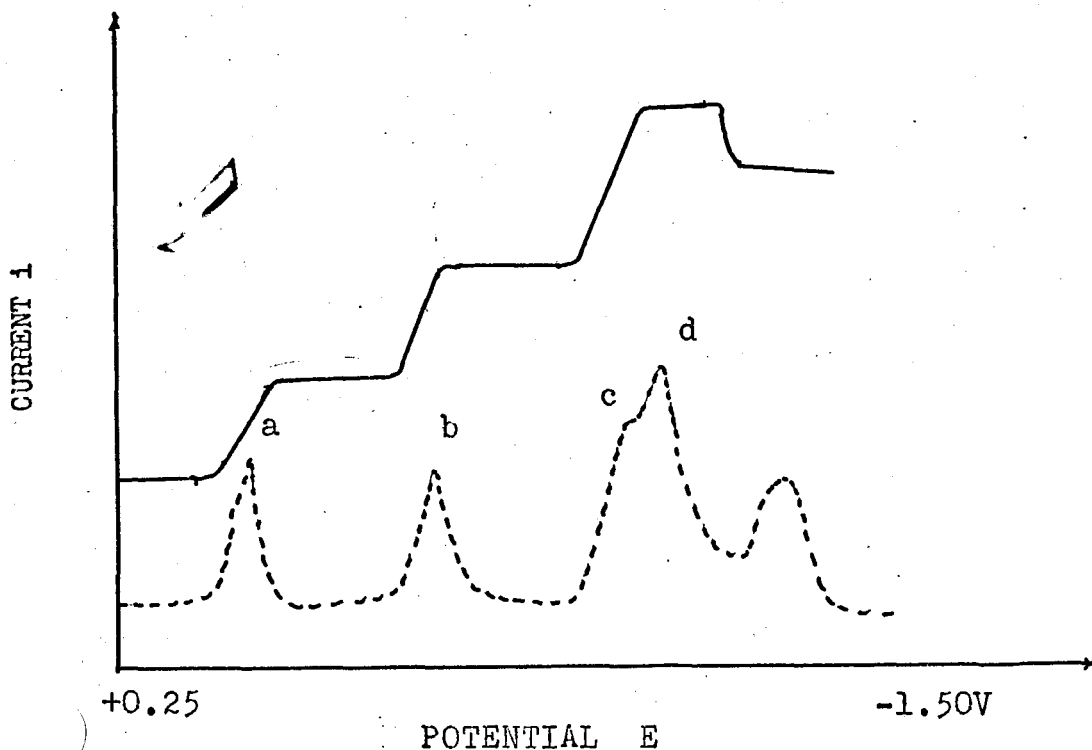


Fig. IV-3 The Polarogram of  $\text{In}(\text{MNT})_2 \cdot 5 \times 10^{-4} \text{M}$  in  $\text{H}_2\text{O}-\text{MeOH}$  solution, 0.1M LiCl as supporting electrolyte.



To get a better a.c. polarogram a low resistance cell must be used, and the compound  $[\text{In}(\text{MNT})_2]^-$  was therefore dissolved in aqueous-methanol solution (ratio 4:1) with lithium chloride as the supporting electrolyte.

Since in the a.c. polarograph (Fig. IV-3, broken line) the waves marked (a), (b) and (c) are all the same height, each of these waves must represent one-electron reductions, and we can therefore identify the shoulder (c) as the third wave without any doubt. The wave (d) is considered to represent the reoxidation of an intermediate product although the actual compound being oxidized cannot be identified.

The discussion of reduced states of metal dithiolate complexes is based on the recent review by Schrauzer<sup>70</sup>. The Group VIII Metal Complexes  $\text{MS}_4\text{C}_4\text{R}_4$  ( $\text{R}=\text{CN}, \text{H}, \text{CF}_3$  or Ph) resemble dithio-quinones in their pronounced affinity for electrons. On reduction  $\text{MS}_4\text{C}_4\text{R}_4^-$  and  $\text{MS}_4\text{C}_4\text{R}_4^{2-}$  are formed, of which the  $\text{MS}_4\text{C}_4\text{R}_4^-$  anion proved to be paramagnetic in the solid state and in solution. Studies of the compound  $[\text{NiS}_4\text{C}_4\text{Ph}_4]^-$  containing  $\text{Ni}^{61}$  showed a small hyperfine splitting in the ESR spectrum due to the delocalization of the odd electron in ligand-metal ring orbitals.<sup>37,71</sup> In addition, in the  $[\text{Ni}(\text{MNT})_2]^-$  ion, the C-C and C-S bond distances are 1.356Å and 1.710Å respectively. These values are intermediate between those

found for single and double bonds. In the  $[\text{Ni}(\text{MNT})_2]^{2-}$  the C-C and C-S distances are 1.33Å and 1.75Å. It was therefore concluded that the unpaired electron occupied a  $\pi$ -MO delocalized over the whole molecule.

The existence of the formal lower oxidation states In(II), In(I) and In(0) have been demonstrated in the polarograms, resulting in the reduction half-wave potentials given in Tables IV-2,3,4. Following the previous explanation, we suggest that in the indium(II), (I) and (0) dithiolate complexes the electrons are accommodated in a  $\pi$ -molecular orbital delocalized over the whole ring system of the molecule.

The measured diffusion current was found to be linearly dependent on the concentration of the complex  $[\text{In}(\text{MNT})_2]^-$  which is to be expected from Ilkovic equation II.

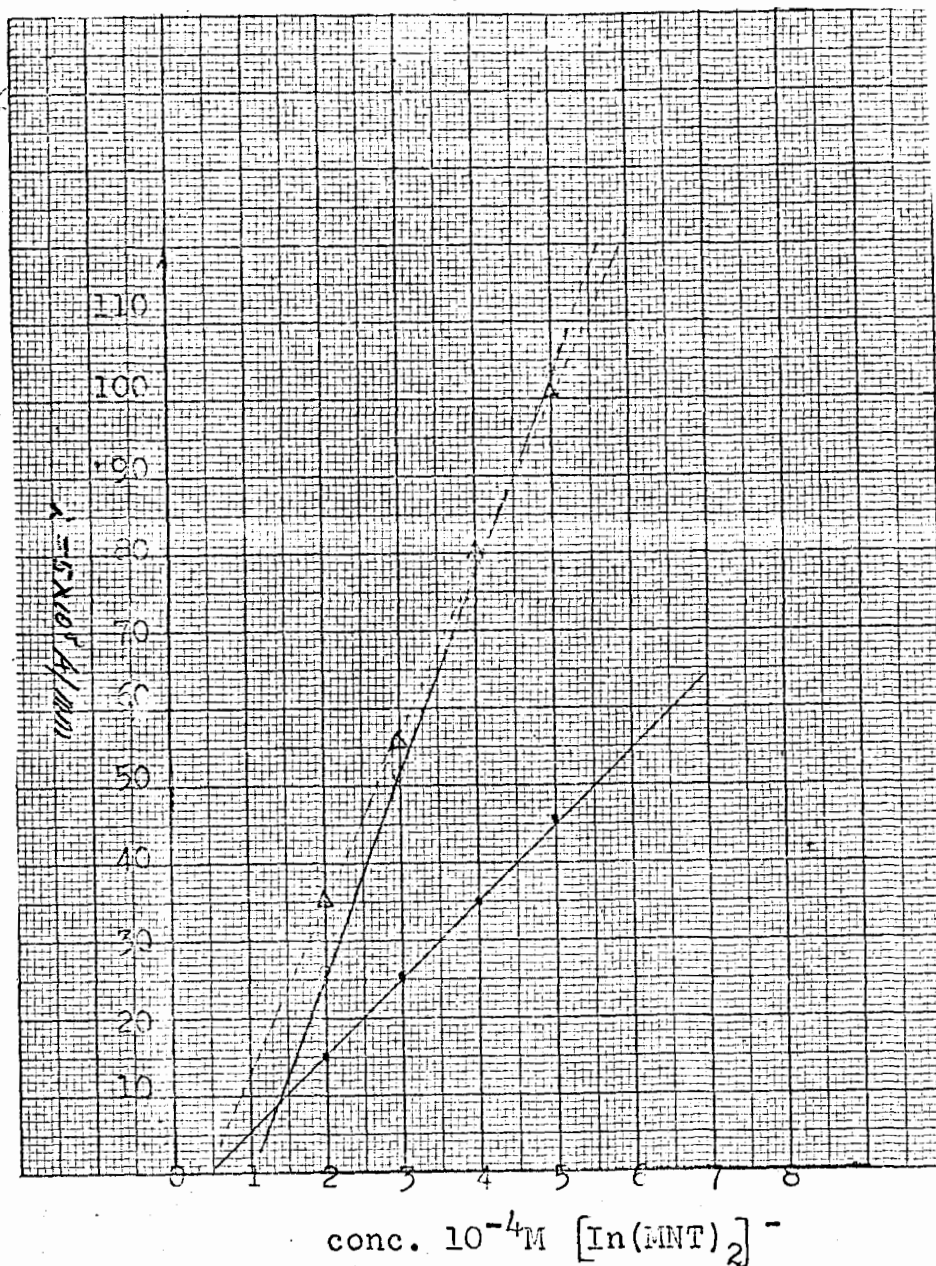


Fig. IV-4 Concentration vs Current.

The three lines did not pass through the original point due to inaccuracies in the concentration measurements.

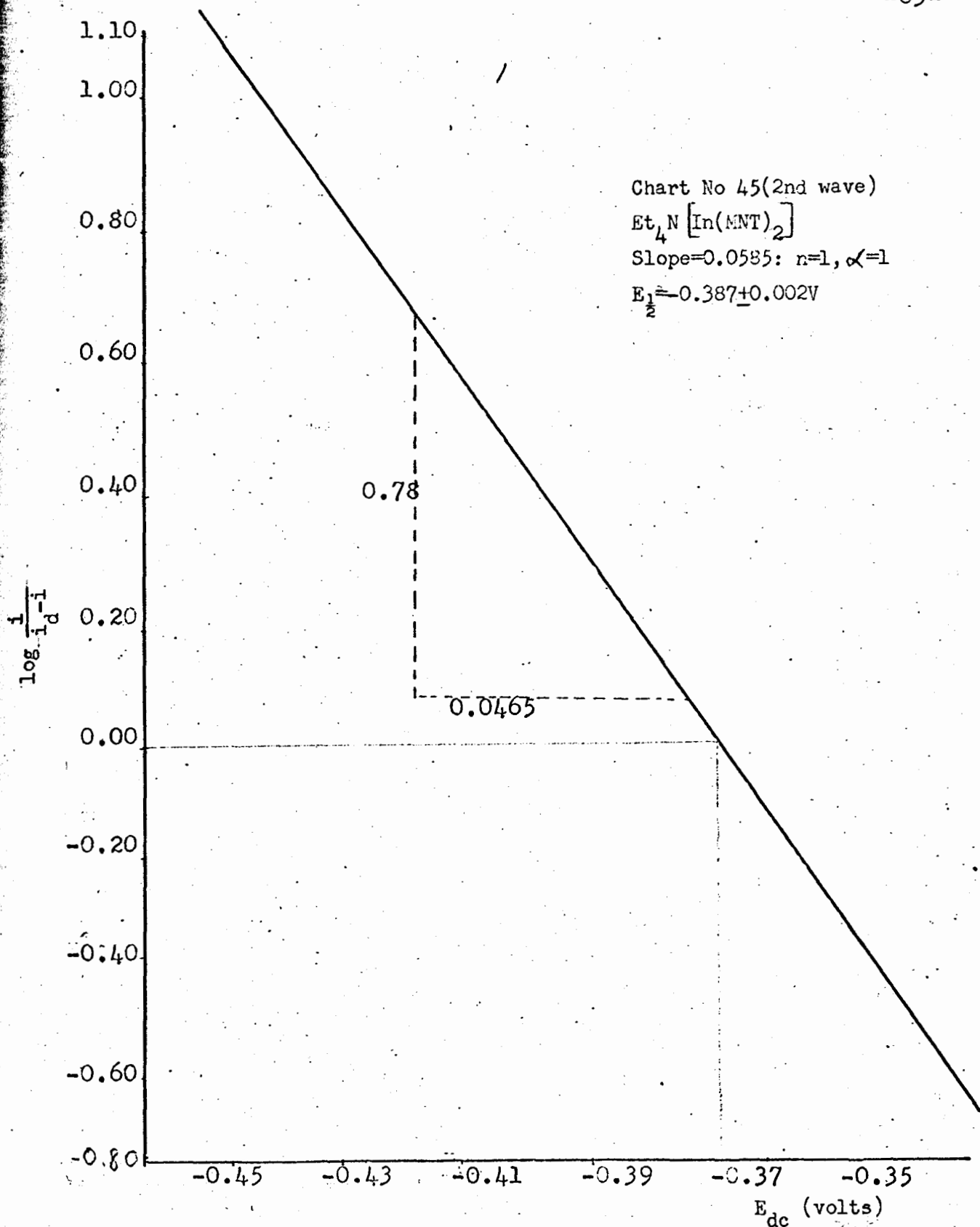


Fig. IV-5  $\log \frac{i}{i_d - i}$  vs  $E_{dc}$  plot

Tables IV-2, IV-3 and IV-4 show the half-wave potentials for the complexes at a concentration of  $5 \times 10^{-4}$  M in acetonitrile. The values were obtained from equation (IV) by plotting  $\log \left( \frac{i}{i_d - i} \right)$  against the potential  $E_{dc}$ , the diffusion current potential. The equation (IV) predicts a straight line with slope 0.0591 at 25°C. The point on this line corresponding to  $i = \frac{i_d}{2}$  gives a precise measurement of the half-wave potential  $E_{\frac{1}{2}}$ . The slope of the tangent to the line shows the reversibility and "n" is the number of electrons transferred. The half-wave potentials, reversibilities and electron transfer numbers of all the indium(III) complexes and their adducts which have been obtained from plots of  $E_{\frac{1}{2}}$  vs  $\log \left( \frac{i}{i_d - i} \right)$  plots are given in Table IV-2, 3 and 4. A typical plot is shown in Fig. IV-5.

Table IV-2 The Half Wave Potential (in Volt) and Reversibility of MNT Complexes

Complexes	First Wave		Second Wave		Third Wave	
	$E_{1/2}$	$\alpha$	$E_{1/2}$	$\alpha$	$E_{1/2}$	$\alpha$
$[\text{In}(\text{MNT})_2]^-$	+0.310	0.985 n=1	-0.379	0.980 n=1	-1.932	0.977 n=1
$[\text{In}(\text{MNT})_2\text{phen}]$	+0.231	0.983 n=1	-1.267	0.859 n=1	-1.851	0.864 n=1
$[\text{In}(\text{MNT})_2\text{bipy}]$	+0.218	+1.43 n=1	--	--	-1.819	0.894
$[\text{In}(\text{MNT})_2\text{on}]^-$	+0.072	.40	-1.071	0.929	-2.062	1.01
$[\text{In}(\text{MNT})_2\text{oxine}]$	+0.058	--	-1.740	--	-2.063	--
$[\text{In}(\text{MNT})_2(\text{dma})_2]^-$	+0.228	$\alpha > 1$	-0.360	1.02	-2.084	1.00
$[\text{In}(\text{MNT})_3]^{3-(a)}$	--	--	--	--	-2.039	1.12 n=1

(a) The polarogram of this compound fail to show a first and second wave

Table IV-3 Tah Half Wave Potential and Reversibility of  $\text{In}(\text{IMNT})$  Complexes

Complexes	First Wave		Second Wave		Third Wave	
	$E_{1/2}$	$\alpha$	$E_{1/2}$	$\alpha$	$E_{1/2}$	$\alpha$
$[\text{In}(\text{IMNT})_2\text{Cl}]^2$	+0.348	0.727	-0.660	1.00	-1.775	1.09
$[\text{In}(\text{IMNT})_2\text{Br}]^{2-}$	+0.418	0.788	-0.645	1.00	-1.737	1.00
$[\text{In}(\text{IMNT})_2\text{I}]^{2-}$	+0.419	0.609	-0.644	0.834	-1.703	0.861
$[\text{In}(\text{IMNT})_3]^{3-}$	+0.494	0.881	-0.176	1.00	-1.795	1.859
$[\text{In}(\text{IMNT})_2\text{phen}]^-$	+0.363	1.00	-1.003	1.00	-1.792	1.18
$[\text{In}(\text{IMNT})_2\text{bipy}]^-$	+0.360	1.00	-1.073	0.623	-1.801	1.13

Table IV-4 The Half Wave Potential (in volt) and Reversibility of TDT Complexes

Complexes	First Wave		Second Wave		Third Wave	
	$E_{1/2}$	$\alpha$	$E_{1/2}$	$\alpha$	$E_{1/2}$	$\alpha$
$[\text{In}(\text{TDT})_2]$	-0.193	0.984	-0.651	0.606	-1.658	0.950
$[\text{In}(\text{TDT})_3]^{3-}$	+1.88	0.977	-0.654	0.948	-1.855	0.963
$[\text{In}(\text{TDT})_2\text{phen}]^{(a)-}$	--	--	--	--	--	--
$[\text{In}(\text{TDT})_2\text{bipy}]^{(a)-}$	--	--	--	--	--	--

(a) Polarogram steps not clear enough for values to be obtained.



