NAME OF AUTHOR/*NOM DE L'AUTEUR* ANTHONY MARK SAKENA

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PERMANENT ADDRESS/*RÉSIDENCE FIXÉ* [redacted]

STUDIES OF MONOSUBSTITUTED TRIOXO- AND OXODIPEROXOCHROMIUM(VI) COMPLEXES

by

ANTHONY MARK AKENA

B.Sc., University of Washington, 1968

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Name: Anthony Mark Akena

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Examining Committee:

Dr. D.G. Tuck, Senior Supervisor

Dr. D. Sutton

Dr. R. G. Korteling

Dr. F.W.B. Einstein, Internal Examiner

Dr. George H. Cady, External Examiner
Professor of Chemistry
University of Washington, Seattle

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OXODIPEROXOCHROMIUM(VI) COMPLEXES

Author:

(signature)

ANTHONY MARK AKENA

(name)

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(date)

ABSTRACT

New monosubstituted trioxo- and oxodiperoxochromium(VI) complexes CrO_3L^-, (for L = Br^-, NCO^-, N_3^-, NCS^- and NO_3^-) and $CrO(O_2)_2.L$ (for L = F^-, NCO^-, NCS^-, N_3^-, NO_3^- and $OP(C_6H_5)_3$), prepared by metathetical reactions in acetonitrile, have been characterized.

The vibrational spectra of the CrO_3L^- (infrared and Raman) and $CrO(O_2)_2L$ (infrared) complexes were measured over the range 200 - 4000 cm^{-1}. Provisional spectral assignments of the Cr-ligand and intraligand vibrations, based on comparisons with similar systems, were made. The vibrational absorption bands near $\simeq$ 900 cm^{-1}, generally assigned to ν_{sym} (Cr-O) (A_1), were studied closely. There was a gradual but regular decrease in the frequency as the substituent L was changed from F^-, Cl^-, NCO^-, Br^-, NO_3^-, N_3^-, to NCS^-, demonstrating that ν_{sym}(Cr-O) could be used as a probe for substituent effects in CrO_3L^{n-} ions.

The electronic charge-transfer spectra of the two sets of complexes CrO_3L^- and $CrO(O_2)_2L$ in the UV-visible region were also recorded. In the case of the CrO_3L^- ions, the spectra showed three absorption bands, one of which (in the 360 mμ region) has a progression of well-defined fine structure with a frequency spacing of ca. 740 cm^{-1}, ascribed to the coupling of electronic transitions with the totally symmetric vibration ν_{sym} (Cr-O). There is a significant red shift in the position of this band maximum as the electronegativity of the substituent L is changed in going from F, Cl, to Br. The substituent effects on the the charge-transfer spectra were discussed in terms of the $Cr-O^{2-}$ and $Cr-O_2^{2-}$ bonding interactions in CrO_3L^- and $CrO(O_2)_2L$, respectively.

Attempts were made to measure the equilibrium constant for the substitution processes of the type

$$CrO_3L^- + L'^- \rightleftharpoons CrO_3L'^- + L^-$$

and

$$CrO(O_2)_2L + L' \rightleftharpoons CrO(O_2)_2L' + L$$

in non-aqueous (dimethylsulphoxide or acetonitrile) solutions, conditions chosen to eliminate competing hydrolytic process which generally occur in aqueous solutions. While the ^{19}F NMR studies showed very slow exchange in the CrO_3F^-/F^- and CrO_3F^-/Cl^- systems, the substitution reactions in CrO_3L^-/F^- for $L^- = Br^-$, N_3^-, NCO^-, NCS^- and NO_3^- were very fast. Attempts to synthesize $CrO(O_2)_2F^-$ or affect exchange in $CrO(O_2)_2L/F^-$ and $CrO(O_2)_2.NC_5H_5/NC_5H_5$ (and d_5) systems were not very successful because of competing decomposition processes.

Repeated attempts to synthesize pure samples of chromium(VI) nitrido complexes by reacting chromium(VI) compounds with nitriding reagents were unsuccessful.

To My Family

and

In Memory of My Father

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I would like to thank my Research Supervisor, Dr. D. G. Tuck, for his concern, constructive comments and financial support through the years of this work.

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In conclusion, I wish to dedicate this effort to the memory of my father who was a continual source of inspiration and understanding.

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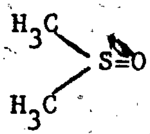
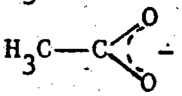
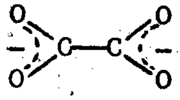
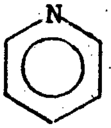
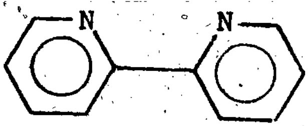
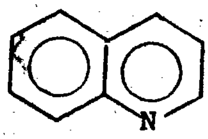
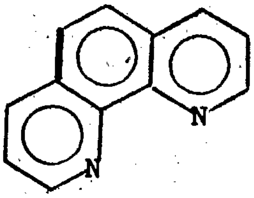
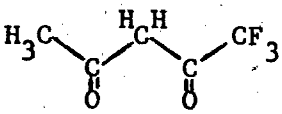
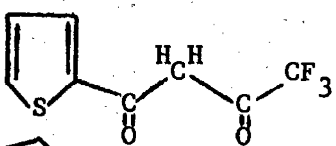
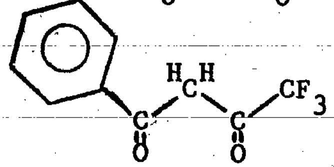
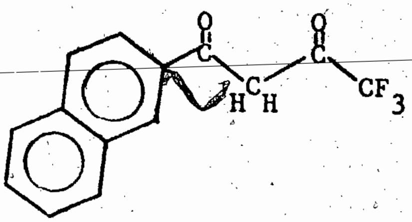
ABBREVIATIONS:

DMSO	Dimethylsulfoxide	
OAc^-	Acetato	
ox^{2-}	Oxalato	
py	Pyridine	
bipy	2-2'-bipyridyl	
quin	Quinoline	
phen	1,10-phenanthroline	
TAA	Trifluoroacetylacetone	
TTA	Thenoyltrifluoroacetone	
BTA	Benzoyltrifluoroacetone	

NTA 2-Naphthoyltrifluoroacetone.



Ps Pseudohalogen

Abbreviations used to describe vibrational bands and corresponding atomic motions.

ν = stretching; δ = deformation; ρ = rocking; f_{M-X} = M-X (stretching) force constant; and λ = wavelength; v, very; s, strong; m, medium; w, weak; sh, shoulder; shr, sharp.

CHAPTER ONE

INTRODUCTION AND REVIEW OF OXO AND PEROXO COMPLEXES OF CHROMIUM(V1)

I.1 INTRODUCTION

The element chromium is widely distributed principally as the ore chromite, $FeCr_2O_4$. It was first discovered in 1797 in the mineral crocoite, $PbCrO_4$, and given its name (from Greek chroma meaning colour) because of its many coloured compounds. In addition to their dominance in the pigment industries, compounds of chromium have also found uses in tanning, pickling, wood preservation, etc. More recently Mertz and Schwarz,[1] and Mertz[2] demonstrated that chromium is a biologically essential trace metal although its exact functions and minimum levels have not yet been established. In short, while chromium chemicals have become a part of our civilization, the problems of toxicity (absorption,[3] distribution,[4] and elimination) of these compounds, especially chromium(VI) compounds, in the body makes the study of chromium coordination chemistry very important.

Chromium (atomic number, $Z = 24$) belongs to the Periodic Group VIA, has six valence electrons ($3d^5 4s^1$) and exhibits oxidation states ranging from -2 to +6. In its lowest oxidation states, stabilized by π-bonding ligands, chromium shows its greatest chemical similarity with molybdenum and tungsten. There is, however, little similarity in the chemical behaviour of these three metals in their highest oxidation state (+6). Many common characteristics are generally expected from members of the same periodic group except where the properties depend on their atomic and ionic radii.

The chemistry of chromium is dominated by literally thousands of Cr(III) complexes. These may be neutral, cationic or anionic and, with a few exceptions, exhibit a maximum coordination number of six. In the higher oxidation states the chemistry of most early transition metals is dominated by oxo species[5] such as MO^{n+}, MO_2^{n+}, MO_y^{n+} and $[M_xO_y]^{n+}$ where n = 0, 1, 2 .... etc. Except for peroxo complexes, the aqueous chemistry of chromium(IV) and (V) have been marred by ready disproportionation and/or reduction to the more stable +3 state. In the oxidation state +6, chromium is highly oxidizing and can only coexist with ligands of high electronegativity. The role of ligands such as O^{2-} and F^- in stabilizing complexes of Os and Ru in the oxidation states between +8 and +4 are known.[5] Gillespie[6] has suggested that, as a mechanism of relieving the high electron density and the strong repulsions between non-bonding electron pairs located on the relatively small oxygen (or fluorine) atom, multiple bonding by the O (or F) should be expected when the ion is bonded to an atom (or a grouping) which can readily accept π-bonding electrons. In the case of terminal oxygen, M-O_t, valency requirements would be a major contributing factor.

All known compounds of chromium(VI) exist, with the exception of CrF_6[7] which decomposes above -100°C, as oxo species such as CrO_4^{2-}, CrO_3, CrO_3L^{n-}, $CrO_2L_2^{n-}$, $CrO_2L_3^{n-}$, $CrO_2L_4^{n-}$ and $CrO(O_2)_2L^{n-}$ where n = 0,1,2....etc. and L is a single atom donor ion or grouping (eg. pseudohalide, hydroxyl or oxyacid anion, neutral or anionic organic donor species). The existence of such a series of compounds has aroused interest in terms of the nature of the metal-oxygen bond. The problems of particular interest are (1) the interaction between two or more M-O oscillators, and (2) from these some quantitative suggestions concerning the relative importance of σ- and π-bonding contributions to the M-O bond strength.

Numerous authors [8,9,10] have tackled various portions of the problem of understanding the nature of metal-oxygen bonds. As usual, we would expect the amount (or degree) of $p\pi$-$d\pi$ donation to depend both on the tendency for the oxygen (or ligand) to donate and of the metal to accept electrons. Consider CrO_3L^-; coordination of ligands (L) which owe their ligational strength primarily to their σ-electron pair (Lewis base) donating ability will increase the electron density on the chromium d-orbitals and cause a reduction in the amount of pπ → dπ donation from the oxygens. For instance, Kidd[11] has shown that a linear relationship exists between the ^{17}O chemical shifts and the degree of Cr-O π-bonding in $O_3CrO^*CrO_3^{2-}$, $CrO^*_4{}^{2-}$, $O^*_3CrOCrO^*_3{}^{2-}$ and $CrO^*_2Cl_2$.

The ideal set-up for studying M-O π-bonding interactions would be a series of complexes in which one of the ligands and the number of coordinated oxygens can be varied gradually, while still keeping the oxidation state and preferably also the coordination geometry around the metal constant. Most second and third row transition metals have the disadvantage of readily extending their coordination number by either polymerization or uptake of donor species, including solvents, into their coordination spheres. Chromium(VI) has most of the properties necessary for such a study. A representative series of complexes for the study would be the well established compounds CrO_2Cl_2, CrO_3Cl^-, $CrO_4{}^{2-}$ and $CrO(O_2)_2Cl^-$, where the number of oxygen atoms coordinated to the chromium is varied from two to five while still retaining the pseudo-tetrahedral configuration around the metal.[12]

The dioxochromium(VI) compounds (or chromyl compounds), $CrO_2L_x{}^{n-}$, for x = 2,3 or 4 and n= 0,1 or 2 present some experimental problems. They are generally very reactive and/or thermally unstable.[13] Among the well

---

* labelled (^{17}O) oxygen

established dioxochromium(VI) compounds,[13,14] CrO_2F_2, the most corrosive of all, has the greatest thermal stability (up to ≈400°C); CrO_2Cl_2 decomposes at approximately 180°C. while the other chromyl compounds, eg. $CrO_2(NO_3)_2$, are unstable around room temperature. Furthermore, almost all known chromyl compounds are decomposed by ultraviolet radiation.

For the other chromium(VI) complexes (CrO_3L and $CrO(O_2)_2L$), except for the vibrational studies of Stemmreich and Sala[15] and others[16,17] on the CrO_3Cl^- and CrO_3F^- ions and the electronic spectral studies of the same compounds by Helmholz and Brennam,[18] there are no vibrational or electronic spectral studies reported on any other stable anionic monosubstituted chromates, CrO_3L^{n-}. The only spectral studies conducted on anionic monosubstituted oxodiperoxochromate(VI) complexes, $CrO(O_2)_2L^{n-}$, are those of Tuck[19] and Griffith.[20]

Research Programme

This thesis intends to contribute to the understanding of the coordination chemistry of chromium(VI) and the metal-oxygen bond by synthesizing a host of monosubstituted trioxo- and oxodiperoxochromate(VI) complexes, CrO_3L^{n-} and $CrO(O_2)_2L^{n-}$, respectively, where the substituent L is a small and simple anionic species. The halides and pseudohalides were found to be particularly well suited ligands for this systematic study. Some kind of a trend would be expected from the vibrational and electronic properties of these species which could be related to the structure and/or changes in the electronic distribution or bonding in the species, CrO_3L^{n-} or $CrO(O_2)_2L^{n-}$. Studies like this suggest the possibility of employing some of the properties of the M-O multiple bond as internal molecular probes to learn more about the nature of other metal-ligand bonds.

A survey of the literature shows that the mechanism of substitution reactions of tetrahedral oxo complexes in non-aqueous solvents have been little studied. The substitution processes

$$CrO_3L^{n-} + L'^{n-} \rightleftharpoons CrO_3L'^{n-} + L^{n-}$$

and

$$CrO(O_2)_2L + L' \rightleftharpoons CrO(O_2)_2L' + L$$

in non-aqueous media (and for non-precipitating systems) were studied to try and obtain information on the kinetics, substitution equilibria, bond type (Cr-O, Cr-N, Cr-S, Cr-F, Cr-Br, Cr-Cl) and the relative stabilities of these chromium(VI) species in solution.

If enough experimental data were obtainable, an evaluation of the thermodynamic parameters, (changes in enthalpy ΔH, entropy ΔS and free energy ΔG), occuring in complex formation might provide useful evidence regarding the nature and strength of the bonding in the complex. These quantities can be determined from the equilibrium constant K and the variation of K with temperature.

The nitride (N^{3-}) and oxide (O^{2-}) ions are isoelectronic, The former has been shown by force constant calculations on ReO_3N^{2-} and OsO_3N^- to have the greater Π-bonding ability. Furthermore, the metal-nitrogen bond reportedly has a remarkable stability to most redox, addition and substitution reactions. I have therefore attempted to synthesize chromium(Vl) nitrido complexes for the purpose of complementing the studies on the methods of synthesis, vibrational and electronic properties, relative stabilities, substitution kinetics and equilibria of oxo-chromium(Vl) complexes.