(b) Stability constant studies.

Indium complexes  $[\text{In}(\text{MNT})_2]^-$ ,  $[\text{In}(\text{MNT})_3]^{3-}$ ,  $[\text{In}(\text{iMNT})_3]^{3-}$ ,  $[\text{In}(\text{TDT})_2]^-$ , and  $[\text{In}(\text{TDT})_3]^{3-}$  have been studied by means of the polarographic method in order to determine the stability of these complexes which are assumed to reduce to indium amalgam in the third wave. The reaction equation and formation constant may be represented by equations (IV), (VII), (IX), (X) and (XI) on page 53.

The standard potential of the Indium ion ( $E_s$ ) is equal to -0.596 Volt relative to the Ag/AgCl electrode in acetonitrile.

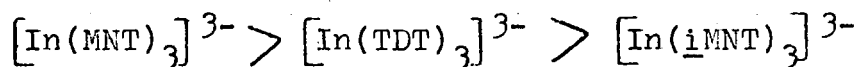
The half-wave potentials (in volts) of the complexes  $[\text{In}(\text{MNT})_2]^-$ ,  $[\text{In}(\text{MNT})_3]^{3-}$ ,  $[\text{In}(\text{iMNT})_3]^{3-}$ ,  $[\text{In}(\text{TDT})_2]^-$ , and  $[\text{In}(\text{TDT})_3]^{3-}$  are equal to -1.982, -2.039, -1.795, -1.658 and -1.855 respectively in acetonitrile solution at  $25^\circ \pm 0.1$ . (See Tables IV-2, IV-3 and IV-4). The formation constants then obtained from equation (XI) are given in the Table IV-5.

Table IV-5

Formation constants of dithiolato complexes

<u>Complexes</u>	<u><math>-E_1</math> (volts)</u>	<u><math>K_d</math></u>	<u><math>i</math></u>
$[\text{In}(\text{MNT})_2]$	1.982	$2.1 \times 10^{-29}$	$4.7 \times 10^{30}$
$[\text{In}(\text{MNT})_3]^{3-}$	2.039	$6.5 \times 10^{-32}$	$1.5 \times 10^{33}$
$[\text{In}(\text{iMNT})_3]^{3-}$	1.703	$3 \times 10^{-27}$	$3.3 \times 10^{28}$
$[\text{In}(\text{TDT})_2]^-$	1.658	$4.4 \times 10^{-23}$	$2.3 \times 10^{24}$
$[\text{In}(\text{TDT})_3]^-$	1.855	$8.1 \times 10^{-29}$	$1.2 \times 10^{30}$

Obviously, the orders of the stability of these complexes are:



and



From the stereochemical point of view, it is quite clear that the  $\text{MNT}^{2-}$  and  $\text{TDT}^{2-}$  compounds involve indium(III) in a five membered ring, whereas the  $\underline{\text{iMNT}}^{2-}$  compound has a four membered ring. Evidently,  $\text{MNT}^{2-}$  and  $\text{TDT}^{2-}$  complexes should be more stable than the  $\underline{\text{iMNT}}$  compound.<sup>72</sup> On the other hand, the MNT complexes are more stable than the TDT complexes, probably because  $\text{MNT}^{2-}$  has an unsaturated double bond, plus the strong electron withdrawing nitrile groups which are responsible for the fact that  $\text{MNT}^{2-}$  ring systems can easily accommodate a number of valence electrons. However, the unsaturated double bond of the TDT ring system is part of a large planar aromatic system. No electron withdrawing group is present. This may account for the MNT complexes being more stable than the TDT complexes.

Although the ring system does not involve a double bond in the  $\underline{\text{iMNT}}$  compound, added electrons can still be accommodated into the ring because of the two strong electron withdrawing nitrile groups; the electron density can presumably drift through the double bond toward the nitrile groups.

(c) Coordination number studies.

The purpose of determining the coordination number of the MNT and TDT complexes of indium(III) polarographically was to test the possibility of  $[\text{In}(\text{MNT})_3]^{3-}$  and  $[\text{In}(\text{TDT})_3]^{3-}$  existing in solution. According to equation (V), the value of  $p$  can be obtained from the slope of a plot of the half-wave potential against the logarithm of the ligand concentration: the third wave half-wave potential was chosen for this purpose. The data and slope are given in Table IV-6,7 and Figure IV-4,5.

Table IV-6

Plot of  $E_{\frac{1}{2}}$  (volts) versus  $\text{MNT}^{2-}$  concentration for  $[\text{In}(\text{MNT})_3]^{3-}$ .

<u>Concn. of MNT(M)</u>	<u><math>-E_{\frac{1}{2}}</math> V (third wave)</u>	<u><math>i_d</math> (amps x <math>10^{-8}</math>)</u>
$10^{-4}$	1.860	59
$10^{-4}$	1.919	60
$10^{-4}$	1.950	64
$10^{-3}$	1.978	67
$10^{-3}$	2.098	66
$10^{-3}$	2.025	65

Table IV-7

Plot of  $E_{\frac{1}{2}}$  (volts) versus  $\text{TDT}^{2-}$  concentration for  $[\text{In}(\text{TDT})_3]^{3-}$ .

<u>Concn. of TDT(M)</u>	<u><math>E_{\frac{1}{2}}</math> V (first wave)</u>	<u><math>i_d</math> (amps x <math>10^{-8}</math>)</u>
$4 \times 10^{-4}$	+0.175	98
$5 \times 10^{-4}$	0.179	97
$6 \times 10^{-4}$	0.187	102
$7 \times 10^{-4}$	0.196	118
$8 \times 10^{-4}$	0.205	110
$9 \times 10^{-4}$	0.218	117
$10 \times 10^{-4}$	0.220	124
$11 \times 10^{-4}$	0.234	125

The solution contained a small amount of absolute methanol.

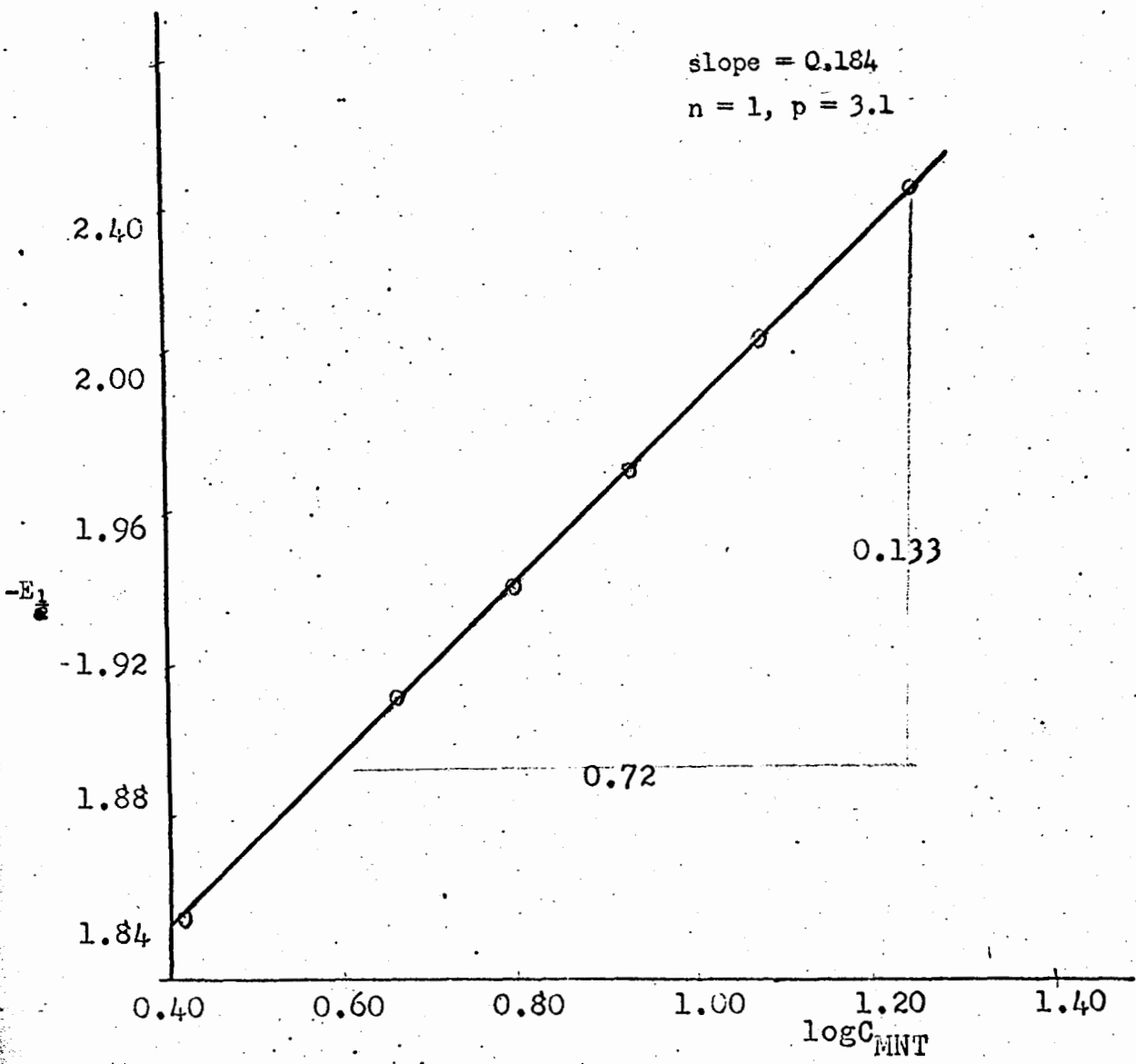


Fig. IV-6 Title as for Table IV-6

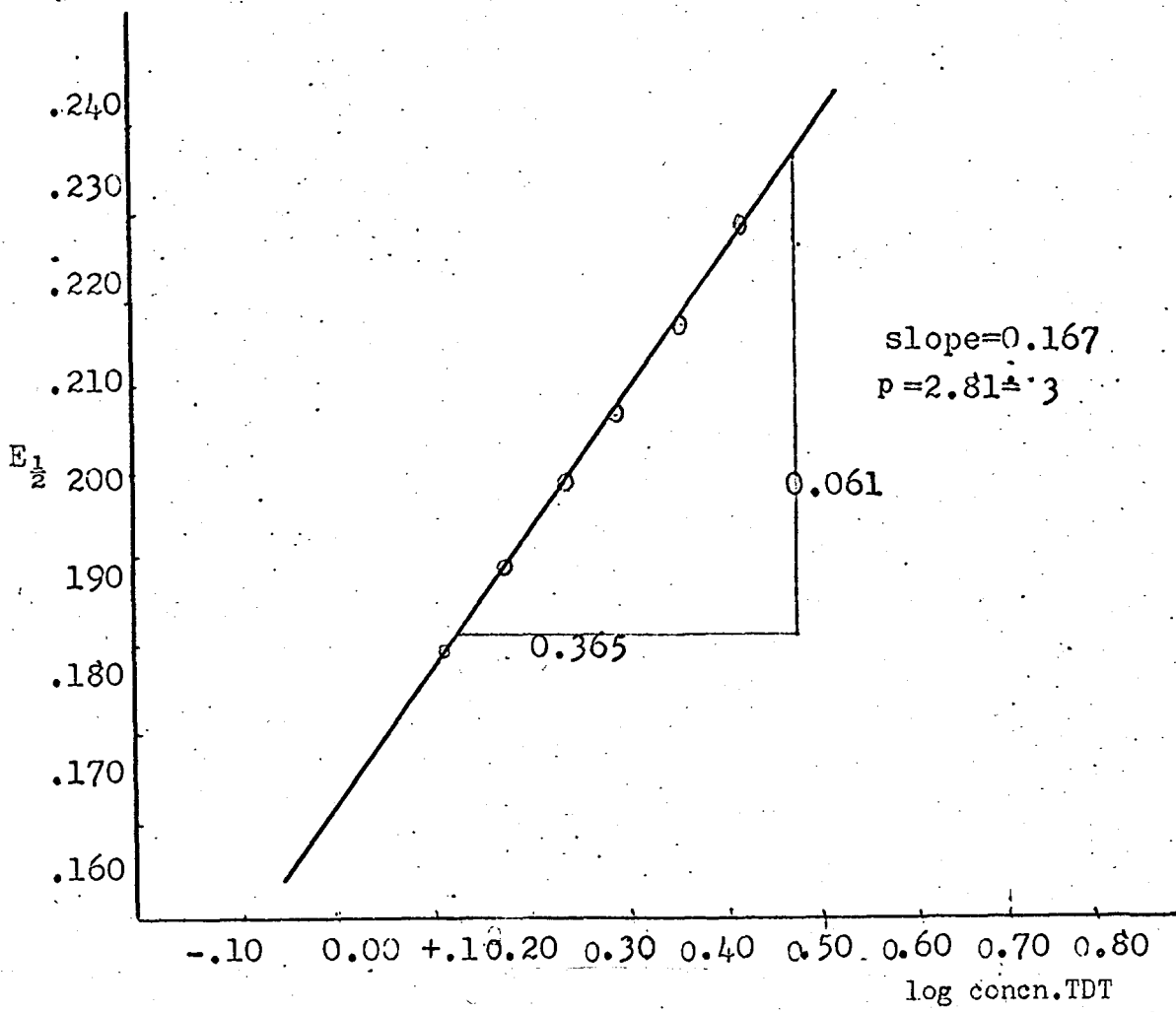


Fig. IV-7 as for table IV-7



From the experimental results the p value is 3 for both the MNT and TDT complexes within experimental error. The compound  $[\text{In}(\text{MNT})_3]^{3-}$  has been prepared as a crystalline salt, but the  $[\text{In}(\text{TDT})_3]^{3-}$  anion could not be isolated possibly because the ligand TDT is easily polymerized as an oil in air. This may also be the reason for the lower p value.

## CHAPTER V

### RESULTS AND DISCUSSION.

#### V. (A) CONDUCTIVITY

The results of molar conductivity measurements for various electrolytes have been classified for acetonitrile, nitromethane, acetone and other solvents, and the value of this method in investigating the ionic nature of complexes is well established. The values for 1:1 electrolytes in nitromethane have been reported to be between 100 to 120  $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$  by Fergusson and Nyholm<sup>73</sup>. The conductivities of the MNT complexes  $\text{Et}_4\text{N Pd}(\text{MNT})_2$ ,  $\text{Et}_4\text{N Ni}(\text{MNT})_2$  and  $\text{Et}_4\text{N Au}(\text{MNT})_2$  have been found to be 83, 81 and 80  $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$  respectively, showing them to be 1:1 electrolytes in nitromethane; for the 1:2 electrolytes  $(\text{Et}_4\text{N})_2[\text{Mn}(\text{MNT})_2]$  and  $(\text{Et}_4\text{N})_2[\text{Fe}(\text{MNT})_2]$ , the values are 307 and 320  $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$  in acetone solution.

The conductance results of  $\text{iMNT}$  complexes<sup>74</sup> in nitromethane are for 1:1 electrolytes 61  $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ , for 1:2 electrolytes around 150-175  $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ , and for 1:3 electrolytes 200-210  $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ . The only conductivity value reported for a TDT complex is for  $(\text{n-Bu}_4\text{N})_2[\text{V}(\text{TDT})_3]$  for which  $\kappa_m$  is 122  $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$  in nitromethane. Table V-1 gives the results on the molar conductivity of In(III) dithiolate complexes with MNT,  $\text{iMNT}$ , and TDT and their adducts, in acetonitrile at room temperature.

Table V-1.

The conductivity of dithiolate complexes of Indium(III).

<u>Complexes</u>	<u>Conductivity</u>	<u>Electrolyte</u>
$\text{Et}_4\text{N} [\text{In}(\text{MNT})_2]$	141	1:1
$(\text{Et}_4\text{N})_3 [\text{In}(\text{MNT})_3]$	401	3:1
$\text{Et}_4\text{N} [\text{In}(\text{MNT})_2\text{phen}]$	115	1:1
$\text{Et}_4\text{N} [\text{In}(\text{MNT})_2\text{bipy}]$	131	1:1
$\text{Et}_4\text{N} [\text{In}(\text{MNT})_2\text{en}]$	132	1:1
$(\text{Et}_4\text{N})_2 [\text{In}(\text{MNT})_2\text{oxine}]$	150	?
$\text{Et}_4\text{N} [\text{In}(\text{MNT})_2(\text{dma})_2]$	126	1:1
$(\text{Bu}_4\text{N})_2 [\text{In}(\underline{\text{iMNT}})_2\text{Cl}]$	214	2:1
$(\text{Bu}_4\text{N})_2 [\text{In}(\underline{\text{iMNT}})_2\text{Br}]$	218	2:1
$(\text{Bu}_4\text{N})_2 [\text{In}(\underline{\text{iMNT}})_2\text{I}]$	225	2:1
$(\text{Bu}_4\text{N})_3 [\text{In}(\underline{\text{iMNT}})_3]$	244	3:1
$(\text{Bu}_4\text{N}) [\text{In}(\underline{\text{iMNT}})_2\text{phen}]$	90	1:1
$(\text{Bu}_4\text{N}) [\text{In}(\underline{\text{iMNT}})_2\text{bipy}]$	91	1:1
$\text{Et}_4\text{N} [\text{In}(\text{TDT})_2]$	140	1:1
$\text{Et}_4\text{N} [\text{In}(\text{TDT})_2\text{phen}]$	126	1:1
$\text{Et}_4\text{N} [\text{In}(\text{TDT})_2\text{bipy}]$	128	1:1

The values in Table V-1 for the complexes of indium(III) dithiolates and their adducts are close to those reported by earlier workers. A comparison of the value of the MNT and iMNT compounds show that MNT complexes have higher conductivities; the lower conductivities of the iMNT compounds may be due to the lower mobility of the very large  $\text{Bu}_4\text{N}^+$  cation. The conductivity of  $(\text{Et}_4\text{N})_2[\text{In}(\text{MNT})_2\text{-oxine}]$  is lower than that for a 2:1 electrolyte, and  $\text{Bu}_4\text{N}[\text{In}(\text{iMNT})_2\text{phen}]$  and  $\text{Bu}_4\text{N}[\text{In}(\text{iMNT})_2\text{bipy}]$  have conductivities similar to those of 1:1 electrolytes. The most important conclusion of the conductance results in the table is that the stoichiometries and ionic formulations of the compounds are correct.

V. (B) THE INFRARED SPECTRA OF INDIUM DITHIOLATE COMPLEXES  
AND THEIR ADDUCTS

Although several transition metal dithiolate complexes are known, little attention has been paid to detailed infrared spectral studies. Davison et al.<sup>38</sup> have assigned

bands to  $\nu(\text{C}=\text{C})$  in some complexes of the type

$[\text{M}(\text{S}_2\text{C}_2(\text{CF}_3)_2)_m]^{n-}$ , (with  $\text{M}=\text{Ni}, \text{Co}, \text{Fe}, \text{Pd}$  and  $\text{Pt}$ , and  $m=2$  or  $3$ ,  $n=0, 1$ , or  $2$ ). Schrauzer and Mayweg<sup>75</sup> have partially assigned bands for  $[\text{Ni}(\text{C}_2\text{S}_2\text{R}_2)_2]^{2-}$  ( $\text{R}=\text{H}, \text{Me}$  and  $\text{Ph}$ ).

The most recent work is that of Adams and Cornell<sup>76</sup>, who made more complete IR studies of the complexes

$[\text{M}(\text{C}_2\text{S}_2\text{R}_2)_2]^{n-}$  ( $\text{R}=\text{H}, \text{CF}_3$  and  $\text{CN}$ ;  $\text{M}=\text{Ni}, \text{Co}, \text{Cu}, \text{Pd}$  and  $\text{Pt}$ ).

Their assignments depend in part upon those of earlier workers.

The significant IR absorption bands of three series of complexes prepared will be discussed and compared to each other, with emphasis on the stretching modes of the  $-\text{CN}$  group in  $\text{MNT}$  and  $\text{iMNT}$  complexes, and on the  $\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}=\text{S})$ , and  $\nu(\text{C}-\text{S})$  modes in general.

The significant bands of the indium(III)  $\text{MNT}$ ,  $\text{iMNT}$  and  $\text{TDT}$  complexes are tabulated in Tables V-2, V-3, and V-4 respectively.

The infrared spectra of the various  $\text{MNT}$  complexes (Table V-2) clearly show the presence of  $\nu(\text{C}\equiv\text{N})$ ,  $\nu(\text{C}=\text{C})$  and  $\nu(\text{C}-\text{S})$  bands. The individual bands of the  $\text{MNT}$  complexes can now be examined. Firstly, the  $(\text{C}\equiv\text{N})$  bands at

Table V-2. I.R. absorption frequencies ( $\text{cm}^{-1}$ )  
for MNT complexes

$\text{Na}[\text{In}(\text{MNT})_2]$	$\text{Et}_4\text{N}[\text{In}(\text{MNT})_2]$	$(\text{Et}_4\text{N})_3[\text{In}(\text{MNT})_3]$	$\text{Et}_4\text{N}[\text{In}(\text{MNT})_2\text{bipy}]$
	2218s	2215s	
2200 s	2200 s	1995(s)	2219 s
			1605 m 1593 m
			1579 m 1567m
1456s	1478 s	1460s	1473 s
1435s	1446 s	1440s	1443 s
			1316 m
1117m	1150 m	1132m	1160 m
1046 m	1030 m	1120 s	1115s
1011 m	1000 m	1032m	1020s
863s	855s	862s	860s
			650 w
			632m
530 s	520m	536 m	530 s
	397 m	395 m	
370 m	373m		315s
322 s	319 s	292 s	309 s
255m	260m	240m	249m
			223s

Table V-2 IR Absorption Frequencies (cm<sup>-1</sup>)  
for MNT Complexes (cont.)

Na <sub>2</sub> MNT	[In(MNT) <sub>2</sub> phen]	[In(MNT) <sub>2</sub> en]	[In(MNT) <sub>2</sub> (dma) <sub>2</sub> ]	[In(MNT) <sub>2</sub> oxine]
		3310s	3658m	
		3242s	2202s	2204s
2200s	2200s	2200s	2200s	2200s
	1624m		1640s(C=O)	1596m
	1603w		1600s(C=N)	
	1585w	1580s		1575s
	1520s			
	1480s	1482s		
1450s	1450m	1445s	1445s	1450s
1438m				1427m
	1367m	1367s		
	1343m			
	1307m		1175m	
1155s	1150s	1145m	1150s	1148s
1115s	1118s		1118s	
1055m	1050m	1066w	1052m	1036m
1015m	1015m	1044s	1030m	1010w
860s	860s	860s	865s	860s
	645m	645m	605s	618m
535s	530m	533m	595s	536m
520s	512s	514s	532m	510s
		495s	480m	
	422m	420m	430m	420w
384w		397w	400w	389w
	314s	310s	328s	318m
	306s	300s		
		240m	267s	
	229s	229m	220m	

Table V-3 IR Absorption Frequencies( $\text{cm}^{-1}$ ) for  $\text{MNT}$  Complexes

$[\text{In}(\text{MNT})_2\text{X}]^{2-}$	$[\text{In}(\text{MNT})_3]^{3-}$	$[\text{In}(\text{MNT})_2\text{dipy}]^-$	$[\text{In}(\text{MNT})_2\text{phen}]^-$	$\text{Na}_2(\text{MNT})$
2200s	2195s	2200s	2200s	2200s
2170sh	2086w	2094w	2092w	2170w
		1604m	1622m	1620s
		1596m	1601w	
			1585m	
			1518s	
1485m	1490w	1486m	1480m	1382s
		1472s		1370s
		1454m		1340s
1230m	1220s	1224m	1220s	1236s
1174w	1167w	1157m	1146m	
1004s	1020s	1020s	1100s	
	972m	969m	968m	985s
945s	946s	937s	946s	970s
	936m			952s
875s	872s	873s	872s	870s
620w	616m	618m	610m	668s
				620s
490s	494m		410m	510s
370m	350s	367s	365s	420m
310w				288m
235s		230s	287m	
220m(X=Cl)		212m	212m	

X = Cl, Br, or I.



Table V-4 IR Absorption Frequencies for TDT Complexes

Na [In(TDT) <sub>2</sub> ]	Et <sub>4</sub> N [In(TDT) <sub>2</sub> ]	Et <sub>4</sub> N [In(TDT) <sub>2</sub> bipy]	Et <sub>4</sub> N [In(TDT) <sub>2</sub> phen]	TDT
2920m	2916m	2910m	2910m	2910m
1588m	1587m	1588m	1596s	2545s(S-H)
1550w	1548m	1580m	1585m	1650m
		1572m	1580m	1595m
1454s	1455s	1488s	1566w	1590m
1378m	1378m		1532w	
	1285m		1453s	1465s
1256m	1250s		1366m	1280m
1210m				1269s
				1212m
1104m	1102s	1100s	1250s	1125s
1030m	1032m	1036s	1136m	1040s
	947s			928s
865m	864m	860s		865s
807s	810s	798s		808s
684w	688m			694m
	680m			
630w	628m	630m		627m
548m	547m	548m		536m
	475w	473m		
438s	438s	436m		430s
		413w		
375w	374s	374m		
	347s			
337m	335m	340w		
		278m		
			340m	

approximately  $2200\text{cm}^{-1}$  are present in all the complexes with little or no shift from the spectrum of  $\text{MNT}^{2-}$  itself, clearly indicating that the neutral donor (e.g. bipy, phen, en, and oxine) has no influences on the  $\text{C}\equiv\text{N}$  group. Secondly,  $\nu(\text{C}=\text{C})$  is normally in the region  $1600\text{-}1680\text{cm}^{-1}$ , but  $\nu(\text{C}=\text{C})$  in our MNT complexes falls at  $1430\text{-}1480\text{cm}^{-1}$ , suggesting that the double bond character is reduced due to delocalization of the  $\pi$ -bonding system (the ring system). The  $\nu(\text{C}=\text{C})$  frequency in the free ligand  $\text{MNT}^{2-}$  is at  $1450\text{cm}^{-1}$ , and Adams and Cornell<sup>76</sup> believe this is due to the anionic nature of  $\text{MNT}^{2-}$ .

Thirdly, the two  $\nu(\text{C}-\text{S})$  bands which are known to be in the regions  $1105\text{-}1120\text{cm}^{-1}$  and  $860\text{-}873\text{cm}^{-1}$  in the compound  $\text{Ni}(\text{S}_2\text{C}_2\text{H}_2)_2$  and  $\text{M}(\text{MNT})_2$  ( $\text{M}=\text{Ni}, \text{Cu}, \text{Pd}$  or  $\text{Pt}$ ), have been assigned by Adams et al.<sup>57</sup> and Schrauzer et al.<sup>75</sup>. In the complex  $[\text{In}(\text{MNT})_2]^-$ , there are two bands at  $1115\text{cm}^{-1}$  and  $1150\text{cm}^{-1}$  and one very strong band at  $855\text{cm}^{-1}$ , believed to be (C-S) stretching modes. The adducts have similar bands in the same regions, and no significant changes are noticed between  $[\text{In}(\text{MNT})_2]^-$  and its adducts (see table V-2).

Fourthly, the range of  $\nu(\text{M}-\text{S})$  has been reviewed by Adams and Cornell<sup>76</sup>. The highest value,  $480\text{cm}^{-1}$ , is found for  $[\text{Mo}-\text{S}_4]^{3-}$  but more typical is the range  $440\text{-}300\text{cm}^{-1}$  for uni- or divalent dithiolate ligand complexes.

For the  $\text{In}(\text{MNT})_2^-$  complex and its adducts the strong bands occur around  $310\text{-}328\text{cm}^{-1}$ ; with  $[\text{In}(\text{MNT})_3]^{3-}$  the band occurs at  $292\text{cm}^{-1}$ . These bands are assigned to the  $\nu(\text{In-S})$  vibration. Medium intensity bands lower than  $(\text{In-S})$  are noted at  $306, 309, 300$  and  $318\text{cm}^{-1}$  in the complexes  $[\text{In}(\text{MNT})_2\text{phen}]^-$ ,  $[\text{In}(\text{MNT})_2\text{bipy}]^-$ ,  $[\text{In}(\text{MNT})_2\text{en}]^-$  and  $[\text{In}(\text{MNT})_2\text{oxine}]^-$  respectively. In the  $200\text{cm}^{-1}$  region another new band is observed at  $220\text{-}280\text{cm}^{-1}$  which is tentatively assigned as an indium-nitrogen vibration. This will be discussed later.

It is well recognized that the vibrational spectra of the free ligand iMNT and its complexes are very similar to that of MNT.<sup>59,77</sup> The vibrational bands of iMNT and its complexes are tentatively assigned in Table V-3. The  $\nu(\text{C}\equiv\text{N})$  bands in all the iMNT complexes are at  $2200\text{cm}^{-1}$  as in the MNT species, so that again the neutral donors evidently have no influence on the  $(\text{C}\equiv\text{N})$  stretching mode. The  $\text{C}=\text{C}$  stretching frequency in the free ligand, iMNT, is at  $1620\text{cm}^{-1}$  but in the complexes this falls to  $1480$  to  $1490\text{cm}^{-1}$ . The reason for this lowering frequency of  $(\text{C}=\text{C})$  might be strain in the  $\text{C}=\text{C} \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{S} \end{array} \text{M}$  ring lowering the double bond frequency.<sup>78</sup>

On comparing the  $\nu(\text{C-S})$  vibration of iMNT complexes ( $876\text{cm}^{-1}$ ) and the corresponding  $\text{In}/\text{MNT}$  complexes ( $860\text{cm}^{-1}$ ), one finds that  $\nu(\text{C-S})$  is higher in the iMNT

case. A probable explanation is in terms of the ring strain effect which results in a higher energy for the four membered than for the five membered ring. There are two new bands at  $350-370\text{cm}^{-1}$  and  $230-235\text{cm}^{-1}$  in the  $\underline{iMNT}$  complexes but no bands were observed, below  $350\text{cm}^{-1}$  for  $[\text{In}(\underline{iMNT})_3]^{3-}$ . Following the earlier discussion, the indium-sulphur bands should be in the  $300\text{cm}^{-1}$  region, but the (In-S) bands of  $\underline{iMNT}$  complexes were found in  $350-370\text{cm}^{-1}$  region, which is a little higher than for the MNT complexes.