I.2 REVIEW OF OXO COMPLEXES OF CHROMIUM(VI)

(a) Unsubstituted Oxochromium(VI) Complexes

Although in the series CrO_3, CrO_4^{2-}, $HCrO_4^-$, ...etc., chromium(VI) has at best superficial stoichiometric similarities with Group VIB elements (S, Se, etc.), the resemblences in the acidity of the MO_3 and the covalent nature and ready hydrolysis of MO_2Cl_2 compounds are profound. The parent oxide, CrO_3, an orange-red substance, is obtained by treating sodium or potassium dichromate with sulphuric acid. Like MoO_3 and WO_3, it dissolves in sodium hydroxide to give the tetrahedral anion MO_4^{2-}. The crystal structure[21] and vibrational spectrum[22,23,24] of the CrO_4^{2-} anion, as salts of K^+, Rb^+, Cs^+, Na^+, Ba^{2+}, Pb^{2+} and NH_4^+, are available. The tetrahedral tetraoxo anions MO_4^{n-} for M = Cr(V), Mo(VI), W(VI), Os(VIII), Mn(V, VI and VIII), Nb(V), Ta(V), Tc(VII), Re(VII), V(V), Fe(VI) and Ru(VI, VII and VIII) have also been established.[24] It has, however, become abundantly clear that the vibrational spectra of these complexes are complicated.[25,26] The complexity has been attributed to the site and factor-group splitting which, for the infrared spectra of powders, are also obscured by strong reflectance spectra. The CrO_4^{2-} [26] crystal structure determination, the single crystal Raman and infrared spectra reported by Adams and colleagues could clear up some of the confusion over assignments of vibrational data for CrO_4^{2-}.

In aqueous acidic solutions VO_4^{3-}, MoO_4^{2-}, WO_4^{2-} and to a lesser extent NbO_4^{3-}, TaO_4^{3-} and CrO_4^{2-}, undergo complex hydrolysis-polymerization reactions.[27] Except for $M^1_2Cr_2O_7$, $M^1_2Cr_3O_{10}$ and $M^1_2Cr_4O_{13}$,[28] chromium does not give rise to the extensive and complex series of polyacids and polyanions characteristic of the somewhat less acidic oxides of V(V), Mo(VI) and W(VI).[9] The relative simplicity of chromate hydrolysis-polymerization is perhaps due to the greater extent of multiple bonding, Cr=0, for the smaller chromium ion. So that while Cr(VI) appears* to be limited to tetrahedral coordination in the oxide structures,[5,31] the larger V(V), Nb(V), Ta(V), Mo(VI) and W(VI) species permit variable coordination numbers. Consequently, the structural possibilities for polyanion formation are much greater for these elements than for Cr(Vl).

The electronic[18] and X-ray[33] structures of the $Cr_2O_7^{2-}$ ion have been studied. As is the case with the CrO_4^{2-} ion, the complete assignment of the vibrational spectrum[34,35] of the $Cr_2O_7^{2-}$ ion is not yet established.

(b) Substituted Dioxochromium(VI) Complexes

Certain ligands are known [5] to replace the oxo (O^{2-}) ion in a complex without changing the oxidation state of the metal or unduly altering the molecular geometry. For instance, in the series of complexes

V^{V}	Cr^{VI}	Mo^{VI}	Re^{VII}
VO_4^{3-}	CrO_4^{2-}	MoO_4^{2-}	ReO_4^{-}
	CrO_3X] ($X^- = F^-, Cl^-, OH^-$)	MoO_3S^{2-}, MoO_3N^{3-}	ReO_3X^{n-} (for X = S, N,F,Cl,Br)
	CrO_2X_2	$MoO_2S_2^{2-}$	
VOS_3^{3-}	$CrO(O_2)_2OH^-$	MoS_4^{2-}	

the isoelectronic nitride (N^{3-}), hydroxide (OH^-) and fluoride (F^-), and also the "pseudoisoelectronic" peroxide (O_2^{2-}) and sulphide (S^{2-}) ions have formally substituted the oxide ligand.

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* The complexes $K_3(CrO_4F)$[29] and $2NaOH.Na_2(CrO_4)$,[30] which may contain the $CrO_4(OH)_2^{4-}$ ion, have been reported.

Except for $CrOF_4$,[32] the most heavily substituted chromium(VI) oxo complexes also contain the peroxo ligands and will be discussed in detail in Section 1.3. On the other hand a large number of complexes are now known in which the dioxochromium moiety CrO_2^{2+} is coordinated to various donor species. Of these the best known are the dioxohalogenochromium(VI) compounds, CrO_2Cl_2 and CrO_2F_2. These complexes are prepared by the action of various halogenating agents on CrO_3 or CrO_4^{2-}.[14,36,37] The structure of CrO_2Cl_2 in vapour[38] has been determined by electron diffraction and both CrO_2Cl_2 and CrO_2F_2 have been subjected to infrared,[39] Raman[40] and mass spectral[41] studies. The electronic structure of CrO_2Cl_2 has also been investigated.[50] The mixed halide complex, CrO_2ClF, has been identified[37,41,42] as a product in the metathetical reaction of the two pure compounds

$$CrO_2CL_2 + CrO_2F_2 \rightleftharpoons 2CrO_2ClF \qquad [1]$$

In addition to other synthetic routes, the reaction of CrO_2Cl_2 with silver borate,[43] hydrogen bromide,[44] silver cyanate,[45] silicon thiocyanate (or $OP(SCN)_3$),[45] dinitrogen pentoxide[46] and peroxodisulphuryldifluoride ($S_2O_6F_2$)[47] have been reported to yield $CrO_2(BO_2)_2$, CrO_2Br_2, $CrO_2(NCO)_2$, $CrO_2(NO_3)_2$, and $CrO_2(SO_3F)_2$ respectively. An equally interesting series of compounds have been reported for reactions with CrO_3. For instance, hydrazoic acid,[49] acetic acid,[51] oxalic acid,[48] acetic anhydride,[52] and various fluorinated anhydrides[53] have been used to prepare $CrO_2(N_3)_2$, $CrO_2(OH)(CH_3COO)$, CrO_2ox, $CrO_2(CH_3COO)_2$, and $CrO_2(R_fCOO)_2$ (for $R_f = CF_3$, ClF_2C and C_3F_7), respectively. In other studies, Gerlach and Gard[54] reported making new five and six coordinate dioxochromium(VI) complexes, $KCrO_2(CF_3COO)_3$ $CrO_2(R_fCOO)_4^{2-}$ (for $R_f = CF_3$ or C_3F_7), and $CrO_2(R_fCOO)_3^-$ (for $R_f = CF_3$ or $ClCF_3$), by reacting the halogenated anhydrides with CrO_3Cl^-, CrO_4^{2-} or

$Cr_2O_7^{2-}$. Reacting[55] CrO_2F_2 with NaF and $NaNO_3$ produced $Na_2CrO_2F_4$ and $Na_2CrO_2F_2(NO_3)_2$, respectively; both compounds contain Cr(VI).

(c) Substituted Trioxochromium(VI) Complexes

A number of kinetic studies[56,57,58,59] have been published on chromium(VI) species in various aqueous solutions. It is well established that in neutral and basic (>pH6) solutions the tetrahedral yellow chromate ion, CrO_4^{2-}, exists; as the pH is lowered the chromate ion is converted via protonation ($HCrO_4^-$) and dimerization to the orange dichromate ion ($Cr_2O_7^{2-}$). Between pH 6 and 2, the ions $HCrO_4^-$ and $Cr_2O_7^{2-}$ are in equilibrium.[56,60]

$$CrO_4^{2-} + H^+ \rightleftharpoons CrO_3(OH)^- \qquad [2]$$

$$2CrO_3(OH)^- \rightleftharpoons Cr_2O_7^{2-} + H_2O \qquad [3]$$

The above reactions represent just two of many situations in which the oxide (O^{2-}) ion in the chromate (CrO_4^{2-}) is replaced by a donor group, in this case hydroxyl (OH^-) or chromato (CrO_4^{2-}) group. The interconversion of $HCrO_4^-$ and $Cr_2O_7^{2-}$ (equation 3) has been shown to bring about oxygen exchange between chromium(VI) species and water. Studies of this exchange process in neutral [61] and basic [62] solutions have also established that they proceed at identical rates. Unfortunately, the rates of oxochromium(VI)-water exchange in reaction [3] do not give information on the structure and bonding in the transition states in such dissociation - condensation equilibria.

Studies carried out in various acidic media [56-63] have also established that the above pH-dependent equilibria exist only in perchloric acid solutions. Using other acids, eg. hydrofluoric, hydrochloric, hydrobromic, acetic, nitric, phosphoric, phosphorous, sulphuric, sulphurous and iodic acids reportedly converts the CrO_4^{2-}, $HCrO_4^-$, and $Cr_2O_7^{2-}$ ions to the corresponding monosubstituted derivative CrO_3L^{n-}, where $L = F^-$, Cl^-, Br^-, $CH_3CO_2^-$, NO_3^-, PO_4^{3-}, (HPO_4^{2-} or $H_2PO_4^-$), PO_3^{3-} (HPO_3^{2-} or $H_2PO_3^-$), SO_4^{2-} (or HSO_4^-), SO_3^{2-} (or HSO_3^-) and IO_3^-, respectively. The possible existence of most of these species (as well as others,[59,63,64] e.g. $CrO_3(S_2O_3)^{2-}$, $CrO_3(NCS)^{2-}$ ..... etc.,) have been suggested on the basis of spectrophotometric (uv-visible) evidence, and only a few have been isolated.

(i) Preparative Studies

Historically, the ruby red crystalline potassium fluorochromate $KCrO_3F$, was first prepared[65] more than a century ago by the action of concentrated hydrofluoric acid on potassium dichromate. The product was purified by recrystallization from the concentrated solution in hot hydrofluoric acid. The preservation of the compound, even of the carefully dried crystals, requires avoiding both exposure to moisture or light and contact with glass or porcelain ware.

Similarly, treating boiling potassium dichromate solution with an excess of dilute hydrochloric acid yields[66] red crystals of potassium chlorochromate, $KCrO_3Cl$. Peligot obtained the same salt by treating stoichiometric amounts of potassium chloride with chromic acid (aqueous solution of CrO_3). Crystal structures of $KCrO_3F$[67] and $KCrO_3Cl$[68] have since been reported and the vibrational[17] and electronic[18] spectra established.

The existence of potassium bromochromate, $KCrO_3Br$, on the other hand, has been questioned.[69,70] Original efforts[71] reported isolating the compound by evaporating, in the cold and in vacuo, either a solution of chromic acid and potassium bromide or the solution of potassium chromate in fuming hydrobromic acid. There are, as yet, no reliable vibrational or structural data on the compound.

Although Guyot[72] claimed having isolated garnet-red crystals of potassium iodochromate ($KCrO_3I$) by reacting potassium chromate and hydroiodic acid, attempts to repeat his reaction have met with failure. Furthermore, the possible coexistence of chromium in the oxidation state +6 and iodide ion has been questioned[73,74] on the grounds of their oxidation-reduction potentials.

The preparation of potassium iodatochromate, $KCrO_3IO_3$, by reacting potassium dichromate and iodic acid in nitric acid, originally reported by Berg and Blomstrand,[75] has since been repeated[76] and the product subjected to an X-ray structural study[77] and a nuclear quadrupole resonance analysis.[78] Meyer and Statecznev[79] have also reported the preparation of the K^+, Na^+, NH_4^+ and Ba^{2+} salts of the trioxosulphatochromate(VI) ion, $CrO_3(SO_4)^{2-}$, and of the free acid, $H_2CrO_3(SO_4)$, by reactions carried out in the absence of water. A typical reaction involved leading SO_3 gas into a cooled suspension of the chromate salt in carbon disulphide and then cautiously warming to 60°C to remove excess SO_3 and CS_2, and drying between porous plates in vacuo for three days.

Finally, Sisler and coworkers[80,81] reported the preparation of a series of 1:1 ($CrO_3 \cdot L$) and 1:2 ($CrO_3 \cdot 2L$) compounds (where L is one molecule of a nitrogen carrying base) by adding chromium(VI) oxide to several anhydrous unhindered heterocyclic nitrogen bases. The 1:2 compounds were isolated for L = pyridine, β-picoline, γ-picoline, quinoline, 2,5-lutidine, 2-ethylpyridine and 4-methylpyridine. On the other hand, α-picoline, acridine and tribenzylamine formed only 1:1

adducts and required lower temperatures to avoid extensive oxidation-reduction reactions. It is believed that the $CrO_3.2L$ adducts formed have trigonal bipyramidal structure with the three oxo ligands forming the equatorial plane and that the predominant factor determining the formula for these addition compounds is steric. The alcohol analogs, $CrO_3.2ROH$, are also known.[82,83]

(ii) Spectroscopic Studies

In addition to the preparative studies, spectroscopic methods have also provided evidence for substituted chromates, at least in solution. For instance, the existence of the aforementioned sulphatochromate-(VI) ion, $CrO_3(SO_4)^{2-}$, along with the condensation copolymers $CrO_3.SO_3$, $H_2CrO_2(SO_4)_2$, $H_2Cr_4O_{13}$ and $H_2Cr_3SO_{13}$, was proposed from spectroscopic evidence obtained from studies of various $CrO_3 — H_2SO_4 — H_2O$ systems.[84]

It is also well known that in dilute aqueous solutions and aqueous acetic acid solutions, chromic acid oxidizes isopropyl alcohol to acetone. The oxidation of various alcohols in aqueous solutions have been extensively studied. Westheimer and coworkers [85] have advanced convincing arguments that these oxidations proceed via the formation of esters of chromic acid; e.g. $(CrO_3.OR)^-$. [86] Similar intermediates $(CrO_3.L)$ have been proposed for the oxidation of aldehydes.[87,88]

The mechanisms for the oxidation of non-metallic oxoanions, such as arsenite,[88] sulphite, phosphite and hydrophosphite,[89] have also been written with a chromium(VI) — oxoanion complex as an intermediate. The association of chromium(VI) species with complexes of other metals in aqueous solutions [90] has renewed interest in inorganic chromium(VI) oxidations.

For instance, the study of the oxidation of complexes of Ce(IV),[91] Fe(II),[92] Fe(III),[93] As(III),[88] Cr(III),[94] Np(IV), Th(IV) and Co(III)[95] suggests that the reaction occurs via the formation of a complex e.g.

$$M^{n+} + HCrO_4^- \rightleftharpoons (M\text{-}CrO_4)^{n-2} + H^+ \qquad [4]$$

The hypothesis is supported by the fact that the solid derivative, $[Cr(NH_3)_5OCrO_3]Cl$,[96] has been isolated, and more recently Coomber and Griffith,[97] reported the vibrational (IR and Raman) spectra of the pentammine and tetrammine cobalt(III) complexes, $[Co(NH_3)_5OCrO_3]Cl$ and $[Co(NH_3)_4O_2CrO_2]NO_3$, and showed that in these solids the chromato group functions as a monodentate and a bidentate ligand, respectively.