The I.R. spectra of the three  $(\text{Bu}_4\text{N})_2[\text{In}(\underline{iMNT})_2\text{X}]$  complexes (X=Cl, Br, and I) are nearly identical except for the chloro compound which has an absorption band at  $220\text{cm}^{-1}$ , probably  $\nu(\text{In-Cl})$ . The value of  $\nu(\text{In-Cl})$  in various compounds has been assigned to the  $200-300\text{cm}^{-1}$  region by other workers.<sup>79,80</sup>

The infrared bands of TDT and its complexes with indium(III) are tentatively assigned in Table V-4. The major changes found on complex formation are that the  $\nu(\text{S-H})$  band at  $2545\text{cm}^{-1}$  disappears on coordination, and that the ring vibration bands at  $1594$ ,  $1590$  and  $1650\text{cm}^{-1}$  are at lower frequencies in the complexes. However, the frequencies of  $\nu(\text{C-S})$  are lower in the complexes than in the free ligand. The reason for this is not clear.

Very recently indium-nitrogen vibration bands have been assigned by Patel and Tuck<sup>5</sup>: The  $\nu(\text{In-NCO})$  vibration is in the  $300\text{-}350\text{cm}^{-1}$  region. With donor ligands such as pyridine and 2,2'-bipyridyl,  $\nu(\text{In-N})$  is at  $200\text{-}235\text{cm}^{-1}$  region. Following the earlier workers, the  $\nu(\text{In-N})$  vibrational bands of indium dithiolate complexes with 1,10-phenanthroline and 2,2'-bipyridyl with MNT, iMNT and TDT, and with ethylenediamine, N,N'-dimethylacetamide and oxine with MNT are tentatively assigned in the region  $220\text{-}280\text{cm}^{-1}$ .

Table V-5 records all assignments of metal-ligand vibrations for the three series of complexes. As noted above, in the bidentate neutral adducts and the oxine complexes the  $\nu(\text{In-S})$  vibration appears as two bands (see Table V-5).

Table V-5  
Comparison of Indium-ligand Vibrational  
Frequencies for Indium(III) Dithiolate  
and Its Adducts: (cm<sup>-1</sup>)

<u>Complexes</u>	<u>In-S</u>	<u>In-N</u>
Et <sub>4</sub> N [In(MNT) <sub>2</sub> ]	319	---
(Et <sub>4</sub> N) <sub>3</sub> [In(MNT) <sub>3</sub> ]	292	--
Et <sub>4</sub> N [In(MNT) <sub>2</sub> phen]	314, 306	229
Et <sub>4</sub> N [In(MNT) <sub>2</sub> bipy]	314, 309	228
Et <sub>4</sub> N [In(MNT) <sub>2</sub> en]	310, 300	229
(Et <sub>4</sub> N) <sub>2</sub> [In(MNT) <sub>2</sub> oxine]	389, 318	252, 221
Et <sub>4</sub> N [In(MNT) <sub>2</sub> (dma) <sub>2</sub> ]	328	267, 220
(Bu <sub>4</sub> N) <sub>2</sub> [In(iMNT) <sub>2</sub> X]	370, 230	--
(Bu <sub>4</sub> N) <sub>3</sub> [In(iMNT) <sub>3</sub> ]	350	--
Bu <sub>4</sub> N [In(iMNT) <sub>2</sub> phen]	365, 287	230
Bu <sub>4</sub> N [In(iMNT) <sub>2</sub> bipy]	364, 230	236
Et <sub>4</sub> N [In(TDT) <sub>2</sub> ]	335	--
Et <sub>4</sub> N [In(TDT) <sub>2</sub> phen]	330, 307	277
Et <sub>4</sub> N [In(TDT) <sub>2</sub> bipy]	340, 300	278

X = Cl, Br, or I.

V. (C) THE NMR SPECTRA STUDY OF 1,10-PHENANTHROLINE  
AND 2,2'-BIPYRIDYL IN INDIUM(III) DITHIOLATE COMPLEXES.

The MNR spectra of the complexes  $\text{Et}_4\text{N}[\text{In}(\text{MNT})_2\text{-phen}]$ ,  $\text{Et}_4\text{N}[\text{In}(\text{MNT})_2\text{bipy}]$ ,  $\text{Bu}_4\text{N}[\text{In}(\text{iMNT})_2\text{bipy}]$ ,  $\text{Et}_4\text{N}[\text{In}(\text{TDT})_2\text{phen}]$ , and  $\text{Et}_4\text{N}[\text{In}(\text{TDT})_2\text{bipy}]$  were studied in order to observe and deshielding effects on the protons of 1,10-phenanthroline and 2,2'-bipyridyl on complex formation. It also proved interesting to investigate the stereochemistry of some species in terms of the cis and trans configuration of the TDT methyl group in these complexes.

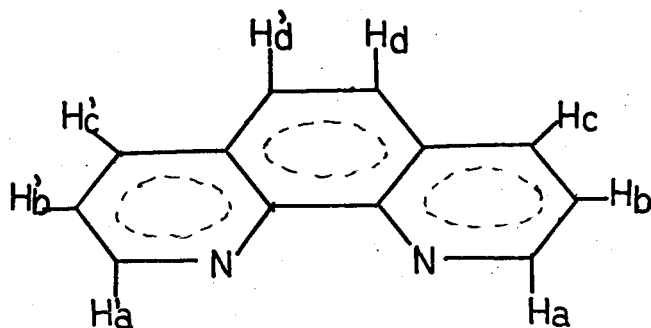
The NMR spectra of 1,10-phenanthroline in acetone<sup>81</sup> and 2,2'-bipyridyl in dichloromethane<sup>82</sup> had been reported previously. The present work has repeated the measurement of 1,10-phenanthroline and 2,2'-bipyridyl in dmsO. The spectral data are given in Tables V-6 and V-7.

The eight protons of 1,10-phananthroline and 2,2'-bipyridyl can be considered as four pairs, viz, Ha and Ha', Hb and Hb', Hc and Hc', and Hd and Hd' which behave as equivalent pairs giving one resonance signal from each pair.

The chemical shift data for the protons of the indium(III) complexes of phen and bipy with MNT, iMNT and TDT run in dmsO-d<sub>6</sub> solution are recorded in Table V-8 and V-9.

Table V-6

NMR data for 1,10-phenanthroline in dmsO at 60Mc/sec.



<u>Proton</u>	<u>Chemical Shift</u> (cps down field from TMS)
Ha, Ha'	554±1
Hb, Hb'	467
Hc, Hc'	512
Hd, Hd'	477

$$J_{\text{Ha-Hb}} = 4.2 \text{ cps}$$

$$J_{\text{Hb-Hc}} = 8.0 \text{ cps}$$

$$J_{\text{Ha-Hc}} = 1.7 \text{ cps}$$

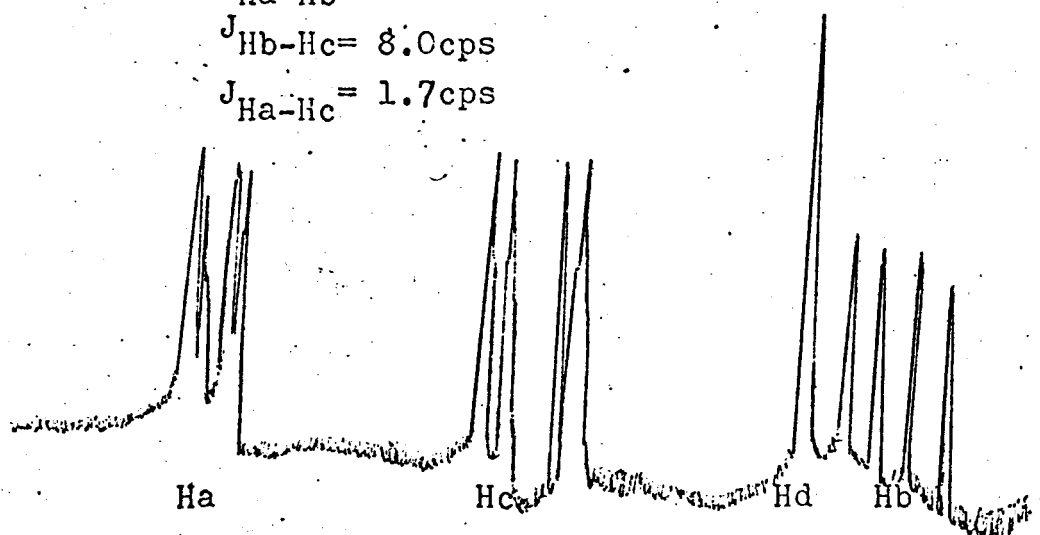
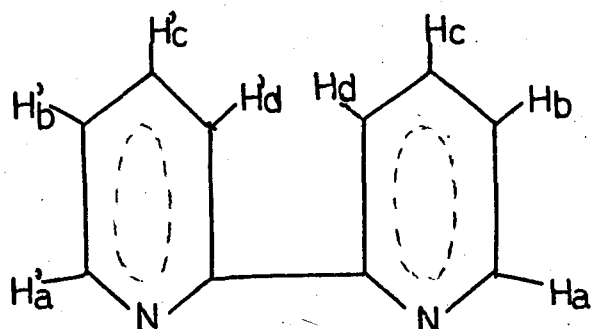




Table V-7

NMR data for 2,2'-bipyridyle in dmao at 60Mc/sec.



<u>Proton</u>	<u>Chemical Shift</u> (cps down field from TMS)
Ha, Ha'	521 $\pm$ 1
Hb, Hb'	444
Hc, Hc'	475
Hd, Hd'	505
$J_{Ha-Hb} = 4.9\text{cps}$	$J_{Ha-Hc} = 2.1\text{cps}$
$J_{Hb-Hc} = 8.0\text{cps}$	$J_{Hc-Hd} = 8.3\text{cps}$
$J_{Hb-Hd} = 1.4\text{cps}$	

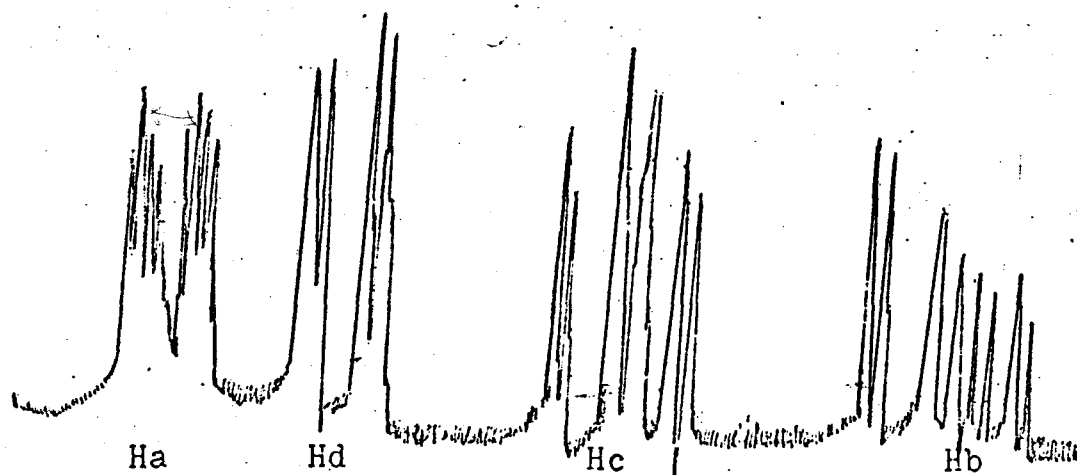


Table V-8

NMR data for indium(III) dithiolate/phen complexes  
in dms<sub>o</sub>-d<sub>6</sub>; chemical shift cps downfield from TMS.

o-phen		$[\text{In}(\text{MNT})_2\text{phen}]^-$	$[\text{In}(\text{iMNT})_2\text{phen}]^-$	$[\text{In}(\text{TDT})_2\text{phen}]^-$
Orange crystal				
Ha, Ha'	554	559 $\Delta\text{Ha}=6$	574 $\Delta\text{Ha}=20$	561 $\Delta\text{Ha}=7$
Hb, Hb'	467	496 $\Delta\text{Hb}=29$	496 $\Delta\text{Hb}=29$	466 $\Delta\text{Hb}=-1$
Hc, Hc'	512	539 $\Delta\text{Hc}=27$	543 $\Delta\text{Hc}=31$	510 $\Delta\text{Hc}=-2$
Hd, Hd'	477	499 $\Delta\text{Hd}=22$	501 $\Delta\text{Hd}=24$	476 $\Delta\text{Hd}=-1$
Yellow crystal				
				568 $\Delta\text{Ha}=14$
				476 $\Delta\text{Hb}=9$
				519 $\Delta\text{Hc}=7$
				486 $\Delta\text{Hd}=11$

$\Delta\text{Ha} = \text{Ha}(\text{phen complex}) - \text{Ha}(\text{phen})$ .

Orange crystals; the  $-\text{CH}_3$  signal of TDT at 11.5 and 117cps  
 (two peaks)

Yellow crystals; the  $-\text{CH}_3$  signal of TDT show only one  
 peak at 113cps.

Table V-9

NMR data of indium dithiolate bipy complexes  
in dms<sub>o</sub>-d<sub>6</sub> ; chemical shift cps downfield from TMS

	bipy	$[\text{In}(\text{MNT})_2\text{bipy}]^-$	$[\text{In}(\text{iMNT})_2\text{bipy}]^-$	$[\text{In}(\text{TDT})_2\text{bipy}]^-$
Ha, Ha'	521	534:ΔHa=13	541:ΔHa=20	520:ΔHa=-1
Hb, Hb'	475	494:ΔHb=19	497:ΔHb=22	472:ΔHb=-3
Hc, Hc'	444	468:ΔHc=24	469:ΔHc=25	448:ΔHc=4
Hd, Hd'	505	519:ΔHd=14	523:ΔHd=18	501:ΔHd=-2

It is quite clear from the data in the tables that in the dithiolate complexes, the eight protons of 1,10-phenanthroline or 2,2'-bipyridyl still show the same resonance pattern, and the proton signals show various downfield shifts. This downfield shift (i.e. decreased shielding) is presumably caused by the coordination of the nitrogen atoms to the central metal indium(III). Since electronic charge is withdrawn toward the nitrogen from all positions in the ring, a downfield shift of the resonance of all the protons is observed.

It is interesting to compare the downfield shift of the four pairs of protons, occurring in the order  $\Delta H_b \approx \Delta H_c > \Delta H_d > \Delta H_a$  in  $[\text{In}(\text{MNT})_2\text{phen}]^-$  and  $[\text{In}(\underline{\text{iMNT}})_2\text{phen}]^-$ , and the order  $\Delta H_c > \Delta H_b > \Delta H_a \approx \Delta H_d$  in  $[\text{In}(\text{MNT})_2\text{bipy}]^-$  and  $[\text{In}(\underline{\text{iMNT}})_2\text{bipy}]^-$ . In other words the biggest deshielding effect is at Hb and Hc in the 1,10-phenanthroline complexes and at Hc in the 2,2'-bipyridyl complexes. It seems possible that the electron distribution in the ring systems is equivalent to establishing a dipole to the nitrogen atom from Hb and Hc positions in 1,10-phenanthroline complexes and from the Hc position in 2,2'-bipyridyl complexes. (See Figure V-1).

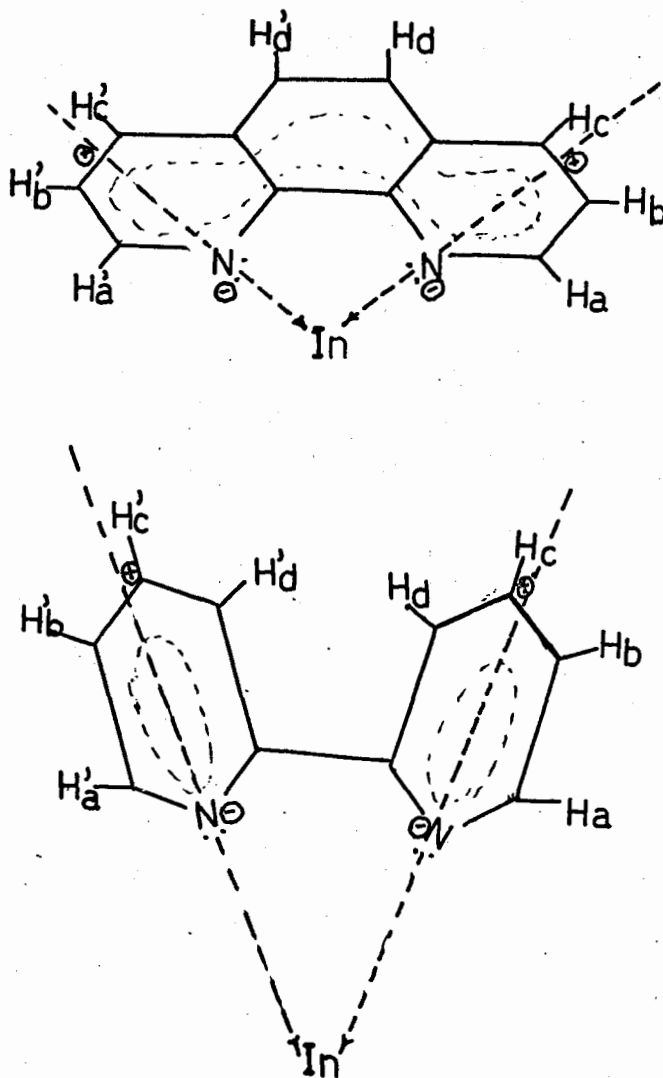


Fig. V-1

The dipole direction in 1,10-phenanthroline and 2,2'-bipyridyl on complexing

A comparison of  $\Delta H_a$ ;  $\Delta H_b$ ,  $\Delta H_c$  and  $\Delta H_d$  for the 1,10-phenanthroline and 2,2'-bipyridyl compounds shows that the  $\Delta H_a$ , etc values of 1,10-phenanthroline are bigger than for the 2,2'-bipyridyl case. This may indicate that 1,10-phenanthroline is more strongly coordinated to indium than 2,2'-bipyridyl. However, in the 1,10-phenanthroline and 2,2'-bipyridyl complexes with  $[\text{In}(\text{TDT})_2]^-$  the chemical shift of the four pairs of protons seems to be the same in both cases. The reasons for this are not clear at present.

The stereochemistry of  $[\text{In}(\text{TDT})_2]^-$ ,  $[\text{In}(\text{TDT})_2\text{phen}]^-$  and  $[\text{In}(\text{TDT})_2\text{bipy}]^-$  has been investigated from the NMR spectra. The complex  $[\text{In}(\text{TDT})_2]^-$  has two possible configurations, cis and trans, but only one signal was recorded at 128 cps (or  $\tau = 7.84$ ) which is to be expected since the two methyl groups in the complex  $[\text{In}(\text{TDT})_2]^-$  have the same environment, (see Figuration V-2)

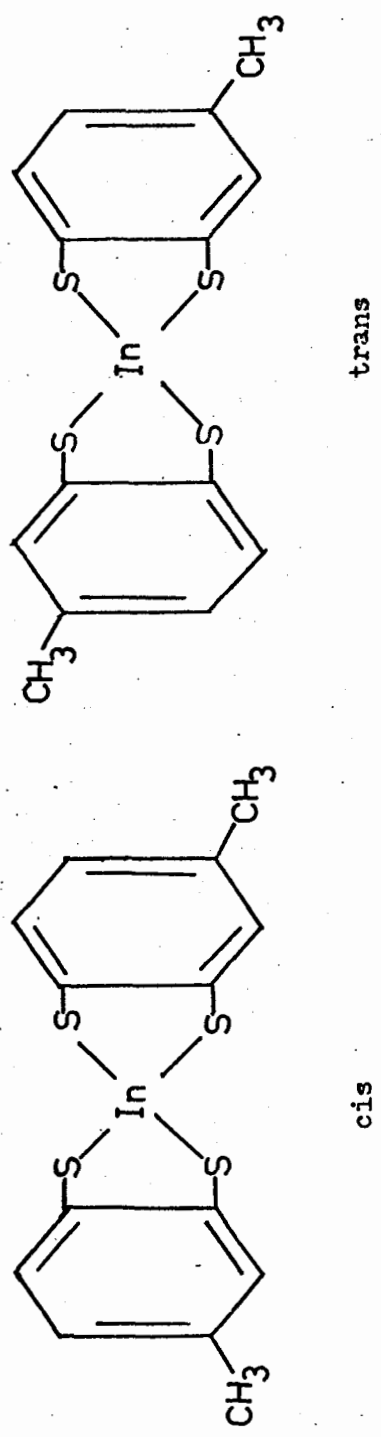


Fig. V-2 The configuration of  $[\text{In}(\text{TDT})_2]^-$  complex

However, in the complexes  $[\text{In}(\text{TDT})_2\text{phen}]^-$  and  $[\text{In}(\text{TDT})_2\text{bipy}]^-$  there are two possible methyl configurations depending upon molecular stereochemistry.

- (1) If  $[\text{In}(\text{TDT})_2]^-$  in the trans configuration coordinate with 1,10-phenanthroline, both the methyl groups of the TDT ligands will be in the same environment.
- (2) If  $[\text{In}(\text{TDT})_2]^-$  in the cis configuration coordinate with 1,10-phenanthroline, the methyl groups of the TDT ligands will not both be in the same environment.

(See Figure V-3).



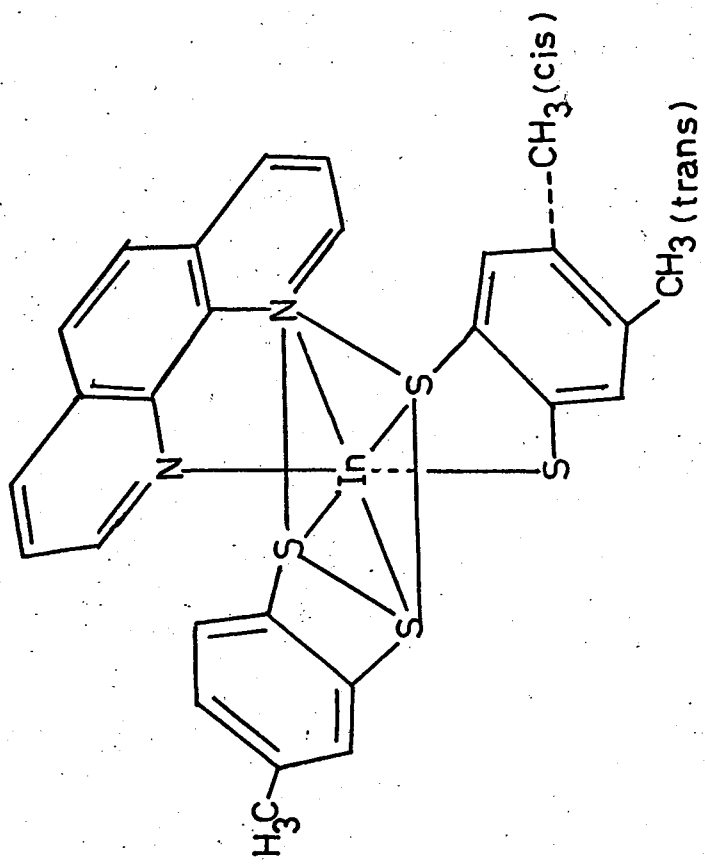


Fig. V-3 The cis or trans configurations in  $[\text{In}(\text{TDT})_2\text{phen}]^-$

The preparation of  $\text{Et}_4\text{N}[\text{In}(\text{TDT})_2\text{phen}]^-$  gave two compounds, obtained as orange crystals and yellow crystals and tentatively identified as two isomers. The former shows two methyl group resonances at 118.5 and 117 cps in NMR spectrum, while the yellow one shows only one methyl peak at 123 cps. The yellow  $[\text{In}(\text{TDT})_2\text{phen}]^-$  might therefore be trans, and the orange  $[\text{In}(\text{TDT})_2\text{phen}]^-$  the cis isomer.

The complex  $[\text{In}(\text{TDT})_2\text{bipy}]^-$  gives only orange crystals, and the methyl group NMR signal is a singlet at 127 cps.

There are two possibilities that can be suggested.

- (1) The bipyridyl complex may exist as a trans configuration only.
- (2) In the bipyridyl structure there is a single bond between two rings which can therefore rotate, in which case the methyl groups could have the same environment.

V (D) THE UV SPECTRA OF INDIUM DITHIOLATES AND THEIR ADDUCTS.

The two main purposes of using UV spectrum in this work were to (a) study the formation of complexes of  $[\text{In}(\text{MNT})_2]^-$  with neutral donor ligands by Job's method, and (b) to study the principal absorptions of indium dithiolate complexes and their adducts.

(a) The study of electronic spectra of the Indium complexes.

The UV spectra of  $[\text{Ni}(\text{MNT})_2]^{2-}$  and  $[\text{Pt}(\text{MNT})_2]^{2-}$  etc. have been reported by Shupack et al.<sup>83</sup> who find five maxima in the region  $10,000-5000\text{cm}^{-1}$  (Fig. V-4). Four of the intense bands have been assigned to the charge transfer transitions  $\text{M} \rightarrow \text{L}$  or  $\text{L} \rightarrow \text{M}$  and  $\text{L} \rightarrow \text{L}^*$ , and the remaining band to a d-d transition. The energy level scheme diagram and electronic spectra (Fig. V-5), Table V-10) are taken from Shupack and Gray's work 39,83.

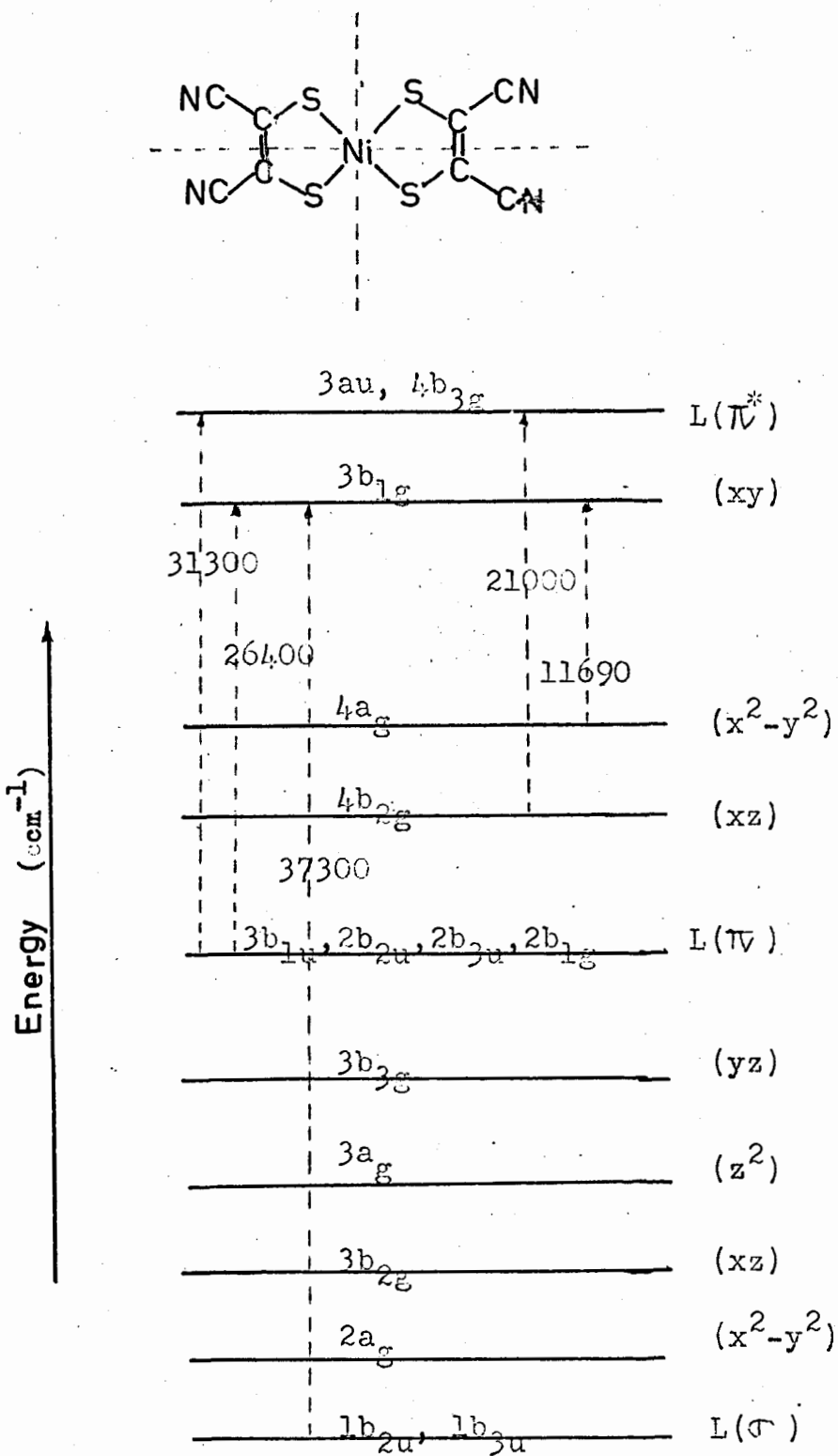


Fig. V-4 Important molecular orbital energy level for  $[\text{Ni}(\text{MNT})_2]^{n-}$