In all these aqueous preparations and spectrophotometric studies, the workers have had competing hydrolytic or protonation processes to contend with. Almost all substituted chromates are easily hydrolysed to the hydrogen chromate, e.g.

$$CrO_3Cl^- + H_2O \longrightarrow CrO_3(OH)^- + H^+ + Cl^- \qquad [5]$$

Because of this a few studies have been attempted in non-aqueous media. Klaning and Symons[98] studied the ultraviolet spectra of dilute solutions of ammonium dichromate, $(NH_4)_2Cr_2O_7$, in various "anhydrous" alcohols (ROH) to draw a relationship between the spectra and the σ^* (Tafts – σ^* function, a measure of the electron withdrawing power) of the group R.[99] From their observations, the authors claimed the identification of monosubstituted esters $CrO_3.OR^-$, in which R is alkyl, substituted alkyl or acyl, and the substitution reaction was represented by equation [6].

$$(NH_4)_2Cr_2O_7 + 2ROH \longrightarrow 2(NH_4)CrO_3OR + H_2O \qquad [6]$$

Although the study was intended to eliminate competing hydrolytic processes, the authors admitted that the equilibrium

$$CrO_3OR^- + H_2O \rightleftharpoons HCrO_4^- + ROH \qquad [7]$$

involving the $HCrO_4^-$ ion was probably unavoidable.

(iii) Bonding

The relation of tetrahedral ligands to the lobes of the metal p or d orbitals is such that none of the orbitals is lying directly along the metal-ligand bonds, but the hybrids sp^3 or sd^3 (specifically the d_{xy} d_{yz} and d_{xz}) do have the correct symmetry for σ-bonding.

Metal and Ligand Orbital Contributions In Tetrahedral Symmetry

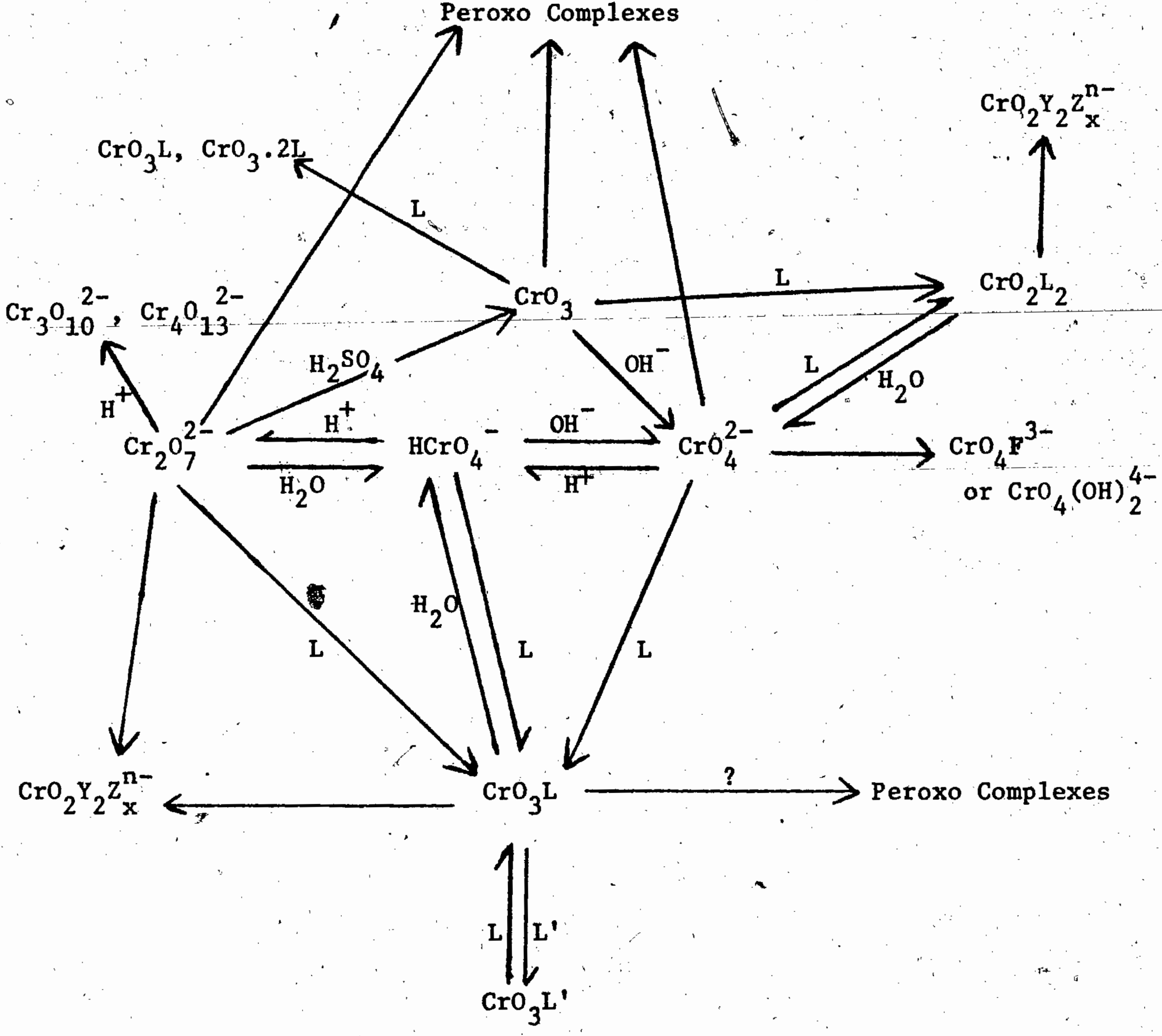
Irreducible Respresentation	Contributions	
	Metal	Ligand
a_1	s	s , pσ
e	$d(z^2, x^2-y^2)$	pπ
t_1	———	pπ
t_2	p(x,y,z), d(xy,xz,yz)	pσ, pπ

In the case of CrO_4^{2-} or CrO_3L^{n-} ions, the chromium $a_1(4s)$ and $t_2(3d_{xy,yz,xz})$ orbitals, which are extensively mixed with the $t_2(4p_x, p_y, p_z)$ orbitals, can take part in the formation of σ bonds; while the e - orbitals can only participate in π-bonding.

Summary

Chromic oxide is an acidic and very reactive species. Although it is more widely used as an oxidant in organic chemistry, formation of 1:1 and 1:2 adducts with certain donor molecules (or ions) and substitution - addition reactions, producing dioxochromium(VI) complexes, are relatively common. Of the dioxo compounds, the chemistry of CrO_2Cl_2 is probably the best studied.

The CrO_4^{2-} and $Cr_2O_7^{2-}$ ions have very extensive aqueous (also leading to peroxo complex) chemistry as far as subsititution and oxidation - reduction reactions are concerned. Unfortunately, however, there is very little information on the structure and bonding in the substituted Cr(VI) products. Of the trioxo complexes, $CrO_3(OH)^-$, CrO_3F^- and CrO_3Cl^- are the best known. The general reactions of the complexes are presented in Scheme 1.1 next page.



Where Y=Z and Y ≠ Z
and $x = n = 0,1$ or 2

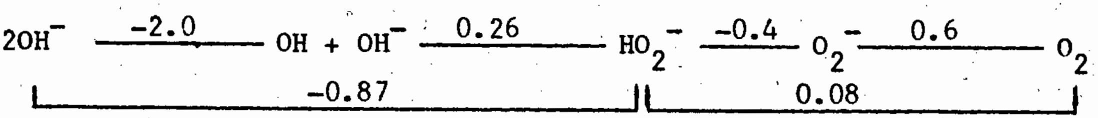
SCHEME 1.1

Reactions of Oxo Complexes of Chromium (VI)

I.3 PEROXO COMPLEXES OF CHROMIUM AND OTHER TRANSITION METALS

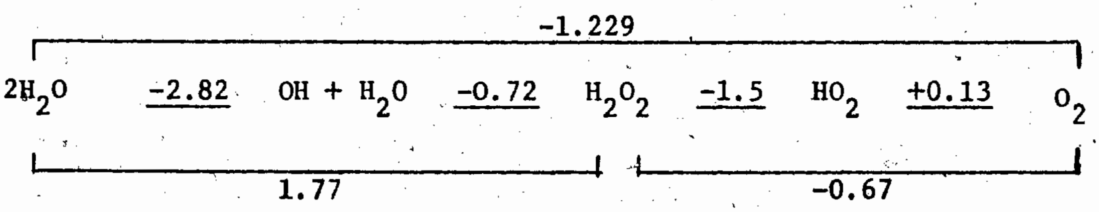
The process whereby transition metal compounds interact with an oxygenating agent, oxygen (O_2), ozone (O_3) or hydrogen peroxide (H_2O_2), to form derivatives in which one or more dioxygen groups (O_2, O_2^- or $O_2^=$) are coordinated to the metal has been known for over 150 years. The co-existence of a dioxygen ligand with other ligands around a central metal atom depends on the conditions (including medium) under which the compound is synthesized. In particular, it depends on the pH of the solution and the oxidation-reduction properties of the ions involved in the reaction.[100]

Basic Solution:



$$\underbrace{2OH^- \xrightarrow{-2.0} OH + OH^- \xrightarrow{0.26} HO_2^-}_{-0.87}\ \underbrace{\xrightarrow{-0.4} O_2^- \xrightarrow{0.6} O_2}_{0.08} \qquad [8a]$$

Acidic Solution:



$$\overbrace{\underbrace{2H_2O \xrightarrow{-2.82} OH + H_2O \xrightarrow{-0.72} H_2O_2}_{1.77}\ \underbrace{\xrightarrow{-1.5} HO_2 \xrightarrow{+0.13} O_2}_{-0.67}}^{-1.229} \qquad [8b]$$

The schemes above represent the redox potentials in volts for O_2 in basic [8a] and acidic [8b] solutions (at 25°C), respectively.[101]

The need to understand the chemistry of coordinated dioxygen species is inspired by the many instances in which they occur. Dioxygen functions both as a ligand and as a reagent in transition metal organometallic chemistry.[102] Because several organometallics initiate the polymerization of many unsaturated compounds in the presence of oxygen or peroxides, a lot of interest has developed in the synthesis, characterization and study of the properties of oxygen and peroxide carriers.[103-105] Dioxygen compounds of transition metals are also of particular importance in relation to metal-catalysed oxidation reactions. Although coordination does not necessarily activate the dioxygen species for reaction, the possibility of such activation, and therefore catalysis by this route, does exist. For instance, relatively fast reactions have been reported[106-108] to occur between certain dioxygen compounds of Group VIII metals and molecular species such as gaseous non-metallic oxides (CO, SO_2, NO, NO_2, CO_2), CS_2, aldehydes, ketones, oxime, and thiourea. These reactions not only represent new avenues for the synthesis of an extended range of compounds but also hope for catalysing the oxygenation of other substrates under ambient conditions.[109-111] Finally, because of the similarity between these reactions and the direct oxygenation of biological substrates (by non-radical pathways) by the metalloenzyme, oxygenase, the coordination chemistry of dioxygen species appear to be a promising model for an understanding of the storage and use of oxygen in biological systems.

The term dioxygen has been used in the preceeding paragraphs to draw attention to the fact that, depending on the electronic environment of the central metal, the dioxygen species, O_2^{n-} for $n = 0$, 1, or 2, on coordination experiences dramatic changes in its electronic structure and therefore the O-O bond length, such that the formal charge on the complexed dioxygen species is frequently different from that in the free ligand. These changes are particularly noticeable in the dioxygen complexes of the low valent Group VIII metals (Fe, Ru, Os, Co, Rh, Ir, Ni, Pd and Pt).[111]

Table 1.1. Formal Charge on the Dioxygen Species:

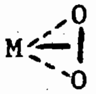
Compound	O-O bond length (A°)	Comparable O_2^{n-} species[d] and their bond lengths (A°)
—	—	O_2 (1.2107 ± 0.0001)
$Ir(O_2)(Cl)(CO)(Ph_3P)_2$	1.30 ± 0.03[a]	O_2^- (1.28 ± 0.02)
$Ir(O_2)(I)(CO)(Ph_3P)_2$	1.509 ± 0.026[b]	O_2^{2-} (1.49 ± 0.01)
$[Ir(O_2)(diphos)_2][PF_6]$	1.625 ± 0.023[c]	—

a. Ref. 112, b. Ref. 113, c. Ref. 114, d. Ref. 115.

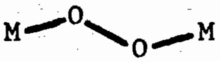
On this basis, it is not certain whether the rigid demarcation in bonding schemes that has been created between molecular oxygen complexes and those of peroxo complexes, based on the difference in the oxidation states of the metal atom, should be allowed to continue. A Löwden and Mulliken populations analysis by Dacre and Elder[116] has shown that each O_2 group in $Cr(O_2)_4^{3-}$ carries a negative charge of only ca. 0.6 electrons while the chromium, far from carrying a charge of +5, is found to be fractionally negatively charged. Furthermore, results from ESCA (electron spectroscopy for chemical analysis) study indicates that from 1.4 to 1.8 electrons are transferred from the metal to the dioxygen ligand in $Pt(O_2)(PPh_3)_2$.[117] It is apparent then that adopting the same basic chemical attitude, including bonding scheme, for both molecular oxygen- and peroxo-complexes would clear-up some of the confusion characterizing this subject.

The compounds studied in this work were all prepared by treating solutions of various chromium(VI) complexes with hydrogen peroxide. Considering the vast amount of literature in the field, it is necessary that the discussion be limited to the dioxygen carrying products of the reaction between H_2O_2 and metals of the early transition series. Because the O-O bond lengths in these complexes are generally around 1.4 — 1.5 A^o, the complexes will be called "peroxo" for the purpose of maintaining uniformity with other papers although IUPAC recommended[118] the use of the nomenclature "peroxido-".

Most transition metal peroxo complexes are unstable, both as solids and (especially) in aqueoues solution. Although a majority of these complexes involve "laterally" coordinated peroxide groups, a few are known in



lateral bonding

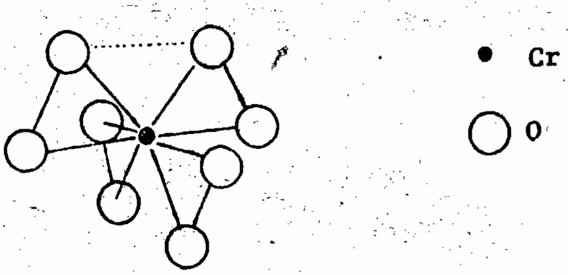


bridging

which the peroxide functions as a bridging ligand or is present as a hydroperoxide (OOH^-) group; and occasionally it is present as the hydrogen peroxide of crystallization.[119,120] Several solid peroxides have been isolated. The use of ion exchangers, electrolytic conductivities, potentiometric titrations and several spectroscopic techniques, including Job's method of continuous variations, to derive the chemical composition of these peroxo species, and especially those present when metal ions are in contact with aqueous hydrogen peroxide, has contributed little toward establishing their formula and structure. This problem is particularly acute in derivatives of molybdenum and tungsten which are less well-defined as a result of the uncertainty in the extent of polymerization in acid solutions,[121] and expecially when varying amounts of hydrogen peroxide (H_2O_2 reduces polymerization) are present. The anionic species obtained by treating acidic molybdates or tungstates with H_2O_2 have variously been given the formulae such as $M_2O_8^{2-}$,[122] $M_2O_9^{2-}$,[123] $HMoO_6$ or $M_2O_{11}^{2-}$.[124]

(a) Unsubstituted Peroxo Complexes: $M(O_2)_4^{n-}$

The NH_4^+ and K^+ salts containing the unsubstituted peroxo anion $M(O_2)_4^{3-}$ are known for M = Cr, V, Nb and Ta.[125] The "red" chromium salt, previously formulated[126-128] as $Cr_2O_{12}^{6-}$, $Cr_2O_{13}^{6-}$, $Cr_2O_{15}^{6-}$, $(Cr_2O_{16}\cdot H_2O)^{6-}$ and now known to contain the mononuclear ion $Cr^V(O_2)_4^{3-}$, is prepared by reacting hydrogen peroxide and a dichromate in strongly alkaline solutions, below 0°C. Structural studies on this compound[129] have shown that the peroxo groups are coordinated laterally and the eight atoms of oxygen are in a dodecahedral (D_{2d}) geometrical arrangement around the Cr — four being at distances of 1.846 A° and the other four at 1.944 A°. The bond length between two oxygen atoms



coordinated as peroxides is 1.405 A°, while the shortest distance between oxygens not belonging to the same peroxide ions, are 2.91, 2.57, 2.75 and 2.74 A°. The magnetic moment of 1.77 BM, corresponding to one unpaired electron, indicates that the chromium is in the +5 oxidation state.