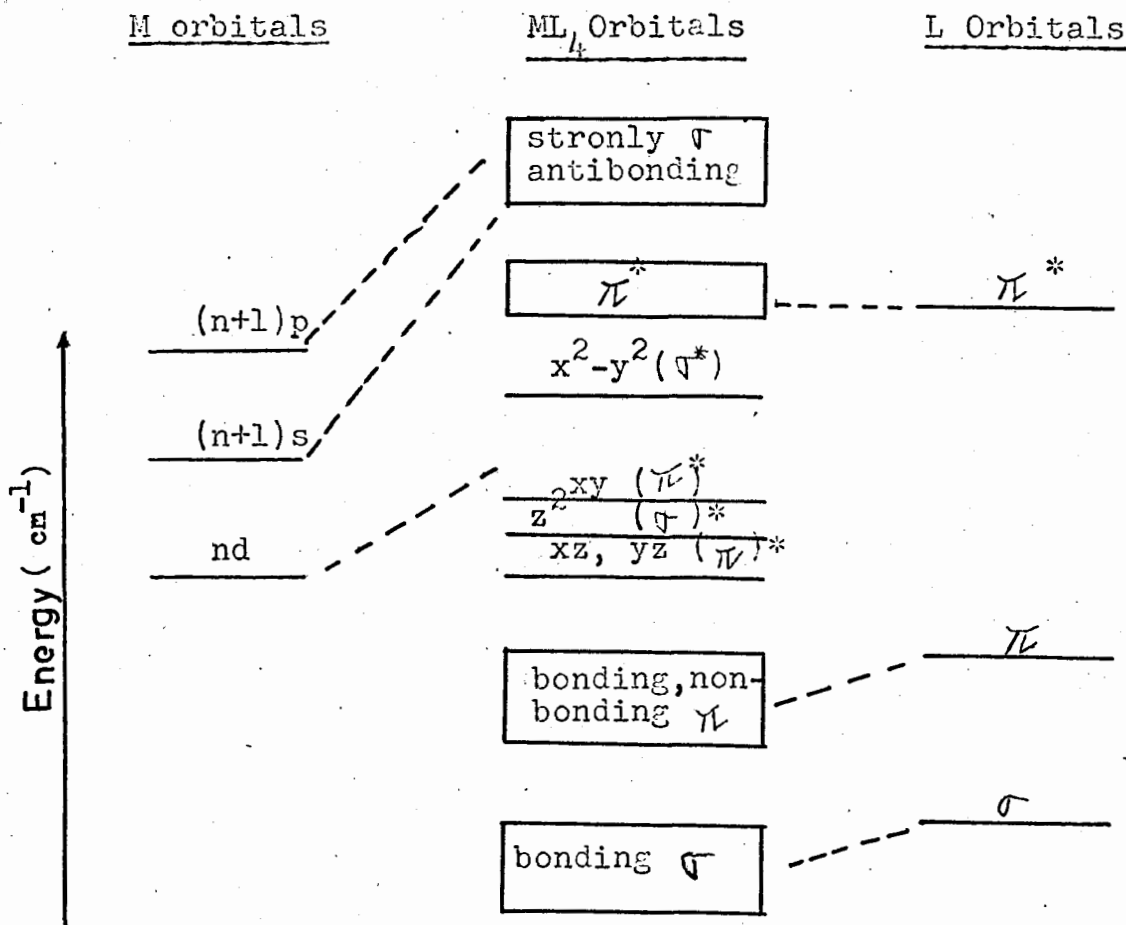


Fig. V-5 Simple energy level scheme for square planar complexes.<sup>39</sup>

Table V-10

Electronic Spectra of  $M(\text{MNT})_2^{2-}$  Complexes 39

	$[\text{Ni}(\text{MNT})_2]^{2-}$	$[\text{Pd}(\text{MNT})_2]^{2-}$	$[\text{Pt}(\text{MNT})_2]^{2-}$
<u>Transitions</u>			
<u>d-d</u>			
${}^1A_g \rightarrow {}^3B_g$ ( $x^2-y^2-xy$ )	not observed	not observed	14410sh $\epsilon=49$
${}^1A_g \rightarrow {}^1B_g$ ( $x^2-y^2-xy$ )	11690 $\epsilon=30$	15700 $\epsilon=64$	18500sh $\epsilon=1220$
${}^1A_g \rightarrow {}^3B_g$ ( $xz-xy$ )	not observed	not observed	15650sh $\epsilon=56$
${}^1A_g \rightarrow {}^1B_g$ ( $xz-xy$ )	17500 sh $\epsilon=570$	not observed	not observed
<u>L→L*</u>			
${}^1A_g \rightarrow {}^1B_{2u}$	31300 $\epsilon=30000$	30800sh $\epsilon=20200$	29700 $\epsilon=15600$
<u>L→M Charge Transfer</u>			
${}^1A_g \rightarrow {}^1B_{2u}, {}^1B_{3u}$ ( $L(\pi) \rightarrow M$ )	26500 $\epsilon=6600$	22700 $\epsilon=5700$	32300 $\epsilon=13400$
${}^1A_g \rightarrow {}^1B_{2u}, {}^1B_{3u}$ ( $L(\sigma) \rightarrow M$ )	37000 $\epsilon=50000$	33900 $\epsilon=47600$	43800 $\epsilon=43500$
<u>M→L Charge Transfer</u>			
${}^1A_g \rightarrow {}^1A_u$	19250 $\epsilon=2250$	25800sh $\epsilon=840$	18500 $\epsilon=1200$
${}^1A_g \rightarrow {}^1B_{2u}$	2100 $\epsilon=2800$	not observed	21100 $\epsilon=3470$

In the spectrum of  $[\text{In}(\text{MNT})_2]^-$  there are three intense bands at  $28400\text{cm}^{-1}$  ( $\epsilon=1.6 \times 10^4$ ),  $29400\text{cm}^{-1}$  ( $\epsilon=1.2 \times 10^4$ ), and  $39500\text{cm}^{-1}$  ( $\epsilon=1.6 \times 10^4$ ). Unfortunately the symmetry of the compound cannot be decided at this stage. Following Shupack's work, however, the three bands have been tentatively assigned according to the energy level and extinction coefficient. The two bands at  $28400\text{cm}^{-1}$  and  $29500\text{cm}^{-1}$  are  $L(\pi) \rightarrow M$  and  $L(\sigma) \rightarrow M$ , charge transfer respectively, and the band at  $29400\text{cm}^{-1}$  is  $L(\pi) \rightarrow L(\pi^*)$ . The  $L \rightarrow M$  transition may involve the ligand  $\sigma$  and  $\pi$  bonding or non-bonding electrons moving to indium(III) 5d empty  $e_g$  orbitals. If the  $[\text{In}(\text{MNT})_2]^-$  is tetrahedral, a simple scheme may be drawn as in Figure V-7 following Gray's work.<sup>39</sup> The spectrum of  $[\text{In}(\text{MNT})_2]^-$  is shown in Figure V-6.

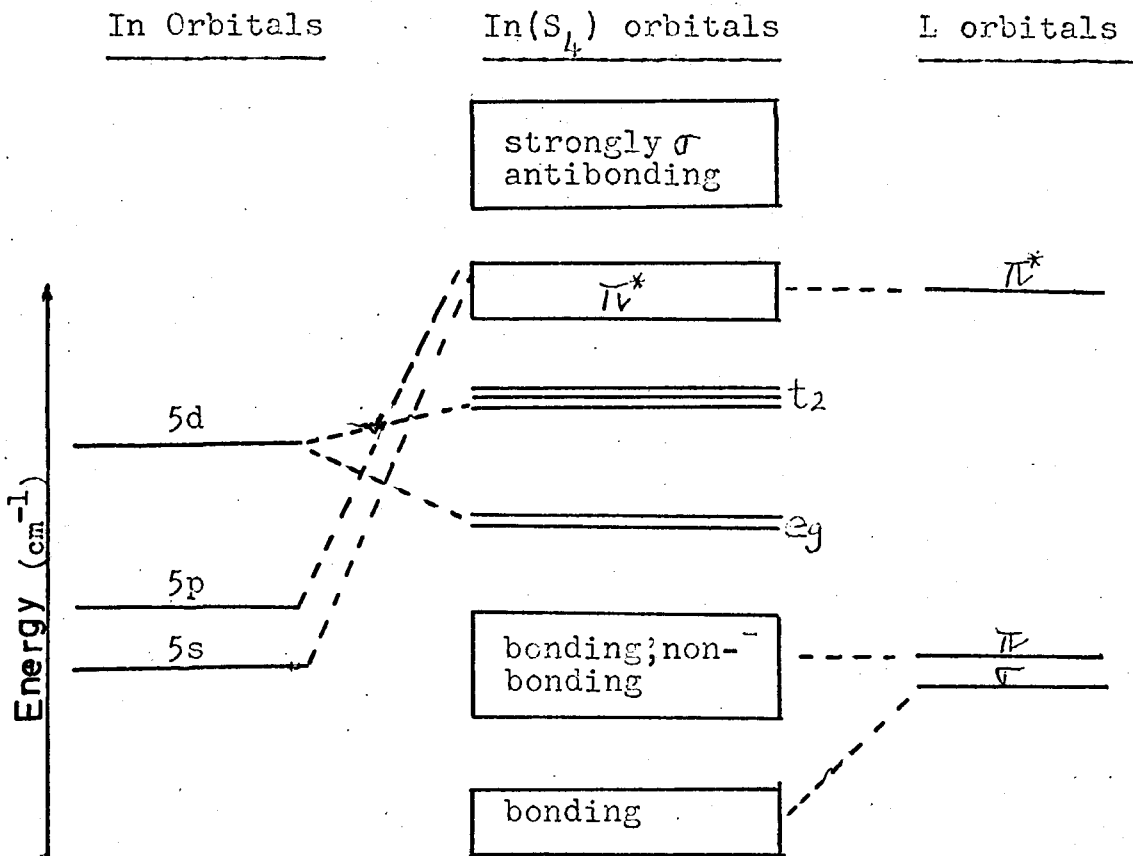
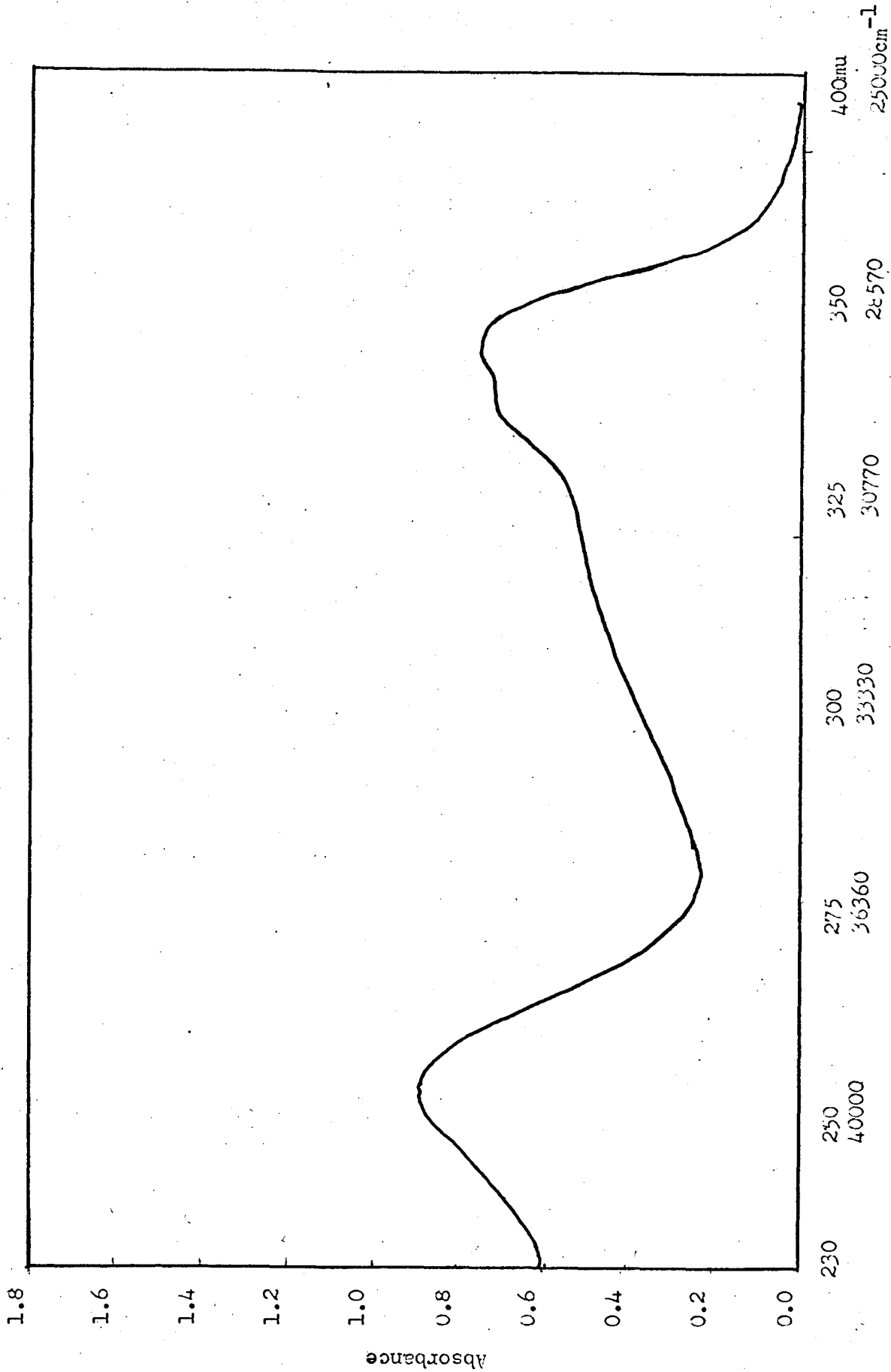


Fig. V-6. Simple energy level scheme for tetrahedral indium complexes



Fig. V-7 Absorption Spectrum of  $[\text{In}(\text{MNT})_2]^-$  Complex in  $\text{CH}_3\text{CN}$



Three intense absorption bands were observed in  $[\text{In}(\text{TDT})_2]^-$  complexes, but, no previous assignments for TDT complexes are available.

The UV spectra of the complexes of Ni(II), Pt(II), Pd(II), Cu(II), Zn(II), Au(III) and Fe(II) with  $\underline{\text{MNT}}$  have been thoroughly studied by Werden et al.<sup>55</sup> and Fackler et al.<sup>77</sup> They assumed that  $[\text{Ni}(\underline{\text{MNT}})_2]^{2-}$ ,  $[\text{Pt}(\underline{\text{MNT}})_2]^{2-}$ ,  $[\text{Pd}(\underline{\text{MNT}})_2]^{2-}$ , and  $[\text{Au}(\underline{\text{MNT}})_2]^-$  have  $D_{2h}$  symmetry, and that  $[\text{Fe}(\underline{\text{MNT}})_3]^{3-}$  and  $[\text{Co}(\underline{\text{MNT}})_3]^{3-}$  are octahedral, and then assigned the absorption bands of the complexes as shown in Table V-11.

Table V-11

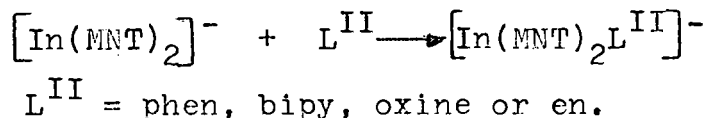
Electronic Spectra of M-iMNT Complexes in CH<sub>3</sub>CN.

Compound	max (cm <sup>-1</sup> )	ε	Assignment
[Fe( <u>i</u> MNT) <sub>3</sub> ] <sup>3-</sup>	15600	8.9x10 <sup>3</sup>	. . .
	19000	5.9x10 <sup>3</sup>	. . .
	19000	5.8x10 <sup>3</sup>	. . .
	26300	2.7x10 <sup>4</sup>	. . .
	29400	7 x10 <sup>4</sup>	L→L*
	36400	22 x10 <sup>4</sup>	. . .
	42300	6 x10 <sup>3</sup> sh	. . .
[Ni( <u>i</u> MNT) <sub>2</sub> ] <sup>2-</sup>	15700	87	d→d
	22100	3 x10 <sup>4</sup>	M→L*
	29600	6 x10 <sup>4</sup>	L→L*
	34400	2 x10 <sup>4</sup>	. . .
	37900	2.3x10 <sup>4</sup>	L→L*
[Pd( <u>i</u> MNT) <sub>2</sub> ] <sup>2-</sup>	22300	300 sh	d→d
	26500	6.6x10 <sup>4</sup>	M→L*
	37800	3.8x10 <sup>4</sup>	L→L*
	39600	1.5x10 <sup>4</sup>	L→L*
	48800	8 x10 <sup>3</sup>	. . .
[Au( <u>i</u> MNT) <sub>2</sub> ] <sup>-</sup>	21700	320	d→d
	25000	660	d→d
	28600	11.7x10 <sup>4</sup>	M→L*
	29800	8.3x10 <sup>4</sup>	L→L*
	31200	5.3x10 <sup>4</sup>	L→L*
	36400	7.4x10 <sup>3</sup>	. . .
	41500	1.2x10 <sup>4</sup>	. . .

The UV/visible spectra of the three compounds  $[\text{In}(\text{iMNT})_2\text{X}]^{2-}$  ( $\text{X}=\text{Cl}, \text{Br}$  and  $\text{I}$ ) (Figure V-9) are identical within experimental error, with absorption bands at  $29200\text{cm}^{-1}$ ,  $30200\text{cm}^{-1}$ ,  $34200\text{cm}^{-1}$  and  $38600\text{cm}^{-1}$ . Following Werden's work, the band at  $29200\text{cm}^{-1}$  and  $38600\text{cm}^{-1}$  may be assigned to the  $\text{L}\rightarrow\text{L}^*$  transition. The UV spectrum of  $[\text{In}(\text{iMNT})_3]^{3-}$  has four intense bands (Figure V-9). Two bands at  $29600$  and  $38600\text{cm}^{-1}$  may be assigned as  $\text{L}\rightarrow\text{L}^*$  transition on the basis of energies and extinction coefficients.

(b) Studies of Complex Formation in Solution.