A comparison of the X-ray powder photographs[130] of other

$M(O_2)_4^{3-}$ ions suggest that the tetraperoxovanadate anion, $V(O_2)_4^{3-}$, is isomorphic with the tetraperoxometallates $M(O_2)_4^{3-}$ for M = Cr, Nb and Ta. This has been confirmed by structural studies on $(NH_4)_3V(O_2)_4$ [131] and $KMg[Nb(O_2)_4].7H_2O$ [132] which reportedly have quasidodecahedral structures similar to that of $K_3[Cr(O_2)_4]$.

Another group of salts containing the tetraperoxo anion, $M(O_2)_4^{2-}$ for M = Cr, Mo and W, has also been reported.[133] Salts of the cations Na^+, K^+, Ca^{++}, Sr^{++}, Ba^{++}, Co^{++} and $Zn(NH_3)_4^{++}$ were prepared by reacting, under very low temperatures, alkaline solutions of the metallates with excess hydrogen peroxide. The molybdenum(VI) and tungsten(VI) tetraperoxo species are chemically stable while the chromium(VI) derivative is highly explosive.

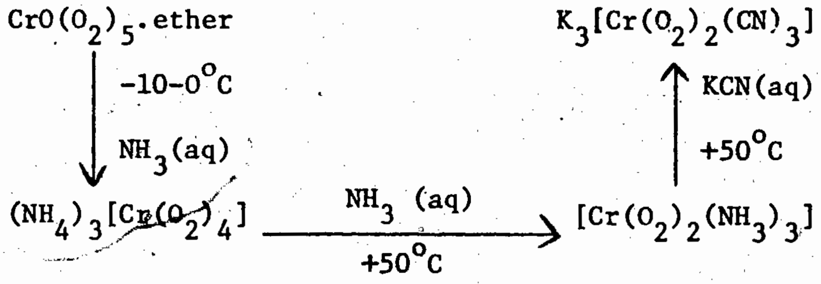
(b) Oxoperoxo Complexes: $M(O_2)_2(O)_y$ and $M(O_2)_x(O)_yL_z$

In addition to the tetraperoxometallates, treating solutions of transition metal salts with various amounts of hydrogen peroxide, and under different conditions of pH and temperature,[129,134,135] produces other complexes in which the ratio of the metal to peroxide varies. For instance, in the series of complexes $V(O_2)_4^{3-}$, $VO(O_2)_3^{3-}$ (or $H_nVO(O_2)_3^{-3+n}$), $VO(O_2)_2^-$ [or $H_nV(O)_2(O_2)_2^{-3+n}$ and polymers like $H_nV_2(O)_3(O_2)_4^{-4+n}$] and $VO(O_2)^+$, the vanadium-to-peroxide ratio varies from 1:4, 1:3, 1:2 to 1:1, respectively.[119] Similar, though not necessarily identical, series of complexes have also been noted for Nb, Ta, Cr, Mo, W and U.[119]

The triperoxo species are relatively uncommon, and where they have been observed (Mo and W) efforts to characterize them have failed.

Although no triperoxochromium compound has yet been isolated,[136] a triperoxouranium(VI) complex exists,[137] and recently structural studies have established the existence of and a dodecahedral geometry in the triperoxoniobate(V) compounds $K[Nb(O_2)_3\cdot phen].3H_2O$ and $K[Nb(O_2)_3\cdot phen].3H_2O.H_2O_2$.[138] The triperoxovanadates are believed[139] to have eight coordination of the metal similar to that observed in the peroxoniobate(V) compounds.

Except for the adducts $Cr^{IV}(O_2)_2.3L$, almost all other chromium diperoxides exist as oxodiperoxides. The chromium diperoxide moiety resembles the tetraperoxo salts, in that it has all its oxygens in peroxo ligands. The triamminochromium diperoxide complex $Cr(O_2)_2(NH_3)_3$ was first prepared in 1897.[140] It exists as a monomer[141] and appears to be the most stable of the peroxochromates, though the coordinated ammonia group can be replaced by cyanide and ethylenediamine. For instance, $K_3[Cr(O_2)_2(CN)_3]$[142] is obtained as a red and rather stable compound when $Cr(O_2)_2(NH_3)_3$ is treated with warm potassium cyanide.



[8]

The olive-green ethylenediamine derivative $[(C_2H_8N_2)Cr(O_2)_2.H_2O].H_2O$ is also known.[143] Structural investigations on the compounds $Cr(O_2)_2(NH_3)_3$,[144] $[Cr(O_2)_2(H_2O)(C_2H_8N_2)].H_2O$[145] and $K_3[Cr(O_2)_2(CN)_3]$[146] have been reported.

The most familiar peroxo compound belonging to this class is the blue perchromic acid formed by the reaction of acidic solutions of chromates (or dichromates) with H_2O_2. The controversy over its composition started when Wiede[147] first isolated a compound which he formulated as M^IHCrO_7. Other workers[148-150] supported the formula. The final formula $CrO(O_2)_2.L$ was not, however, resolved until the works of Evans,[151] Glasner and Stainberg,[152] and Tuck and Walters.[12] The compound $CrO(O_2)_2.H_2O$ is very unstable in water but can be extracted into organic solvents such as ethers, alcohols, ketones, and nitriles, where it is more stable. The species formed by such solvation could be $CrO(O_2)_2.H_2O\leftarrow:L$ or, alternatively, one formed by the complete substitution of the water molecule by the donor solvent (L) to give $CrO(O_2)_2.L$. It is also known that perchromic acid can react with nitrogenous organic bases such as pyridine (py),[153] 2,2'-bipyridyl (bipy),[140] 1,10-phenanthroline (phen),[151] aniline and quinoline,[154] the compounds so formed being relatively stable solids. The dimethyl ether adduct, $CrO(O_2)_2.O(CH_3)_2$, which is stable below -50°C explodes above -30°C.[155] The three stable adducts $CrO(O_2)_2.L$ for L = pyridine, 2,2'-bipyridyl and 1,10-phenanthroline, have low electrolytic conductivities and small magnetic moments (0.4 to 0.9 BM).[130] The small moments indicate the absence of a "spin" component and are probably due to the temperature independent paramagnetism.

The crystal structures of the compounds $[CrO(O_2)_2.py]$,[156] $[CrO(O_2)_2.bipy]$[157] and $[CrO(O_2)_2.phen]$[158] have been determined and shown to bear close resemblences to oxodiperoxo adducts of other early transition metals. For instance, the mononuclear oxodiperoxoamminovanadate(V) complex $NH_4[VO(O_2)_2NH_3]$ is shown to have a distorted pentagonal pyramidal geometry analogous to that of the oxodiperoxopyridinochromium(VI) complex. In addition to the infrared and Raman spectral studies of Griffith and Wickins,[120] an X-ray structural study reported on the polynuclear anions $[M_2(O)_2(O_2)_4(\mu O)(H_2O_2]^{2-}$ for M = Mo(VI)[159] and W(VI)[160] showed that the two complexes and $[(O)(O_2)_2Mo^{IV}(\mu(OOH)_2)Mo^{IV}(O_2)_2(O)]^{2-}$ have pentagonal bipyramidal coordination with two peroxo groups and a bridging atom forming the pentagonal plane.

(c) Substituted Anionic Peroxo and Oxoperoxo Complexes

(i) Other Transition Metals

Elements of the Periodic Group IVA, VA and VIA also form substituted peroxo complexes. The most stable species of this type are usually anionic and involve other electronegative ligands such as oxides, chlorides, hydroxide, fluoride, sulphate or carboxylate. Chromium is known to form substituted peroxo (or oxoperoxo) complexes with only the first three. However, some of the best characterized peroxo complexes of early transition metals include peroxo-oxalates and peroxocarboxylates. The oxalate ion, particularly, is interesting because, like the peroxide it is compact and each ion generally occupies two adjacent coordination sites in a complex. So that the coordination number of the central metal is the same in the peroxo-oxalato (or oxoperoxo-oxalato) as it is in the unsubstituted peroxo (or oxoperoxo) complex of the same ligand-to-metal stoichiometry. Griffith[161] and Griffith and Wickins[120,162] have studied the peroxo-oxalates $[MO(O_2)_2Ox]^{2-}$ (M = W, Mo); $[M(O)_2(O_2)(Ox)(H_2O)]^{2-}$ (M = Mo, W, U), $[M(O_2)(Ox)_3]^{3-}$ (M = Nb, Ta) and $[M(O_2)(Ox)_2(H_2O)]^{2-}$ (M = Ti, Zr) by means of infrared and Raman spectroscopy on the solids and concluded that the oxalato ligands were bidentate.[163,164] The crystal structure of the compound $(NH_4)_3[Nb(O_2)_2(Ox)_2].H_2O$,[132] originally formulated as $(NH_4)_3[Nb(O_2)(Ox)_3]$[162] supports this conclusion and further shows that, like the $Nb(O_2)_4^{3-}$, the complex exhibits a dodecahedral coordination geometry around the niobium.

Although no monoperoxo or cationic peroxo complexes of chromium are known, recently the X-ray crystal structure of two monoperoxocarboxylatometallates, $[(O)(Ti(O_2)(H_2O)(C_5H_3N(COO)_2))_2]^{2-}$[166] and $[V(O)(O_2)(H_2O) -$

$(C_5H_3N(COO)_2)]^-.xH_2O(x=1.3)$[165] have been reported, and the coordination geometry around each metal in the chelated complex shown to be that of a distorted pentagonal bipyramid. It is argued[166] that in the non-chelated form these complexes could be assumed to have the composition $[V(O)(O_2).4H_2O]^+$ and $[Ti(O_2).4H_2O]_2O^{2+}$, respectively. The possible existence of such species is further supported by spectroscopic, conductrimetic and pH studies of weakly acid solution of vanadium(V)[167] and titanium(IV)[166] salts treated with hydrogen peroxide.

Some low molecular symmetry peroxo-fluorometallates have also been characterized. The first peroxofluorides of both molybdenum and tungsten were prepared in 1892 by Piccini[168] who isolated them either by dissolving the oxofluorometallates (Mo or W) in warm hydrogen peroxide, or by treating the solution of the molybdate or tungstate in diluted hydrofluoric acid with hydrogen peroxide. These reactions have since been repeated and/or modified and the following complexes isolated [120,160,162,169]

$[M(O_2)F_5]^{n-}$ for M(IV) = Ti and Zr, M(V) = Nb and Ta; $[M(O)(O_2)F_4]^{2-}$ for M(VI) = Mo or W; and $[Mo(O)(O_2)_2F_2]^{2-}$. The last three complexes $[M(O)(O_2)_2F_4]^{2-}$ and $[Mo(O)(O_2)_2F_2]^{2-}$ have also been made by the action of H_2O_2 on the salt carrying the corresponding $[M(O)_2F_4]^{2-}$ anion. The X-ray crystal structure[170] of $K_2[Mo(O)(O_2)F_4].H_2O$ has been published. Griffith and Wickins[120] have also reported the infrared spectra of the oxoperoxotetrachloromolybdate(VI) complex $Cs_2[MoO(O_2)Cl_4]$ and the peroxodisulphatotitanium(IV) complex $[Ti(O_2)(SO_4)_2]^{2-}$. The relatively small number of chloroperoxo and sulphatoperoxo compared to oxalato- or fluoroperoxo complexes probably reflectes the relative instability of these ligands to oxidation by hydrogen peroxide.

$$E^{\circ}(2X^- = X_2 + 2e^-) \text{ volts}, \qquad X = Cl(1.36) \text{ and } F(2.87)$$

(ii) Substituted Anionic Oxoperoxochromium(VI) Complexes

The anionic oxodiperoxochromium(VI) complexes $CrO(O_2)_2L$ resemble the neutral adducts $CrO(O_2)_2.L$ in every aspect except that the former species generally occurs with small univalent anion in the place of the organic donor group.

In 1904, Hofmann and Hindlemaier[171] isolated blue-violet salts, which they formulated as $HCrO_6$, from the reaction of the neutral or very slightly acidic solutions of the corresponding dichromates with H_2O_2. Wiede[147] obtained relatively purer compounds by reacting perchromic acid ($CrO(O_2)_2.H_2O$) solutions with potassium cyanide or hydroxide. Years later, magnetic susceptibility measurements[172] demonstrated that the potassium salt, originally formulated as $KCrO_6$ or $K_2Cr_2O_{12}$, was very feebly paramagnetic. The molar conductivity of the ammonium salt (≈110 ohm^{-1} cm^2, in H_2O or MeOH)[127] showed conclusively that ~~the~~ compound was a 1:1 electrolyte. More recently, Griffith[150] showed that the violet perchromate, obtained by treating an anhydrous ethereal solution of $CrO(O_2)_2.H_2O$ with a deficiency of ethanolic potassium hydroxide solution at -10°C, contained two peroxo groups per chromium. On the basis of these data, infrared spectra, elemental analysis, and molecular weight measurements, the formula $K[CrO(O_2)_2(OH)]$ was suggested for the potassium salt. This formulation was also supported by the observation[20] that aqueous acid solutions convert the anion into perchromic acid.

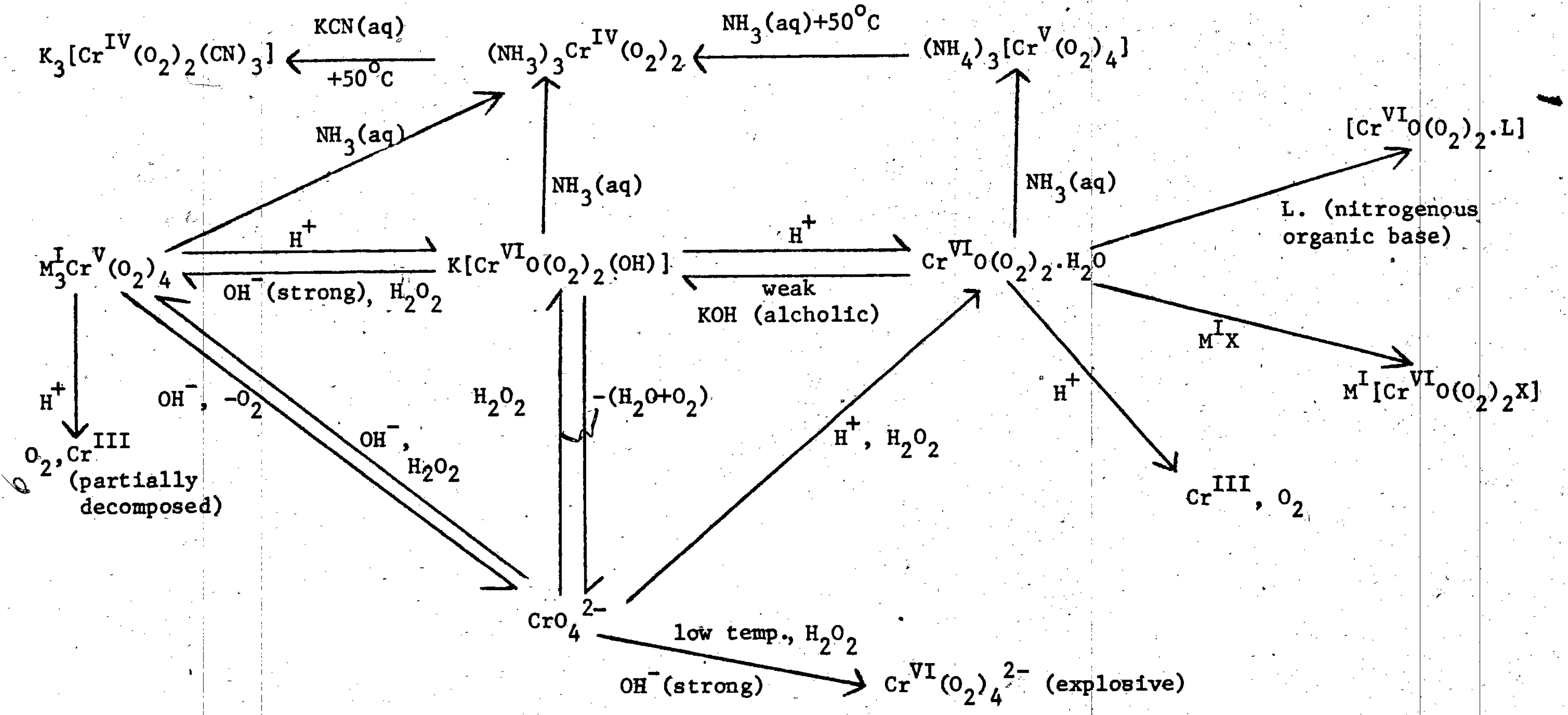
$$CrO(O_2)_2OH^- + H^+ \longrightarrow CrO(O_2)_2.H_2O \qquad [9]$$

The only other related anionic chromium(VI) peroxo species has been characterized and reported by Tuck and Faithful.[19] The royal blue anionic chlorodiperoxochromium(VI) complex $CrO(O_2)_2Cl^-$ was prepared by treating the tetraphenylarsonium chlorochromate, Ph_4AsCrO_3Cl, dissolved in ethyl acetate solution, with ice cold 30 percent hydrogen peroxide. The molar conductivity (97 ohm^{-1} cm^{2}) in nitromethane shows that this compound too is a 1:1 electrolyte. The infrared spectra of the $CrO(O_2)_2Cl^-$ species showed a band at 430 cm^{-1} assignable to Cr-Cl stretch and two strong higher frequency vibrations (950 cm^{-1} and 940 cm^{-1}), one of which must be due to the Cr=O mode. The molecular formula $Ph_4AsCrO(O_2)_2Cl$ was also supported by chemical analysis.

Although the structural data on these anionic species are scarce, an attempt will be made, in a later section, to discuss the possible mode of bonding of the peroxo group in the complex, $CrO(O_2)_2L^{n-}$.

Summary

It is obvious from preceeding accounts that the preparations and/or decompositions of chromium peroxo complexes are interelated[119] in the particularly interesting way shown by the scheme on the next page. It shows that the blue perchromic acid, $Cr^{VI}O(O_2)_2.H_2O$, is formed when H_2O_2 is added to acidified solutions of CrO_4^{2-} or $Cr_2O_7^{2-}$; while in strongly alkaline solutions the stable peroxo compound is $M_3^ICr(O_2)_4$, a derivative of chromium(V). The chromium(V) compound decomposes in alkaline solution to CrO_4^{2-} while it is only in acidic solutions that the blue chromium(VI) species undergo the complex reduction to Cr(III). Treating $CrO(O_2)_2.H_2O$ with donor molecules or ions yields the substituted derivatives, $CrO(O_2)_2.L$, and reacting the peroxochromates with NH_3, CN^- or aqueous ethylenediamine gives the Cr(IV) species, $Cr(O_2)_2L_3$. From these accounts it is probable that protonation or ligand basicity plays an important part in the oxidation-reduction relationships amongst these compounds.



S C H E M E 1.2

Reactions of Peroxo Complexes of Chromium.

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CHAPTER TWO

PREPARATION AND CHARACTERIZATION OF SUBSTITUTED ANIONIC TRIOXO CHROMIUM(VI) COMPLEXES

II.I INTRODUCTION

The accounts in Chapter I show that, except for the much earlier work involving the isolation of the halochromates, CrO_3L^- (for $L^- = F^-$ or Cl^-), sulphatochromate, $CrO_3(SO_4)^{2-}$, and the iodatochromate, $CrO_3IO_3^-$, and the growing interest in the association of chromium(VI) with various anionic, cationic and organic molecular species, no new anionic monosubstituted chromates seem to have been isolated and identified since the early 1920's. Attempts to prepare pseudohalogenochromates from aqueous solutions probably failed because these substrates are readily oxidised by chromium(VI). For instance, in acidic solutions, I^- and NCS^- ions have been shown to be readily oxidised by chromium(VI) to iodine (I_2)[1] and thiocyanogen $(SCN)_2$,[2] respectively.

The present work was aimed, therefore, at avoiding the complicating hydrolytic side reactions often involved in aqueous studies by working exclusively in non-aqueous media. Metathetical methods were used to prepare the new compounds, and, whenever possible, attempts were made to investigate the solution and solid state bonding interactions between the chromium and the ligands, O^{2-} and L^{n-}. In this attempt only one of the four ligands was varied such that the electronic properties of the fourth ligand, L, for $L^{n-} = F^-$, Cl^-, Br^-, NCO^-, NCS^-, NNN^-, NO_3^-, $CH_3CO_2^-$, $C_2O_4^{2-}$, NO_2^-, and IO_3^-, scan a large sector of the inductive drift of bonding electrons by either σ- or π-bonding.

II.2 EXPERIMENTAL

(a) Apparatus and Materials.

Preparative work was generally carried out in an acetone bath whose temperature was maintained by a Stir Kool Model SK 12 (Thermoelectronic Unlimited Inc.).

The infrared spectra in the region 200—4000 cm^{-1} were obtained at room temperature on a Beckman IR 12 double-beam grating spectrophotometer or a Perkin-Elmer 457 instrument. Solid samples were studied in the form of KBr discs or as Nujol mulls deposited on CsI windows. There was no apparent reductive reaction. Reproducibilities of ±2 cm^{-1} were obtained.

The Raman spectra of the solids and/or solutions in dimethylsulphoxide (DMSO) were obtained on the Cary model 81 Laser-Raman spectrophotometer with 60mW Spectra Physics model 125 He/NE laser excitation. The samples were contained in capillary tubes. Preproducibilities of ±1 cm^{-1} were obtained.

The UV-visible spectra were recorded on the Cary 14 and sometimes on the Unicam SP 800 spectrophotometer, using 0.1 or 1.0 cm cells. The C, H and N analyses were performed in the department on a microanalyser. The CrO_3L^{n-} compounds were found by, magnetic measurements, to be diamagnetic.

Tetraphenylarsonium chloride hydrate was obtained from the Aldrich Chemical Company. Potassium dichromate, silver cyanate, silver nitrate, silver oxalate, sodium oxalate, tetraethylammonium perchlorate, cesium chloride, sodium azide, cesium bromide and ammonium thiocyanate were used without further purification. Reagent grade tetraethylammonium halides, Et_4NF and Et_4NCl, supplied by Eastman Kodak, were recrystallized in vacuo from absolute EtOH, and stored over phosphorus pentoxide. The chlorine content, determined by precipitation as AgCl, was 11.2% (Et_4NCl requires 11.5% Cl). Analysis of the fluoride, using the Orion Specific Ion Activity Electrodes, gave a low figure - 11.6% F, found (Et_4NF requires 12.8% F). Reagent grade acids H_2SO_4, HNO_3, HCl, HF and HIO_3 were used as supplied, but the HBr was first shaken with 5% tri-n-butyl phosphate in chloroform, to remove any traces of free bromine or HBr_3 before use.[3]

Reagent grade acetonitrile (CH_3CN or MeCN) was distilled twice from P_2O_5 before use. The other solvents, carbon tetrachloride, methylene dichloride, benzene, hexane, cyclohexane and chloroform were redistilled reagent grade solvents kept dry using molecular sieves. The DMSO was distilled three times from calcium hydride. The water content of the purified DMSO was shown by gas-liquid chromotography to be ≃ 0.03% by weight.

The chromium contents were determined by atomic absorption technique or by iodometric titration. In the latter method the chromium was first reduced to Cr(III) by bubbling SO_2 through the aqueous alkaline solution of the complex. After the reduction was complete the solution was acidified with 2M H_2SO_4 and boiled to expel any excess SO_2; $K_2S_2O_8$ was then added to the solution and boiled further to oxidise the chromium back to Cr(VI) and standard iodometric ti[illegible]ion procedures followed.

(b) Syntheses of Monosubstituted Chromates

(i) Trioxochloro- and Trioxofluorochromate Anions, CrO_3Cl^- and CrO_3F^-.

Potassium and Cesium Salts:

The potassium salts of trioxochloro- and trioxofluorochromates, CrO_3Cl^- and CrO_3F^-, were prepared and preserved in the manner described on page 10. The cesium salt, $CsCrO_3Cl$, was prepared for spectroscopic purposes by treating stoichiometric amounts of CsCl and CrO_3, dissolved in minimum amounts of water, with 3M HCl; yellow crystals eventually formed.

$$CsCl + CrO_3 + HCl\ (3M) \longrightarrow CsCrO_3Cl \qquad [1]$$

Analysis for Cl in $CsCrO_3Cl$ gave 13.3% compared to 13.4% (theoretical).

Tetraphenylarsonium Salts:

The tetraphenylarsonium chlorochromate was prepared either by the method of Tuck and Faithful[4] or by cation exchange in dry redistilled acetonitrile. The latter route was found to be less extravagant, fast and a more convenient way of producing Ph_4AsCrO_3Cl. On treating a dilute solution of $Ph_4AsCl.xH_2O$ in MeCN with stoichiometric amounts of $KCrO_3Cl$, also dissolved in MeCN, a white crystalline precipitate of KCl is formed immediately.

$$KCrO_3Cl + Ph_4AsCl \longrightarrow Ph_4AsCrO_3Cl + KCl \qquad [2]$$

Crystalline Ph_4AsCrO_3Cl can be isolated by adding 1:1 benzene-hexane (or CCl_4) solution to the filtrate.

To obtain tetraphenylarsonium fluorochromate, an aqueous solution of Ph_4AsNO_3 was first isolated by reacting the corresponding chloride with silver nitrate.

$$Ph_4AsCl + AgNO_3 \longrightarrow Ph_4AsNO_3 + AgCl \qquad [3]$$

Treating the aqueous nitrate solution with a solution of $K_2Cr_2O_7$ in 2M HF yields a yellow precipitate.

$$2Ph_4AsNO_3 + K_2Cr_2O_7 + 2HF \longrightarrow 2Ph_4AsCrO_3F + 2KNO_3 + H_2O \qquad [4]$$

The yellow precipitate was filtered, redissolved in a 1:1 chloroform - acetone mixture and reprecipitated with low boiling petroleum ether.

Analysis (%), calculated for Ph_4AsCrO_3F: C, 57.4; H, 4.0; As, 14.9; Cr, 10.4; F, 3.5. Found: C, 57.2; H, 4.1; As, 14.9; Cr, 10.3 and F, 3.5.

(ii) Trioxocyanatochromate Anion, CrO_3NCO^-.

Potassium Salt.

Potassium chlorochromate (0.286 gm) was dissolved in 10 ml of dry redistilled MeCN. To the solution a suspension of AgNCO (0.246 gm) in MeCN was added dropwise with stirring. After 5 to 10 minutes stirring at 25 °C, a fluffy white precipitate formed in a strongly orange-yellow solution.

$$KCrO_3Cl + AgNCO \longrightarrow KCrO_3(NCO) + AgCl \qquad [5]$$

The precipitate, containing AgCl (found 0.0579 gm Cl compared to 0.0582 gm expected), was filtered off and the $KCrO_3(NCO)$ recrystallized from MeCN solution either by adding dry CCl_4 or 1:1 CH_2Cl_2-petroleum ether, and washing with low boiling petroleum ether.

Analysis (%), calculated for $KCrO_3(NCO)$: Cr, 28.7; C, 6.6; N, 7.7. Found: Cr, 28.6; C, 6.6 and N, 7.5.

Tetraphenylarsonium and Cesium Salts.

The tetraphenylarsonium salt, $Ph_4AsCrO_3(NCO)$, and the cesium salt, $CsCrO_3(NCO)$, were prepared by treating the corresponding chlorochromates with AgNCO in MeCN and adding ice-cold 1:2 benzene-hexane mixture to the filtrate.

Analysis (%), calculated for $CsCrO_3(NCO)$: Cr, 18.9; C, 4.4; N, 5.1. Found: Cr, 18.7; C, 4.7 and N, 4.9.

(iii) Tetraphenylarsonium trioxoazidochromate, $Ph_4AsCrO_3N_3$.

Ph_4AsCrO_3Cl (2.498 gm) dissolved in redistilled MeCN was treated with a cold (-10°C) solution of NaN_3 (0.316 gm) also in MeCN. After 1 hr stirring, a white crystalline precipitate formed in the yellow solution.

$$Ph_4AsCrO_3Cl + NaN_3 \longrightarrow Ph_4AsCrO_3N_3 + NaCl \qquad [6]$$

The precipitate, NaCl, was filtered off and the solution treated with an ice-cold 1:2 benzene-hexane mixture to isolate the product.

Analysis (%), calculated for $Ph_4AsCrO_3N_3$: Cr, 9.9; C, 54.8; H, 3.8; N, 8.0. Found: Cr, 10.1; C, 54.8; H, 3.9 and N, 7.7.

(iv) Trioxothiocyanatochromate Anion, $CrO_3(NCS)^-$.

Tetraphenylarsonium Salt.

The $Ph_4AsCrO_3(NCS)$ complex was prepared from Ph_4AsCrO_3Cl (0.352 gm) and NH_4NCS (0.052 gm) in a way similar to that of $Ph_4AsCrO_3N_3$; except that here the reaction is slower (2 hr allowed for reaction time) and the product less stable.

$$Ph_4AsCrO_3Cl + NH_4NCS \longrightarrow Ph_4AsCrO_3(NCS) + NH_4Cl \qquad [7]$$

The solid NH_4Cl was filtered off in the dry box and in the dark; the $Ph_4AsCrO_3(NCS)$ complex was obtained in the solid state by pumping off the MeCN on a vacuum line.

Analysis (%), calculated for $Ph_4AsCrO_3(NCS)$: Cr, 9.6; C, 55.5; N, 2.6; H, 3.7. Found: Cr, 9.8; C, 55.8; N, 2.6 and H, 3.8.

Potassium and Cesium Salts.