The spectroscopic method has been used extensively in investigations of complex formation and the measurement of formation constants. Job's method has been used in the present work, with the assumption that only one complex was present in solution:



When a neutral bidentate ligand  $\text{L}^{\text{II}}$  was added in solution to the  $[\text{In}(\text{MNT})_2]^-$  complex in the ratio

$[\text{In}(\text{MNT})_2]^- : \text{L}^{\text{II}} = 1:0, 1:0.5, 1:1.0, 1:2.0$  and  $1:3.0,$

the UV spectrum showed that the combining ratio of  $[\text{In}(\text{MNT})_2]^-$  with  $\text{L}^{\text{II}}$  was 1:1 (see Fig. V-10).

Fig. V-8 Absorption Spectrum of  $[\text{In}(\text{iMNT})_2]^-$  ( X=Cl, Br, and I ) in  $\text{CH}_3\text{CN}$

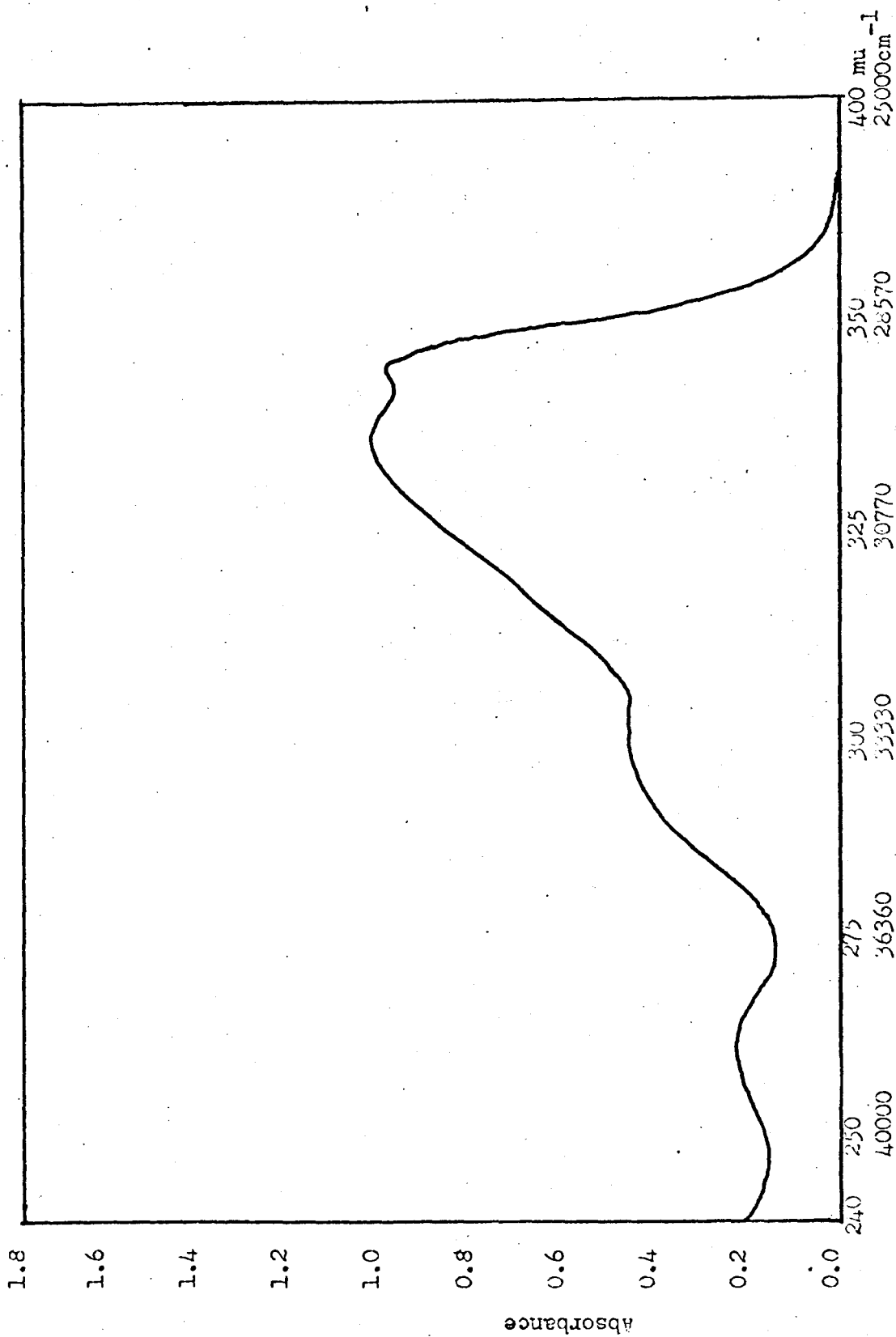
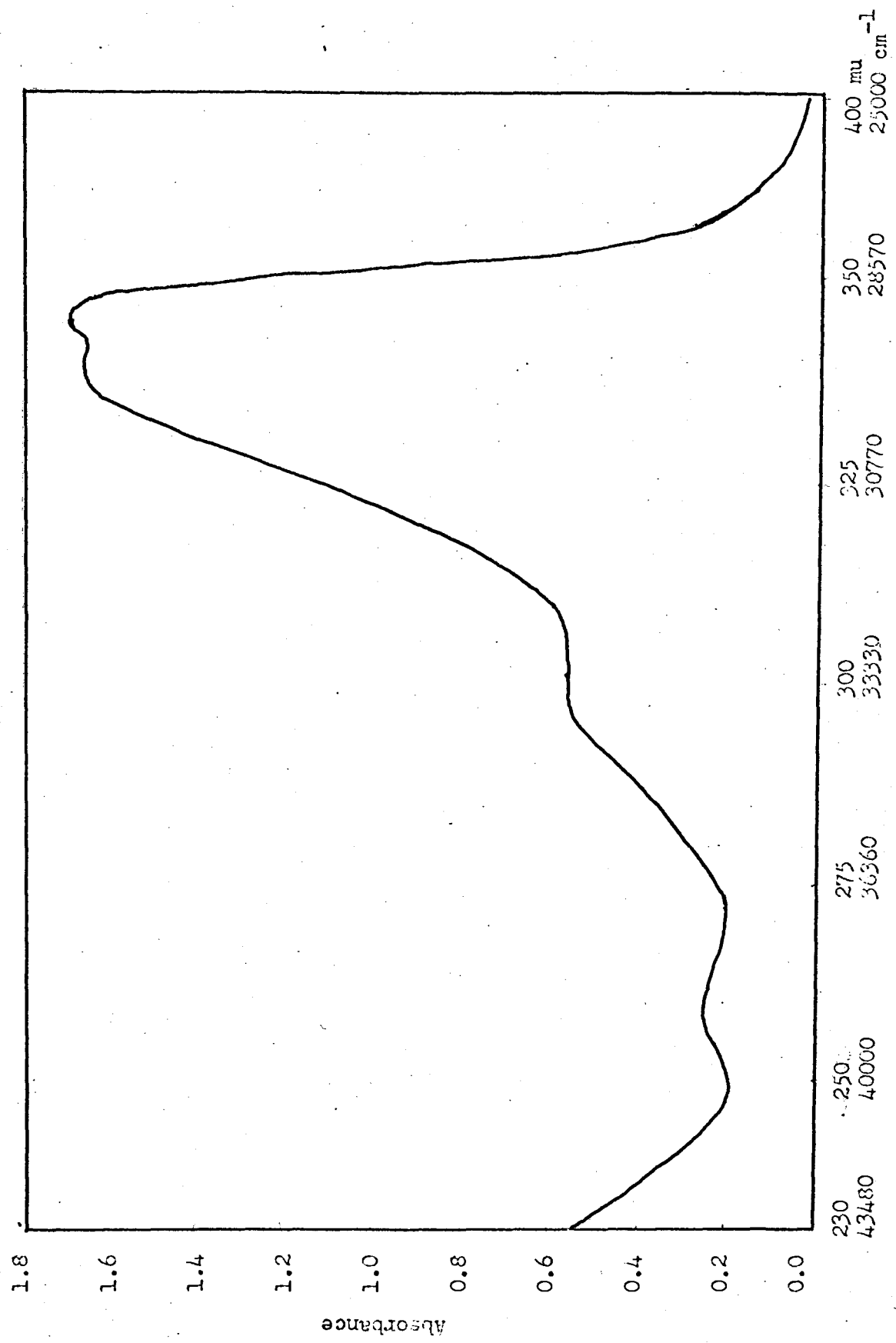


Fig. V-9 Absorption Spectrum of  $[\text{In}(\text{iMNT})_3]^{3-}$  in  $\text{CH}_3\text{CN}$



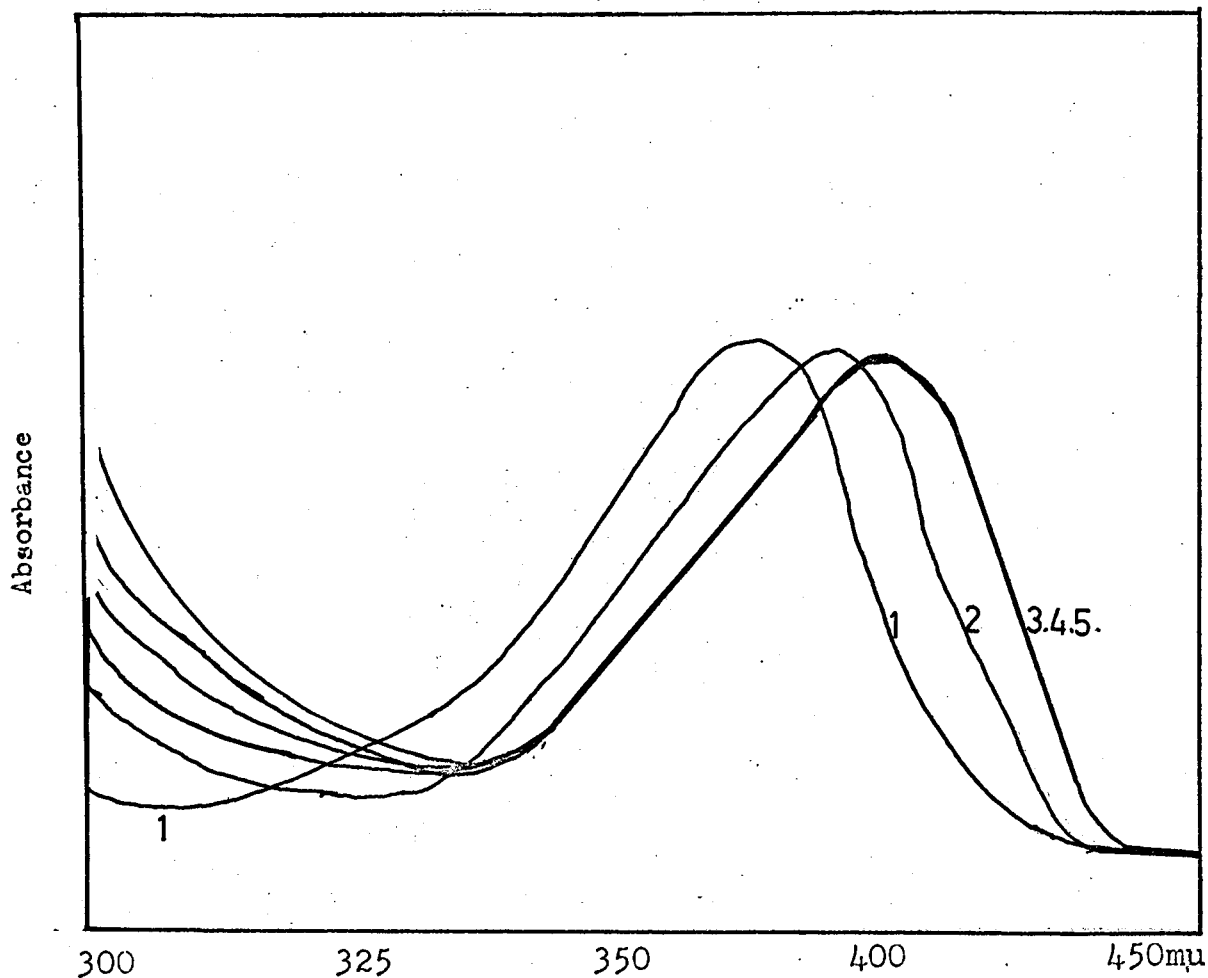


Fig. V-10

The absorption spectrum of  $[\text{In}(\text{MNT})_2]^-$  with differing amounts of 1,10-phenanthroline

- (1)  $[\text{In}(\text{MNT})_2]^-$  : phen = 1:0.0 (mole ratio)
- (2) = 1:0.5
- (3) = 1:1.0
- (4) = 1:2.0
- (5) = 1:3.0

The concentration of  $[\text{In}(\text{MNT})_2]^-$  is  $5 \times 10^{-4} \text{ M}$  in acetonitrile.

The two bands at  $28400\text{cm}^{-1}$  and  $29400\text{cm}^{-1}$  disappeared as the bidentate ligand was added (i.e. four coordinate structure was changing to pseudo-octahedral six coordinate structure). Two new bands were found in the  $27000\text{-}29000\text{cm}^{-1}$  region (see Table V-12).

The UV spectra of the  $[\text{In}(\text{TDT})_2]^-$  and  $[\text{In}(\text{iMNT})_2\text{X}]^{2-}$  complexes were not detectably changed during the addition of the bidentate ligand. The absorption bands of the indium(III) dithiolate complexes and their adducts are listed in Table V-12.



Table V-12

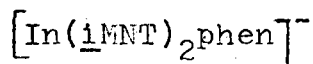
The UV spectra of Indium dithiolate complexes in  $\text{CH}_3\text{CN}$ .

Compound	$\lambda_{\text{max}}$ ( $\text{cm}^{-1}$ )	$\epsilon$	Assignment
$\text{Na}_2(\text{MNT})$	25700	$1.8 \times 10^4$	
	39500	$1.6 \times 10^4$	
	26500	$1.5 \times 10^4$	
	37300	$8 \times 10^3$	
$[\text{In}(\text{MNT})_2]^-$	28400	$1.3 \times 10^4$	(L( $\pi$ ) $\rightarrow$ M)
	29400	$1.2 \times 10^4$	(L $\rightarrow$ L*)
	39500	$1.6 \times 10^4$	(L( $\sigma$ ) $\rightarrow$ M)
$[\text{In}(\text{MNT})_3]^{3-}$	27800	$1.9 \times 10^4$	
	36900	$2.7 \times 10^4$	
$[\text{In}(\text{MNT})_2\text{bipy}]^-$	27300	$1.4 \times 10^4$	
	28800	$1.7 \times 10^4$	
	32500	$1.0 \times 10^4$	
	34100	$1.5 \times 10^4$	
	37800	$2.8 \times 10^4$	(L( $\sigma$ ) $\rightarrow$ M)
$[\text{In}(\text{MNT})_2\text{phen}]^-$	27300	$1 \times 10^4$	(L( $\pi$ ) $\rightarrow$ M)
	28400	$1 \times 10^4$	(L $\rightarrow$ L*)
	34000	$1.2 \times 10^4$	
$[\text{In}(\text{MNT})_2\text{en}]^-$	27700	$2.2 \times 10^4$	(L( $\pi$ ) $\rightarrow$ M)
	28200	$2.0 \times 10^4$	(L $\rightarrow$ L*)
	37900	$2.5 \times 10^4$	(L( $\sigma$ ) $\rightarrow$ M)

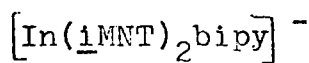
Table V-12 cont.