Treating a cold (-10°C) $KCrO_3Cl$ or $CsCrO_3Cl$ solution (in MeCN) with NH_4NCS also in MeCN produces white crystals, NH_4Cl, and a yellow solution containing the $CrO_3(NCS)^-$ anion.

$$CrO_3Cl^- + NH_4NCS \longrightarrow CrO_3(NCS)^- + NH_4Cl \qquad [8]$$

The NH_4Cl is filtered off under N_2 or vacuum and the $KCrO_3(NCS)$ or $CsCrO_3(NCS)$

can be precipitated by adding ice-cold benzene to the MeCN solution. A flaky yellow powder was formed. Unfortunately, both compounds decompose, sometimes exposively (especially when heated), and are also easily hydrolysed. The hydrolysis/decomposition reaction is so fast that the weight of the sample changes appreciably during the time it takes to make a weighing. Exhaustive efforts to obtain the infrared spectra (in KBr or nujol) of the freshly prepared compounds were abortive.

Analysis (%), calculated for $KCrO_3(NCS)$: Cr, 26.4; C, 6.1; N, 7.1. Found: Cr, 24.5 (28.8); C, 7.9 and N, 9.3.

The yellow compounds, $KCrO_3(NCS)$, dissolves in water giving a yellow solution which slowly turns brownish-green. When 2M H_2SO_4 is added to the aqueous solution, it immediately turns completely green — a Cr(III) complex.

(v) Trioxonitratochromate Anion, $CrO_3NO_3^-$.

Tetraphenylarsonium Salt.

Ph_4AsCrO_3Cl (0.296 gm) was dissolved in MeCN and treated in the dark with $AgNO_3$ (0.097 gm) also in MeCN. The AgCl precipitate (found, 0.0820 gm Cl compared to 0.0823 gm expected) was immediately filtered off under nitrogen and the filtrate pumped in the dark on the vacuum line. It was noticed that the compound decomposed slowly under light and more readily when in contact with moisture or easily oxidisable organic solvents.

Analysis (%), calculated for $Ph_4AsCrO_3NO_3$: Cr, 9.6; C, 52.7; H, 3.7; N, 2.6. Found: C, 51.7 (51.5, 51.4) H, 3.4(3.3, 3.6); N, 2.8 (2.5, 2.4) and Cr, 9.0.

Tetraethylammonium Salt.

When $KCrO_3Cl$ (0.826 gm) in MeCN was treated with a solution of tetraethylammonium perchlorate (1.090 gm), a white precipitate of $KClO_4$

forms in a yellow solution of $\mathrm{Et_4NCrO_3Cl}$. Filtering the white precipitate off and treating the yellow solution with $\mathrm{AgNO_3}$ (0.805 gm) dissolved in MeCN causes AgCl to precipitate out. The $\mathrm{Et_4NCrO_3NO_3}$ solution was then pumped on the vacuum line. This leaves a dark orange light- and moisture-sensitive oil.

$$\begin{tikzcd}
\mathrm{KCrO_3Cl} + \mathrm{Et_4NClO_4} \arrow[r, "-10^\circ C"] & \mathrm{Et_4NCrO_3Cl} + \mathrm{KClO_4} \arrow[d, "\begin{array}{l}\mathrm{AgNO_3}\\ -10^\circ C\end{array}"] \\
 & \mathrm{Et_4NCrO_3NO_3} + \mathrm{AgCl}
\end{tikzcd} \qquad [9]$$

Analysis (%), calculated for $\mathrm{Et_4NCrO_3NO_3}$: Cr, 17.8; C, 32.9; H, 6.8; N, 9.6. Found: Cr, 18.0; C, 32.2; H, 6.8 and N, 8.2.

Attempts to precipitate $\mathrm{Et_4NCrO_3NO_3}$ or $\mathrm{Ph_4AsCrO_3NO_3}$ from the MeCN solution by adding $\mathrm{CHCl_3}$, $\mathrm{CH_2Cl_2}$ or benzene resulted in decomposition.

(vi) Trioxobromochromate Anion, $\mathrm{CrO_3Br^-}$.

Tetraphenylarsonium Salt.

$\mathrm{Ph_4AsCrO_3Br}$ is prepared from $\mathrm{KCrO_3NO_3}$ and $\mathrm{Ph_4AsBr.H_2O}$ by the reaction

$$\mathrm{KCrO_3NO_3} + \mathrm{Ph_4AsBr} \xrightarrow{\mathrm{MeCN},\ -10^\circ C} \mathrm{Ph_4AsCrO_3Br} + \mathrm{KNO_3} \qquad [10]$$

The $\mathrm{Ph_4AsBr.H_2O}$ used in the reaction is prepared by passing a solution of $\mathrm{Ph_4AsCl.xH_2O}$ (3.0 gm), in a minimum amount of water, through a Dowex 1-X4 (the hydroxide form) ion exchange column. The column was washed three times and the eluant plus washings treated with 10 ml of 1M HBr and the crystals of $\mathrm{Ph_4AsBr.H_2O}$ (melting point 279°C) thus formed, were dried in an oven at 110°C.

Analysis (%), calculated for $\mathrm{Ph_4AsBr.H_2O}$: C, 60.0; H, 4.6; Br, 16.6. Found: C, 60.7; H, 4.6 and Br, 16.7.

The $KCrO_3NO_3$ used in the reaction was prepared by reacting $KCrO_3Cl$ (2.190 gm) in MeCN with $AgNO_3$ (2.120 gm) also in MeCN

$$KCrO_3Cl + AgNO_3 \xrightarrow{-10^{\circ}C} KCrO_3NO_3 + AgCl \qquad [11]$$

The AgCl precipitate formed was immediately filtered off and the $KCrO_3NO_3$ used (immediately) in the next step. The MeCN solution could only be stored in the dark at $-10^{\circ}C$; the compound decomposes slowly in solution, even under these conditions, and more readily when exposed to light and/or at room temperature. Attempts to precipitate the $KCrO_3NO_3$ from the MeCN by treatment with benzene, ethers, tetrahydrofuran, CH_2Cl_2, $CHCl_3$ or CH_2Cl_2- petroleum ether mixture resulted in decomposition to a brownish powder. This decomposition also occurs when the MeCN solution is pumped on the vacuum line.

The reaction of a MeCN solution of $KCrO_3NO_3$, at −10°C, with $Ph_4AsBr.H_2O$ (6.00 gm) yields a white crystalline precipitate containing KNO_3 and a yellow solution according to reaction [10]. The KNO_3 precipitate was filtered off and the solid Ph_4AsCrO_3Br isolated by treating the filtrate with ice-cold 1:1 benzene-hexane mixture.

Analysis (%), calculated for Ph_4AsCrO_3Br: Cr, 9.2; C, 51.2; H, 3.6 Br, 14.2.
Found: Cr, 8.6 (7.8, 8.0); C, 50.9; H, 3.5 and Br, 13.9.

Because of the poor chromium analyses, it was found necessary to seek better ways of preparing other compounds containing the CrO_3Br^- anion.

Cesium Salt.

It was possible to prepare cesium trioxobromochromate by a method similar to that used for $CsCrO_3Cl$, viz. treating a chilled solution of CsBr in dilute HBr with chromic acid (CrO_3 dissolved in a minimum amount of water). The mixture was allowed to react for 5 minutes, chilled with crushed dry ice and the crystals of $CsCrO_3Br$ collected by filtration under nitrogen. This compound was found to be easily hydrolysed and decomposed even in the absence of moisture or light.

Triphenyl(n-butyl)phosphonium Salt.

When triphenyl(n-butyl)phosphonium bromide, $Ph_3(n\text{-}Bu)PBr$ gm), was dissolved in $CHCl_3$, treated with an aqueous solution containing CrO_3 (2.00 gm) and dilute HBr (2M), and allowed to stir for 5 minutes, the yellow product formed by the reaction [12]

$$Ph_3(n\text{-}Bu)PBr + CrO_3 + HBr(2M) \longrightarrow Ph_3(n\text{-}Bu)PCrO_3Br \qquad [12]$$

is extracted into the chloroform layer. The chloroform layer was collected, washed with 20 ml of 2M HBr and the $n\text{-}BuPh_3PCrO_3Br$ precipitated from the $CHCl_3$ solution by adding low boiling petroleum ether. The precipitate was washed with more petroleum ether and pumped dry in the dark on the vacuum line. Because the compound is very susceptible to hydrolysis it was necessary to keep it out of contact with moisture.

Analysis (%), calculated for $n\text{-}BuPh_3PCrO_3Br$: Cr, 10.4; C, 53.3; H, 4.8; Br, 16.0. Found: Cr, 10.0; C, 53.7; H, 4.9 and Br, 16.1.

(vii) Other Attempts at Preparing CrO_3L^{n-} (L = acetate, oxalate, selenocyanate, cyanide, nitrite and thiosulphate).

Potassium Acetatochromate.

Attempts to prepare $K[CrO_3(acetate)]$ by treating $KCrO_3Cl$ (0.651 gm) solution with a slurry of Ag(OAc)(0.631 gm) in MeCN, for 15 minutes, gave a quantitative yield of AgCl (weight of Cl found was 0.1320 gm compared to 0.1322 gm expected), but any $K[CrO_3(acetate)]$ that might have formed decomposed (acetic acid was given off) in solution.

$$KCrO_3Cl + Ag(CH_3CO_2) \longrightarrow K[CrO_3(CH_3CO_2)] + AgCl \quad [13]$$

When the AgCl was filtered off immediately and the MeCN pumped off on the vacuum line, the elemental analysis of the yellow powder that remained gave Cr, 28.9%; C, 0.6% and H, 0.0% compared to Cr, 26.3%; C, 12.1% and H, 1.5% expected for $KCrO_3(CH_3CO_2)$. There were no absorptions in the infrared spectra assignable to C-H or C=O stretching modes - the only bands observed being: 940vs, 905s, 885s, 790sh, 570m-w,sh, 375m cm^{-1}.

Others:

Attempts were made to prepare potassium oxalatochromate by treating a slurry of silver (or sodium) oxalate in MeCN with $KCrO_3Cl$ and allowing the mixture to stir for 24 hr. There was no AgCl precipitate or change in the chemical analysis or vibrational spectra of the starting materials.

Attempts to prepare $CrO_3(NCSe)^-$ by reacting $KCrO_3Cl$, Ph_4AsCrO_3Cl or $CrO(O_2)_2py$, in MeCN, with KNCSe (greenish-yellow) gave greenish-yellow or grayish-green precipitates and a repugnant smell. The mixture was allowed to stir for 24 hr, filtered and washed twice with MeCN. The dried precipitate had no infrared absorptions assignable to any of the vibrations of the NCSe group.

A solution of Ph_4AsCrO_3Cl in MeCN was also treated with AgCN, slurried in MeCN, for 48 hr. The mixture was filtered and the yellow compound precipitated out using 1:1 benzene-hexane mixture. From the elemental analysis and infrared spectra, the yellow solid was Ph_4AsCrO_3Cl.

Attempts to prepare $CrO_3(S_2O_3)^{2-}$ by reacting MeCN solutions of Ph_4AsCrO_3Cl with a slurry of $(NH_4)_2S_2O_3$ (or $Na_2S_2O_3$) also in MeCN gave no evidence of a reaction. It was not possible to prepare $(Ph_4As)_2S_2O_3$ for use in alternative reactions.

II.3 DISCUSSION OF THE VIBRATIONAL SPECTRA OF CrO_3L^{n-} COMPLEXES.

(a) Trioxohalogenochromates.

The stereochemistry of the ions CrO_3F^- and CrO_3Cl^- have been shown by X-ray diffraction [5,6] to belong to the point group C_{3v}. For the CrO_3Cl^- ion, the interatomic distances r(Cr-Cl) and r(Cr-O) were found to be 2.16 and 1.58A°, respectively, with all interbond angles approximately those of a regular tetrahedron. Studies of the salts $KCrO_3F$ and $CsCrO_3F$ showed that the structure of the CrO_3F^- ion is close to that of a perfect tetrahedron with r(Cr-O) = r(Cr-F) = 1.53A°. With C_{3v} symmetry point group for all complexes CrO_3L^{n-}, for L a monoatomic ligand (eg. F^-, Cl^- and Br^-), the vibrational spectra of the penta-atomic species should give six fundamental modes, $3A_1 + 3E$, all active in Raman and in the infrared, with the A_1 modes Raman polarized.

In order to establish the frequencies of some of the fundamentals arising from the CrO_3L^{n-} ions, it seemed appropriate to compare the spectra of the compounds prepared in the present study with those reported for CrO_3F^- and CrO_3Cl^-. [7, 8] Tables II.1 and II 2 show that, except for the small shifts, these results are consistent with the studies of Dupuis(IR),[8] Stammreich et al (IR and R) [7] and Carter and Bricker (R)[9]. The spectra (IR) of $CsCrO_3Cl$ and Ph_4AsCrO_3F were also recorded.

$CsCrO_3Cl$ (IR): 969s, 943vs, 908s, 446s, 399w, 380w, 370w, 358vw, 338vw, 306m-w, 283w, 249w and 228w.

Ph_4AsCrO_3F (IR): 950vs, 923m, 910m, 639m-s and 380w.

Table II.1 The Raman and Infrared Spectra of $KCrO_3F$, (cm^{-1})

Raman(Intensity)[a] aqueous soln.	IR(solid)[a]	IR(solid)[b]	IR(solid), this work	Assignments
955(4)	952vs	946	957vs	$\nu_4(E)$, $\nu_{(Cr-O)}$,
910(10)P	912s	910	915s	$\nu_1(A_1)$, $\nu_{(Cr-O)}$,
—	888mw	—	—	$\nu_2 + \nu_6 = 890$
—	—	—	745w	$2(\nu_5) = 750$
—	635s	620	639s	$\nu_2(A_1)$, $\nu_{(Cr-F)}$
—	—	—	487w	?
—	—	460	—	(SiF_6^{2-})
370(7)	370m	—	375w,br	$\nu_5(E)$, $\delta(\mathrm{O{-}Cr{-}O})$
—	338ms	340	343m	$\nu_3(A_1)$, $\delta\left\{\begin{matrix}\mathrm{O{-}Cr{-}O}\\ \mathrm{O{-}Cr{-}F}\end{matrix}\right\}$
261(6)	257m	260	250w	$\nu_6(E)$, $\nu(\mathrm{O{-}Cr{-}F})$

a. H. Stammreich et. al.; Spectrochimica Acta, 19, 593 (1963).
b. T. Dupuis Compt. rend., 246, 3332 (1958).

Table II.2 The Infrared and Raman Spectra of $KCrO_3Cl$, (cm^{-1})

Raman (Intensity)[a] solution*	IR (solid)[a]	IR (solid), this work	Assignments
954(4)	963 948]vs	964 953]vs	$\nu_4(E)$, $\nu_{(Cr-O)}$
907(10)P	915s	914s	$\nu_1(A_1)$, $\nu_{(Cr-O)}$
—	735vw	—	$\nu_2 + \nu_3 \simeq 733$
—	726vw	—	$2\nu_5$
438(2)P	438s	445ms	$\nu_2(A_1)$, $\nu_{(Cr-Cl)}$
365(7)	378 364]w	397m	$\nu_5(E)$, $\delta(\mathrm{O{-}Cr{-}O})$
295(0.5)	—	300w 281w	$\nu_3(A_1)$, $\delta\left\{\begin{matrix}\mathrm{O{-}Cr{-}O}\\ \mathrm{O{-}Cr{-}Cl}\end{matrix}\right\}$
209(10)	—	—	$\nu_6(E)$, $\delta(\mathrm{O{-}Cr{-}Cl})$

* Solutions in CH_3COCH_3, $CH_3COC_2H_5$ or $C_2H_5COC_2H_5$. a. H. Stammreich Spectrochimica Acta, 17, 226 (1961).

Tables II.1 and II.2 give the frequencies of the normal modes of vibration of the CrO_3F^- and CrO_3Cl^- ions with the descriptions of the approximate intramolecular motions involved.

The A_1 modes are particularly interesting. The totally symmetric stretching vibration of the CrO_3 group, ν_1, is apparently sensitive to the nature of the substituent and, as will be shown later, couples with the electronic charge-transfer transition. Although the descriptions of most intramolecular motions are generally considered merely approximate, definite meanings can be associated with vibrational modes whose frequencies are widely separated from the rest - as appears to be true of the Cr-O stretching modes in the present case. Because the values of the symmetric stretching frequency, $\nu_{sym}CrO_3$, may be dependent in part on the formal covalent bond orders, the symmetric CrO_3 stretching frequencies of the different substituted CrO_3L^{n-} derivatives, have been investigated and will be discussed in Section II(d). Vibrational spectra[10] and the normal-coordinate analyses[11] for the trioxorhenium(VII) complexes, ReO_3X^{n-} for $X^{n-} = F^-, O^{2-}, Cl^-, Br^-, S^{2-}$ and N^{3-}, support this approach.

Stammreich and coworkers[7] have shown, by normal coordinate analysis, that the ν_2 and ν_3 modes of CrO_3Cl^- are strongly coupled: both involve considerable deformation of all interbond angles, except that in the latter vibration the Cr and Cl move in the same direction along the principal axis, while in ν_2 the motion of the same atoms are in opposite directions along this axis. Thus the observed ν_2 frequency cannot be regarded as truly characteristic of the Cr-Cl bond stretching frequency. Furthermore, Miller and coworkers[12] have suggested that in CrO_2Cl_2 the 'true' frequencies, of the two unperturbed A_1-modes, ν_2 and ν_3, ν(Cr-Cl) and (δ(O-Cr-O)), should fall close to 400 cm^{-1} but are probably spread apart by resonance interaction. In the case of the CrO_3F^- ion, however, the ν_2- and ν_3-modes would be less mixed [7] since ν_2(Cr-F) occurs at 637 cm^{-1}.

For CrO_3Br^-, the six frequencies ascribed to the fundamental modes of vibration of the CrO_3L group were observed and assignments made, in a straightforward manner, by comparison with those reported for the CrO_3Cl^- and CrO_3F^- ions (See Tables II.3a and 3b). The positions of the CrO_3 stretching and deformation bands would not be expected to change greatly between CrO_3Cl^- and CrO_3Br^-. The band occuring rather consistently at ≈380 cm^{-1} was assigned to $\nu_2(A_1)$ and, by analogy with the CrO_3Cl^- spectrum, the absorption at ≈360 cm^{-1} is assigned to $\nu_5(E)$. The doubly degenerate mode, ν_5, essentially a deformation of the O-Cr-O angles, has sometimes been hard to observe for the Ph_4AsCrO_3L compounds reported in this study because the Ph_4As^+ cation has a strong absorption in the same region. But the frequencies of such vibrations in CrO_2Cl_2 [13], CrO_4^{2-} [14], $Cr_2O_7^{2-}$ [15], CrO_3Cl^- [7] and CrO_3F^- [7] are quite characteristic and are generally found around 360 cm^{-1}, and a band at this frequency is assigned accordingly.

The vibrational properties of the cesium salt, $CsCrO_3Br$, were also recorded primarily to attempt to avoid any cation interferences (See Table II.3(b). The cesium salt gave better resolution of the weak low frequency (<400 cm^{-1}, the region of bending modes) absorptions; significant shifts in the frequencies of most vibrations between Cs^+ and Ph_4As^+ salts suggest that the CrO_3Br^- ion experiences cation-dependent lattice and polarizing effects.

Table II.3(a), The Vibrational Spectra of the CrO_3Br^- Anion, (cm^{-1})

Infrared (solid)		Raman (solid)	Assignment
Ph_4AsCrO_3Br	$n\text{-}BuPh_3PCrO_3Br$	Ph_4AsCrO_3Br	
950s 920m	946vs	951s 929w,br	$\nu_4(E)$, $\nu_{(Cr-O)}$
905m	902m	903vs	$\nu_1(A_1)$, $\nu_{(Cr-O)}$
380s	382s	379m	$\nu_2(A_1)$, $\nu_{(Cr-Br)}$
360m,sh	368w	361s	$\nu_5(E)$, $\delta(\mathrm{O}\diagup^{\mathrm{Cr}}\diagdown\mathrm{O})$
		272w	$\nu_3(A_1)$, $\delta\left\{\begin{matrix}\mathrm{O}\diagup^{\mathrm{Cr}}\diagdown\mathrm{O}\\ \mathrm{O}\diagup\mathrm{Cr}\diagdown\mathrm{Br}\end{matrix}\right\}$
		234m	$\nu_6(E)$, $\delta(\mathrm{O}\diagup^{\mathrm{Cr}}\diagdown\mathrm{Br})$
		180m-s	?

Table II.3(b), IR Spectra and Possible Assignments for $CsCrO_3Br$, (cm^{-1})

959vs	ν_4	379w	ν_{5a}
908s	ν_1	363w	ν_{5b}
670vw	?	315w	ν_{3a}
665vw	?	307w	ν_{3b}
393s	ν_2	282w	ν_{3c}
		247w	ν_6

(b) Trioxonitratochromate Anion.

The free NO_3^- ion has a highly symmetrical planar structure, all its N-O bond lengths equal and an interbond angle of 120°. It interacts with metal ions displaying several different mode of coordination,[16] the most common of which are the symmetrical bidentate and unidentate nitrato groups.

Table II.4 Correlation Table for ZXY_2 Molecule in D_{3h}, C_{2v} and C_s Symmetries.

Point Group	$\nu_1(\nu_{XZ})$	$\nu_2(\pi ZXY_2)$	$\nu_3(\nu_{sy}(XY), \nu_{as}(XY))$	$\nu_4(\delta(ZXY))$
D_{3h} (free ion)	A_1'(R)	A_2''(ir)	E'(ir,R)	E'(ir,R)
C_{2v} (unidentate) (bidentate) (bridging)	A_1(ir,R)	B_1(ir,R)	A_1(ir,R) + B_2(ir,R)	A_1(ir,R)+B_2(ir,R)
C_s (unidentate)	A'(ir,R)	A"(ir,R)	A'(ir,R) + A"(ir,R)	A'(ir,R)+A"(ir,R)

The free NO_3^- ion has bands at ca. 1390 (R,IR), 1050 (R), 830 (IR) and 720 (R, IR) cm^{-1}. Depending on the mode of coordination, systematic changes occur in the vibrational selection rule of the ion. In all cases, however, the number (six) and the activity of the fundamental vibrational modes are the same. To deduce the mode of coordination a detailed spectral analysis would be required. A normal coordinate analysis[17,18] for unidentate bonding shows that the stretching mode $\nu_3(B_2)$ has higher frequency than the $\nu_3(A_1)$ component. Conversely, this analysis predicts that the position of the frequencies for these same components would be reversed in the bidentate bonded case. The difference between the A_1 (Raman polarized) and B_2 (Raman depolarized) modes cannot, however, be identified by infrared spectroscopy alone. Raman shifts, together with their depolarization ratios, currently provide the most acceptable means. Unfortunately, both

Table II.5 The Infrared Spectra of the $CrO_3(NO_3)^-$ Anion (cm^{-1}) †

$Ph_4AsCrO_3NO_3$ (KBr)	Tentative Assignments	$(C_2H_5)_4NCrO_3NO_3$ (Smear, CsI)
1580(w-m)		1585m
1550(s)	$\nu_3(\nu NO)$	1550s
1380(vs,br)		1370(m,sh)
1340(s,sh)	"	1340(s,br)
1315(m,sh)		1310(s,sh)
1287(s,sharp)	"	1280(vs,br)
1210(w,sh)		
		1095(s,br)
	ν_1 in NO_3^-	1050(m,sh)
975(m,sh)		975(s)
945(vs)	$\nu_{asy}(CrO_3)$	945(vs)
925(m,sh)		
905(s,sharp)	$\nu_{sym}(CrO_3)$	905(s,sh)
		850(vs)
835(m,sharp)	$\pi(NO_3)[\nu_2(A_2''$ in free $NO_3^-)]$	
780(m-s)	$\delta(ONO)[\nu_4(E'$ in free $NO_3^-)]$	780(vs,br)
		685(m)
		620(m)
540(w-m,br)	$\nu_{asy}(CrON)$ or $\nu_{asy}(\mathrm{Cr}\langle^{O}_{O}\rangle\mathrm{N})$	540(m-br)
		470(w)
435(w)	$\nu_{sym}(CrON)$ or $\nu_{sym}(\mathrm{Cr}\langle^{O}_{O}\rangle\mathrm{N})$	435(w)
380(m)		420(w)
		390(w)
(350)?	$\delta(\mathrm{O}{\diagup}^{\mathrm{Cr}}{\diagdown}\mathrm{O})$	350(m,sh)

† There is the possibility of NO_3^- ion impurities from exchange with the windows.

$Ph_4AsCrO_3NO_3$ and $(C_2H_5)_4NCrO_3NO_3$ are readily decomposed by the Ne/He exciting laser and other criteria[16] have not proved adequate.[19]

The spectra and assignments for the complex ion $CrO_3NO_3^-$ in $Ph_4AsCrO_3NO_3$ and $(C_2H_5)_4NCrO_3NO_3$ are given in Table II.5.

By comparison with the spectra of CrO_3L^- for L = F^-, Cl^-, and Br^-, the absorptions between 900 and 1000 cm^{-1} have been assigned to $\nu(CrO_3)$. Although one of these bands could also arise from the symmetric stretching mode, ν_1, of the coordinated nitrate - cf. $Me_3Sb(NO_3)_2$ (945 cm^{-1}),[20] $SbF_3(NO_3)_2$ (940 cm^{-1}), SnF_3NO_3 (965 cm^{-1}) and $[As(NO_3)_4]^+[AsF_6]^-$ (915 cm^{-1}).[21]

A definite assignment of the ligand deformation modes ν_2 and ν_4 is also difficult because the region 650 - 850 cm^{-1}, where they are expected to occur, is partially obscured by cation modes. As a result only the two bands, 780 cm^{-1} and 835 cm^{-1}, which are assigned to $\nu_4(\delta(ONO))$ and $\nu_2(\pi ONO_2)$ respectively, have been identified. Comparing the values observed for ν_4 with those of the hexanitrato complexes, $[M^{IV}(NO_3)_6]^{2-}$ for M = Zr, Hf and Sn,[22] and for SnF_3NO_3 and $SbF_3(NO_3)_2$[21] suggests that the second ν_4 band probably occurs around 700 to 600 cm^{-1}. The assignments of the far-infrared spectra, which may contain the chromium - nitrate stretching modes, are not possible at the moment.[23,24]

The highest frequency bands, 1600 - 1100 cm^{-1}, have generally been used to deduce the coordination geometry of the nitrate group. According to Curtis and Curtis[25] the distinction between symmetrically bidentate and unidentate nitrato groups is based on the separation of the two highest frequency bands, symmetrically bidentate giving rise to greater separation than unidentate coordination. In addition Field and Hardy [26] have suggested that occurance of two strong bands, one at a frequency greater than 1570 cm^{-1} and the other at a frequency less than 1280 cm^{-1} may indicate the presence of bridging nitrato groups. The position of the highest frequency band in the $CrO_3NO_3^-$ complex is such that no definite conclusions can be drawn regarding the type of nitrate coordination. The $CrO_3NO_3^-$ absorptions at 1585, 1550, 1380, 1340, 1315, 1287, and 1210 cm^{-1} are similar to those reported for anhydrous rare-earth metal nitrates.[24] Although the list [19] of compounds, containing nitrato groups, with established structures indicate that the nitrato groups prefer coordination through two oxygens, either bridging or as bidentate nitrate, the predominance of tetrahedral coordination in trioxochromium(VI) complexes (page 7), would suggest that bond formation is probably limited to only one $Cr-O(NO_2)$ bond in the $CrO_3NO_3^-$ ion. The nitrate coordination in $CrO_2(NO_3)_2$, which also contains chromium(V1), has not yet been established.[27]

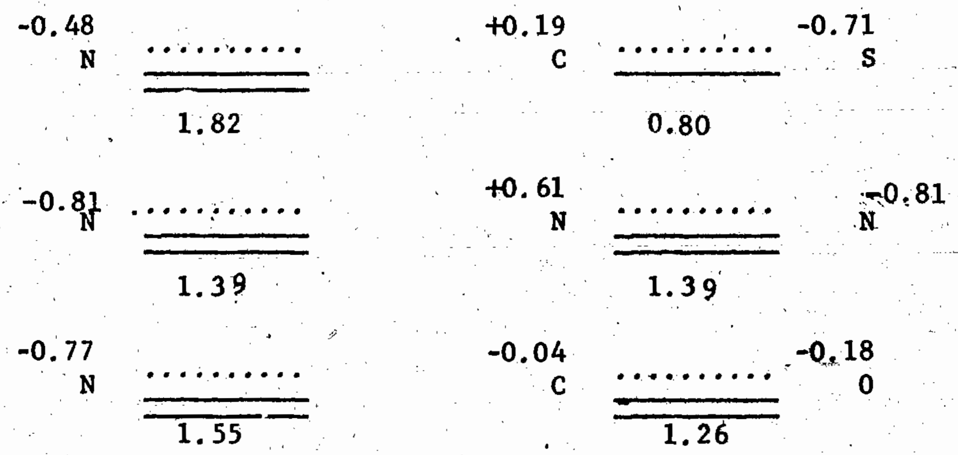
(c) Trioxopseudohalogenochromate(VI) Complexes:

(i) Electronic and Geometrical Structures of Pseudohalides.

In discussing the vibrational spectra of the complexes CrO_3Ps^-, where Ps^- stands for a pseudohalide grouping,[28] NYZ, where YZ = NN, CO or CS, it is necessary to discuss some characteristic structural (electronic and geometrical) features of the pseudohalides and pseudohalide complexes.

Norbury and Sinha[29] have used contributions from various reasonance forms to explain the fact that each of these ions, in the "free" state, approaches a linear triatomic configuration. Variations in the mode of coordination of these ions have been rationalized in terms of the constituent charge distributions calculated by Wagner;[30]

Table II.6 Calculated Atomic Charges and π-bond Orders for NYZ^- (Wagner[30])



where the numbers above the atoms represent the resulting π-electron charges on the atoms, and the numbers written under the bonds represent the π-bond orders. We would expect the NCS^- ion, which shows only a moderate charge difference between the two potential donor sites, to be more likely to exhibit ambidentate behaviour, while NCO^-, with the greater part of its charge localized on the N atom, would probably favour bonding through the N. One calculation[30a], which included σ-bonding, found equal charge densities on the N and O atoms.