$[\text{In}(\text{MNT})_2\text{oxine}]^{2-}$	26900	$1.6 \times 10^4$
	27600	$1.9 \times 10^4$
	38200	$6.4 \times 10^4$
$[\text{In}(\text{MNT})_2(\text{dma})_2]^-$	27800	$4.4 \times 10^3$
	TDT <sup>2-</sup>	
	43400	
	44400	
$[\text{In}(\text{TDT})_2]^-$	36900	$1.4 \times 10^4$
	41500	$1.4 \times 10^4$
	46800	$1.4 \times 10^4$
	21300	$7 \times 10^4$
$[\text{In}(\text{TDT})_2\text{bipy}]^-$		
	$[\text{In}(\text{TDT})_2\text{phen}]^-$	
	38000	$36 \times 10^4$
	41000	$6.4 \times 10^4$
	43300	$6.5 \times 10^4$
$\text{Na}_2(\text{iMNT})_2$	29100	$1.4 \times 10^4$
	31400	$1.1 \times 10^4$
	38600	$2.5 \times 10^3$
	39600	$2.7 \times 10^3$
	47500	$1 \times 10^4$
$[\text{In}(\text{iMNT})_3]^{3-}$	29100	$8.5 \times 10^5$
	29600	$8.5 \times 10^5$
	33800	$2.3 \times 10^5$
	38600	$8 \times 10^4$

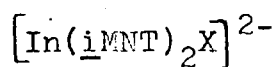
Table V-12 cont.



29200	$4.9 \times 10^5$
30100	$5.5 \times 10^5$
33600	$2.7 \times 10^5$
36900	$3.9 \times 10^5$
44100	$4.8 \times 10^5$



29200	$5 \times 10^5$
30200	$5.16 \times 10^5$
31900	$4.6 \times 10^5$
34500	$3.1 \times 10^5$
38600	$1.2 \times 10^5$
41000	$1.5 \times 10^5$



X=Cl, Br or I

29200	$4.8 \times 10^5$
31200	$5 \times 10^5$
24100	$2.1 \times 10^5$
38600	$8 \times 10^4$

## V (E) STRUCTURAL DISCUSSION

The structure of complexes of dithiolate ligands  $\text{MNT}^{2-}$ ,  $\text{TDT}^{2-}$ ,  $\text{S}_2\text{C}_2\text{Ph}_2$  and  $(\text{S}_2\text{C}_2\text{H}_2)^{2-}$  with the transition metal ions  $\text{Ni(II)}$ ,  $\text{Co(II)}$ ,  $\text{Co(III)}$ ,  $\text{Cu(III)}$ ,  $\text{Au(III)}$ ,  $\text{V(VI)}$ ,  $\text{Re(VI)}$ , etc., have been determined by x-ray crystallography<sup>52,77,84</sup>. The complexes have coordination numbers of four, five, and six. The geometry of all the four coordinate complexes studies showed that the sulphur atoms surround the metals in an essentially square-planar structure. The complexes of  $\text{Co(III)}$  and  $\text{Fe(III)}$  exist as both five coordinate monomers and five coordinate dimers. The five coordinate complexes of  $[\text{Co}(\text{MNT})_2\text{py}]^-$ ,  $[\text{Fe}(\text{MNT})_2\text{py}]^-$  and  $[\text{Co}(\text{MNT})_2\text{PPh}_3]^-$  have the proposed square pyramidal structure<sup>85</sup> shown in Figure V-11.

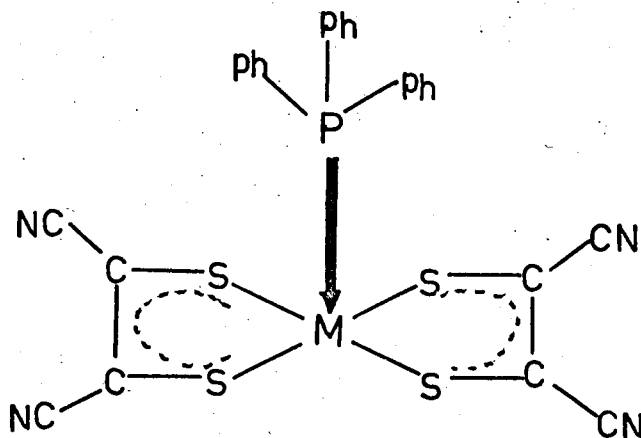


Fig. V-11

Proposed structure of the phosphine adducts of MNT complexes.

The structure of the dimeric form of the complexes  $[\text{Co}(\text{TDT})_2]^-$ ,  $[\text{Co}(\text{S}_2\text{C}_2(\text{CF}_3)_2)]^-$ ,  $[\text{Co}(\text{MNT})_2]^-$  and  $[\text{Fe}(\text{MNT})_2]^-$  have been established by x-ray methods. The arrangement of the five coordinates square pyramidal dimers<sup>86</sup> is shown in Figure V-12.

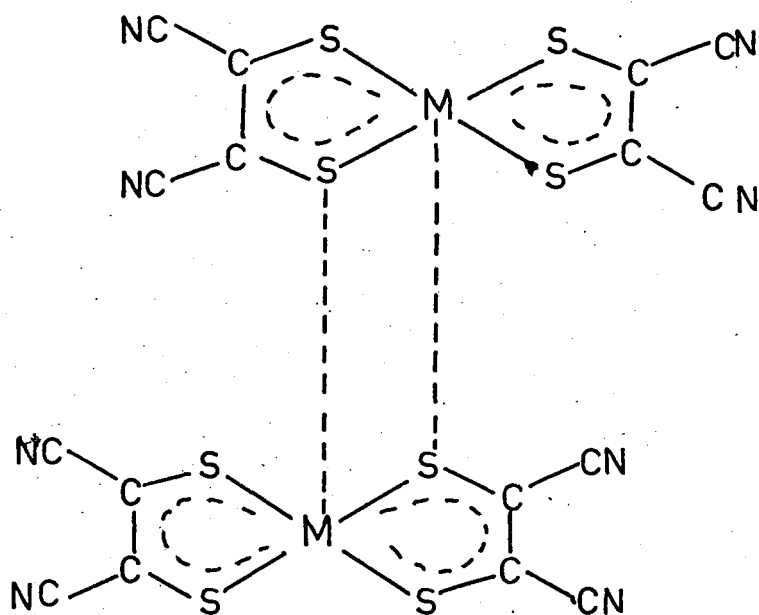


Fig. V-12

The dimeric structure of MNT complexes.

The six coordinate complexes e.g.  $V(S_2C_2Ph_2)_3$ ,  $Mo(S_2C_2H_2)_3$ , etc., have been found to have perfect or nearly perfect trigonal prismatic structures ( see diagram on page 23 Fig. II-2).

In the compound  $[Co(MNT)_2phen]^-$ , the six coordination is apparently not octahedral<sup>85</sup>.

Complexes of  $\underline{i}MNT$  studied by Fackler<sup>70</sup> with the bivalent ions Ni(II), Pd(II), Pt(II) and Cu(II) are square-planar. With trivalent ions  $[Fe(\underline{i}MNT)_3]^-$  and  $[Co(\underline{i}MNT)_3]^-$  it is possible that the sulphur atoms are arranged either in a trigonal-prismatic or an octahedral configuration. The UV and IR spectra of  $[Cr(\underline{i}MNT)_3]^-$ , which is isomorphous with the Fe(III) and Co(III) complexes, suggests strongly that these compounds have a pseudo-octahedral arrangement of six sulphur surrounding the metal.

The indium dithiolate complexes and their adducts have coordination numbers of four, five, and six. The structure of four coordination indium(III) complexes  $[In(MNT)_2]^-$  and  $[In(TDT)_2]^-$  is possibly tetrahedral or distorted tetrahedral, since the square-planar structure appears to be restricted to the diamagnetic  $d^8$  complexes such as Ni(II), Au(III), Rh(I), etc., and a few paramagnetic square-planar Co(II) and Cu(II) species.<sup>83</sup>

The complexes  $[\text{In}(\underline{\text{iMNT}})_2\text{X}]^{2-}$  ( $\text{X}=\text{Cl}, \text{Br}$  and  $\text{I}$ ) apparently have coordination numbers of five which presumably gives either a square-pyramidal or trigonal bipyramidal structure. Following work on the structure of the complexes  $[\text{Co}(\text{MNT})_2\text{PPh}_3]^-$ ,  $[\text{Fe}(\text{MNT})_2\text{PPh}_3]^-$  and  $[\text{Co}(\text{MNT})_2\text{py}]^-$ ; and recent work<sup>32</sup> on the compound  $\text{InCl}_5^{2-}$  (see diagram page 15 Figure II-1), it is suggested that the structure of these compounds is probably tetragonal pyramidal, so that the anion  $[\text{In}(\underline{\text{iMNT}})_2\text{X}]^{2-}$  may have the structure shown in Figure V-13.

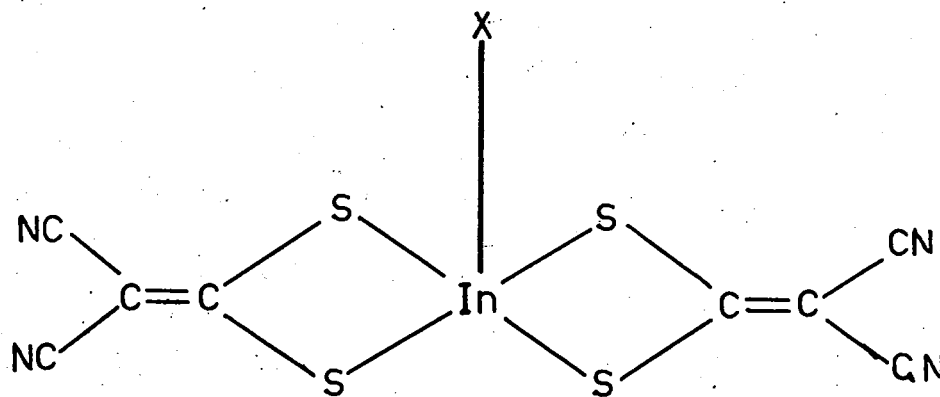


Fig. V-13

Proposed structure of  $[\text{In}(\underline{\text{iMNT}})_2\text{X}]^{2-}$  complexes  
 $\text{X}=\text{Cl}, \text{Br},$  and  $\text{I}.$

A study of the details of the structure of this complex would be very valuable. The structure of the six coordination complex,  $[\text{In}(\underline{\text{iMNT}})_3]^{3-}$ , is tentatively suggested to be octahedral, following Fackler's work.

The complex  $[\text{In}(\text{MNT})_3]^{3-}$  has been studied by x-ray single crystal methods<sup>87</sup>, which has shown that the  $\text{InS}_6$  kernel in this anion has a distorted octahedral structure, with the In-S bond length 2.59Å. The S-In-S angle within the chelate ring is  $80^\circ$  and the S-S distance in the ring 3.39Å. (Figure V-14).



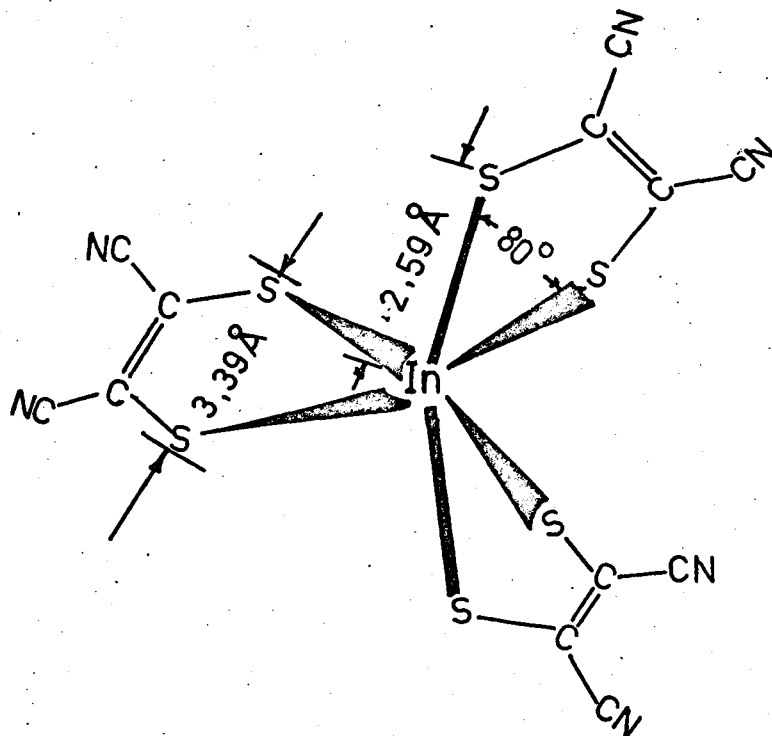


Fig. V-14 The distorted octahedral structure of  $[\text{In}(\text{MNT})_3]^{3-}$

The complexes  $[\text{In}(\underline{\text{iMNT}})_2\text{phen}]^-$ ,  $[\text{In}(\underline{\text{iMNT}})_2\text{bipy}]^-$ ,  $[\text{In}(\text{TDT})_2\text{phen}]^-$ , and  $[\text{In}(\text{TDT})_2\text{bipy}]^-$  may be six coordinate, with distorted octahedral structure. It was emphasised earlier that the complex  $[\text{In}(\text{TDT})_2\text{phen}]^-$  may have the cis and trans isomers, following the NMR studies.

## CHAPTER VI

SUGGESTION FOR FURTHER RESEARCH

The structure of some  $[\text{In}(\text{MNT})_2]^-$ ,  $[\text{In}(\text{TDT})_2]^-$ , and  $[\text{In}(\underline{\text{iMNT}})_2\text{X}]^{2-}$  complexes are worth studying by x-ray crystallography, which will show whether the compounds have tetrahedral, or distorted tetrahedral structures, and also how strong is the influence of the chelating ring system. Of special interest is the possibly five-coordinate  $[\text{In}(\underline{\text{iMNT}})_2\text{X}]^{2-}$ , in terms of the actual geometry, and of the bond lengths In-X (X=Cl, Br and I) which should be compared with known structures.

It would be very useful to study in detail the infrared and Raman spectra of the complexes in order to identify the In-S and In-N, In-O stretching modes unambiguously.

Attempts to isolate the different oxidation states of  $[\text{In}(\text{MNT})_2]^-$ ,  $[\text{In}(\text{MNT})_3]^{3-}$ ,  $[\text{In}(\text{TDT})_2]^-$ ,  $[\text{In}(\underline{\text{iMNT}})_2\text{X}]^{2-}$ ,  $[\text{In}(\text{MNT})_3]^{3-}$  and their adducts, as possible In(0), In(I) and In(II) complex species, represents a big challenge. The study of magnetic properties in the different oxidation states of the compounds, possibly by ESR method, would be very significant.

During the preparation of 8-hydroxyquinoline adducts with  $[\text{In}(\text{MNT})_2]^-$ , it was found that a compound with an indium content of 16.7% was isolated. This is close to

the composition of either  $\text{Et}_4\text{N}[\text{In}(\text{MNT})_2\text{oxine}]$  (17.01%) or  $[\text{In}(\text{MNT})(\text{oxine})_3]$  (16.64%). The IR spectrum has shown the compound containing MNT ligand and the oxine, and the NMR spectrum has clearly shown the absence of the cation  $\text{Et}_4\text{N}^+$ . It may be of interest to study the structure of such indium-oxine-dithiolate complexes in more detail.

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LIST OF ABBREVIATIONS

- bipy = 2,2'-bipyridyl
  - dma = N,N'-dimethylacetamide
  - DME = dropping mercury electrode
  - dmf = dimethylformamide
  - dmsO = dimethylsulphoxide
  - en = ethylenediamine
  - oxine = 8-hydroxyquinoline
  - 1MNT = 1,1'-dicyanoethylene-2,2'-dithiolate
  - L = ligand
  - $\Lambda$  = molar conductivity
  - MNT = maleonitriledithiolate
  - Ox. = Oxidation
  - phen = 1,10-phenanthroline
  - 5-nitro-o-phen = 5-nitro-1,10-phenanthroline
  - py = pyridine
  - pic = picoline
  - Red = reduction
  - TDT = toluene-3,4-dithiolate
  - soln = solution
  - X = halides
  - s = strong
  - m = medium
  - w = weak
  - sh = shoulder
  - cps = cycles per second
- } in infrared spectra