The free pseudohalide has three characteristic fundamental vibrations, the pseudoasymmetric stretch (νNYZ(asy) or ν_{NY}), the pseudosymmetric stretch (νNYZ(sym) or ν_{YZ}) and a doubly degenerate deformation mode δ(NYZ). The infrared spectra of these ions are given in the Table II.7 below.

Table II.7 Infrared Spectra of the "free" Pseudohalide Ions (as K+ salts)

Ion	$\nu_{NYZ(asy)}$ (cm^{-1})	δ(NYZ) cm^{-1}	$\nu_{NYZ(sym)}$ (cm^{-1})	Ref
NNN^-	2041	645	1344	a
NCO^-	2165	637 628	1254 ↗1301 ↘1207	b
NCS^-	2053	486 471	746	c

a. F. Basolo and G.S. Hammaker, J.A.C.S. 82, 1001 (1960); Inorg. Chem. 1, 1 (1962). b. A. Maki and J.C. Decius, J. Chem. Phys. 28, 1003 (1958); 31, 772 (1959). c. P. O. Kinnell and B. Strandberg Acta. Chem. Scand. 31, 1607 (1959).

The pseudo-symmetric vibration, ν_{sym}(NCO), expected at 1254 cm^{-1}, in the same region as the first overtone 2δ(NCO), is shifted to give two bands, 1301 cm^{-1} and 1201 cm^{-1}, as a result of Fermi resonance interaction and a "mixing" of the two modes.

The available experimental data[31] show that changes in the frequencies of the normal vibrations of the pseudohalide (NYZ) depend on, among other things, the mode of coordination (eg. M-NYZ, M-ZYN, M'→NYZ-M", $\begin{smallmatrix}M'\\M''\end{smallmatrix}\!>$ZYN-M') and the acceptor character of the central metal. The hard-soft acid-base concepts of Pearson[32] has failed, however, in predicting the prefered bonding modes in a large number of complexes. For instance, Pd(II), a soft acid (class "b"),[33] forms the S-bonded complex $Pd(SCN)_4^{2-}$ [34] but in the presence of π-bonding ligands (eg. PEt_3, bipy) N-bonded complexes eg. $Pd(Et_3P)_2(NCS)_2$ [35] as well as linkage isomers [36] of the type cis - $Pd(NCS)(SCN)(Ph_2P(CH_2)_2PPh_2)_2$ are formed. The electronic effects apparent from the coordination behaviour of the NCS^- ion in mixed ligand complexes have been analysed by Norbury,[37] who showed that each coordinating atom (N or S) in the NCS^- ion has both "soft" and "hard" character.

	σ -Donor (or hard) ligand	σ -Donor and π -acceptor (or soft) ligand
Class "a" acceptor	-NCS	-SCN
Class "b" acceptor	-SCN	-NCS

Thus it appears likely that in the trioxochromium(VI) complex, $CrO_3(NCS)^-$, and the oxodiperoxo analog, $CrO(O_2)_2(NCS)^-$, the theocyanate ion will be N-bonded, but it is also possible that small energy modifications (e.g. by solvation) may affect [38,39] the mode of coordination. It is also known [40,41] that steric conditions imposed by other ligands, counter ions [42] or even the solvent in a complex do induce the incoming pseudohalide(s) to assume specific configurations in the M-XYZ skeleton. Bulky groups favour the linear (or nearly linear) M— N-C-S over the angular linkage $M^{\nearrow S-C-N}$.

The cyanate ion has received less attention. Norbury and Sinha [29] studied complexes of the type $ML_2(NCO)_2$, where M = Pd(II) or Pt(II), and used various ligands (L) with a wide range of ligand σ- and π-bonding properties, but failed to change the bonding mode, as has been done with NCS and $NCSe^-$ ions. More recently Norbury et al [29a] claimed the isolation of the first examples, $Rh(PPh_3)_3NCO$ and $Rh(PPh_3)_3OCN$, of solid cyanate linkage isomers.

(ii) Discussion of Vibration Spectra of Trioxopseudohalogenochromates

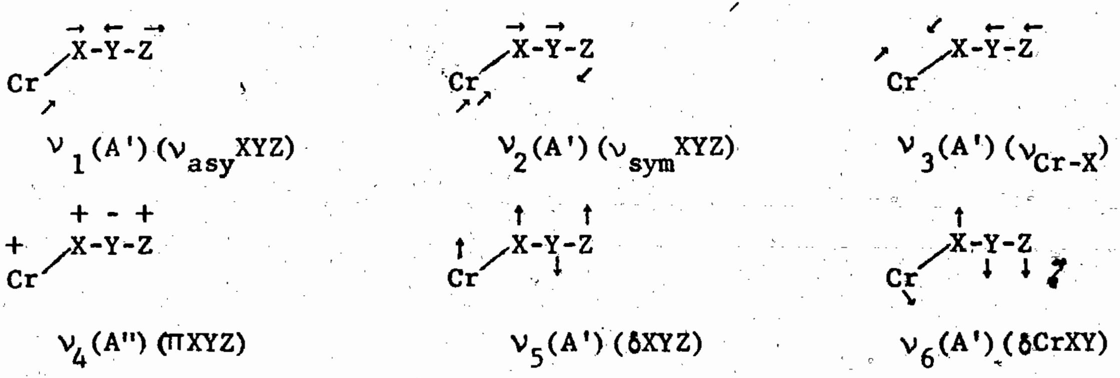
Because there is no structural information on the complexes, CrO_3Ps^- for Ps = NCO, NNN and NCS, we will apply some of the arguments used on the germyl pseudohalide GeH_3Ps, for Ps = N_3,[43] NCO[44] and NCS,[45] . Where the complex has a linear skeleton, i.e., the angle Cr-X-Y in $CrO_3(XYZ)^-$ is 180°, it will belong to C_{3v} point group; for other angles, the maximum possible symmetry is C_s. Table II.8 gives the vibrational modes expected for the pseudohalide complex, $CrO_3(XYZ)^-$, for the alternative assumptions of C_{3v} or C_s symmetry.

Table II.8 Vibrational Modes and Symmetry Classes for Structures of $CrO_3(XYZ)^-$

Vibrations	Point Group			
	C_{3v}		C_s	
	Class A_1	Class E	Class A'	Class A"
XYZ str. (asy)	ν_1		ν_1	
XYZ str. (sym)	ν_2		ν_2	
CrO_3 str. (asy)		ν_6	ν_3	ν_{11}
CrO_3 str. (sym)	ν_3		ν_4	
XYZ bend (π(XYZ) and δ(XYZ))		ν_7	ν_5	ν_{12}
Cr-X(YZ) str.	ν_4		ν_6	
CrO_3 def. (asy)		ν_8	ν_7	ν_{13}
CrO_3 def. (sym)	ν_5		ν_8	
CrO_3 rock		ν_9	ν_9	ν_{14}
CrXY bend and CrO_3 torsion		ν_{10}	ν_{10}	ν_{15}

For C_s symmetry (only one plane of symmetry) all 15 vibrations are allowed in both the Raman and infrared. The 10A' vibrations are symmetric to the plane and are Raman polarized while the 5A" modes are antisymmetric and depolarized. The C_{3v} point group on the other hand would give rise to 10 fundamentals all active in both the Raman and IR. The 5A modes are Raman polarized while the 5E modes give depolarized Raman lines. The difference between the spectra of the CrO_3Ps^- complexes and those of the analogous halides lies in the introduction of additional fundamentals arising from the Cr-X-Y-Z moiety. A planar non-linear four-atom species of this type has 6 fundamental modes of vibration.[46]

Figure II.1 Normal Modes of Vibration for a Planar Non-linear Cr-XYZ Moiety.



$\nu_1(A')(\nu_{asy}XYZ)$ $\nu_2(A')(\nu_{sym}XYZ)$ $\nu_3(A')(\nu_{Cr-X})$

$\nu_4(A'')(\pi XYZ)$ $\nu_5(A')(\delta XYZ)$ $\nu_6(A')(\delta CrXY)$

Both steric effect and the hybridization on the bonding atom X (or Z) may vary the angle MXY (or MZY) from 109° to 180°,[47] thus affect the degeneracy of certain vibrations. The structure and bonding in CrO_3Ps^- complexes are discussed on pages 71 - 72.

Tetraphenylarsonium Trioxothiocyanatochromate.

While the Ph_4As^+ salt was moderately stable, the K^+ and Cs^+ salts decomposed relatively rapidly in both air and in vacuo. Obtaining the complete vibrational spectrum of the $CrO_3(NCS)^-$ ion was hindered both by the superposition of the Ph_4As^+ vibrations over those of the anion (Table II.9) and by the decomposition of the complex. The analysis of the vibrational spectra of $Ph_4AsCrO_3(NCS)$, therefore, had to involve the spectra of the freshly prepared cesium and potassium salts (Table II.10).

The intense band at 2060 cm^{-1} in the $Ph_4AsCro_3(NCS)$ complex is assigned to $\nu(CN)$. The small increase from the free ion value of 2053 cm^{-1} suggests Cr-NCS coordination, according to an analysis by Tramer.[48] Increases of 50 - 70 cm^{-1} have generally been assigned to M-SCN, and larger increases (70 - 120 cm^{-1}) to strong bridging. Distortions from regular geometry, brought about by non-linearity in Cr-NCS, as well as cation[49] or lattice effects may be responsible for the splitting of $\nu(CN)$. The larger increase in the $\nu(CN)$ mode in the K^+ or Cs^+ salts is probably a result of the greater polarizing effects of these cations relative to Ph_4As^+.

The pseudosymmetric stretch, ν_{CS}, is somewhat harder to assign. The position and intensity of this mode in a variety of thiocyanate complexes is known to be very dependent on the environment of

Table II.9 The Vibrational Spectra of the $CrO_3(NCS)^-$ Anion in $Ph_4AsCrO_3(NCS)$

Raman (cm^{-1})	Infrared (cm^{-1})	Assignments
	2060s,sh	$\nu_{asy}(NCS)$
	1260(w)(?)	
969w	950s(sharp)	$\nu_{asy}(CrO_3)$
960w		
914s	912m-s(sharp)	$\nu_{asym}(CrO_3)$ or $\nu_{sym}(CrO_3)$ or $\nu_{sym}(NCS)$
884w	885w	$\nu_{sym}(CrO_3)$ or $\nu_{sym}(NCS)$
495s(broad)		δ(NCS)
	415(m-s)	ν(Cr-N) or ν(Cr-S)

Table II.10 Spectra of the $CrO_3(NCS)^-$ Ion at Different States of Decomposition

$CsCrO_3(NCS)$ Nujol, fresh	$CsCrO_3(NCS)$ KBr, 24 hrs. later	$CsCrO_3(NCS)$ in MeCN, 1 hr. later	$KCrO_3(NCS)$ Nujol, partly decomposed	$KCrO_3(NCS)$ KBr, partly decomposed
	3100w,br		3180m,v-br	3100s,v-br
			2320vw	2340w,sh
			2300vw	
			2260vw	2200m,sh
	2100sh		2200vw	
2060s,sh	2060vs,br	2085vs	2080vs	2080vs,br
2020vs,br			2010s,sh	
	1600w		1610w	1610w,br
	1400w		1410s	1400vs,br
1150w,br	1130w		1150w,br	1130s,br
	1030w		1080w	1080m,br
940vs	940vs	955s,sh	940vs,br	930vs
920s,sh	920s,sh	927m,sh		970-700 v-br
890m,sh	890m,sh	889m,sh	900m	
	780m,br	810m,br	770s,br	780vs
			660vw	660w
			610vw	600m
	480w	485w	485m	480m
			445m	
420m	420w	420m	430sh	430m
			370s	360s,v-br
			350-330sh	

the NCS group. For instance, in HNCS the band is at 995 cm^{-1}, in the gas the absorption shifts to 851 cm^{-1} [50], and to 845 cm^{-1} in the CS_2 solution (with a band at 962 cm^{-1} unassigned).[51] The same band in GeH_3NCS is at 962 cm^{-1}.[45] Furthermore, a review[31] of transition metal thiocyanate complexes positions this vibration in the range 690 - 940 cm^{-1}. In view of the low (2060 cm^{-1}) C-N stretching frequency of the $CrO_3(NCS)^-$ complex, and the reciprocal relationship found for C-N and C-S stretching frequencies for organic isothiocyanates, it is reasonable to assign the 912 cm^{-1} absorption to the C-S stretching mode in the PH_4AS^+ salt. This assignment favours a N-bonded thiocyanate for which, according to Tramer, ν_{CS} would occur between 780 and 860 cm^{-1} compared to 690 and 720 cm^{-1} for S-bonded thiocyanates.

The bending modes, ν_4 and ν_6, would be expected in the far-infrared region and therefore outside the range of the spectrophotometer used.

The ligand bending vibration, ν_5, has sometimes been used as a diagnostic criterion for assigning modes of coordination of the NCS^- ion. According to Sabatini and Bertini[49] a single sharp band near 480 cm^{-1} is taken as indicative of N-bonding, while S-bonding is characterised by several bands of lower intensity around 420 cm^{-1}. The splitting is once again caused by symmetry reduction. Freshly prepared compounds containing the CrO_3NCS^- anion, show bands at 415 or 420 cm^{-1}, while older (or partially decomposed) samples exhibit multiple bands of medium intensity between 500 and 330 cm^{-1}. Unfortunately, the Cr-N stretching frequency is also expected to occur in this region. The frequencies of ν_{Cr-N} in $CrO_3N_3^-$, CrO_3NCO^- and CrO_3ClN_3[52] are consistently observed at $\simeq 495\ cm^{-1}$, and it is generally argued that the metal-ligand vibration becomes less pure M-N as the pseudohalide becomes heavier in the series NCO, NCS and NCSe, so that the Cr-N vibration for Cr-NCS could well be lower than $495\ cm^{-1}$. For instance in the $Ph_4AsCrO_3(NCS)$ spectrum, the $415\ cm^{-1}$ absorption can be assigned to the Cr-N stretching mode and the weak absorptions at $480 - 475\ cm^{-1}$ to the δ(NCS) deformation. The position and intensity of this mode in other transition metal isothiocyanates[53,54] support the assignment.

In general, the vibrational spectrum of the $Ph_4AsCrO_3(NCS)$ complex is compatible with a $CrO_3(NCS)^-$ anion of C_{3v} symmetry.

Tetraphenylarsonium Trioxocyanatochromate

The criteria for assigning the bonding modes of cyanate complexes have been more difficult to establish, partly because of lack of structural determinations, and partly because of the greater mixing of the stretching modes. By analogy with thiocyanates, an increase is expected in the C-N stretching mode if the bonding occurs through the oxygen and the reverse for N-bonding. Although ambiguity is sometimes expected for the C-N stretching of the N-C-O unit, as is found with thiocyanate complexes,[55] larger increases have generally been observed for isocyanates by Forster and Goodgame[56], and Bailey and Kozak.[57] In Table II.11, the frequency of the band at 2206 cm^{-1} in $Ph_4AsCrO_3(NCO)$ and 2276 cm^{-1} in $KCrO_3(NCO)$ clearly shows the presence of a coordinated NCO group; in the case of $KCrO_3NCO$ the evidence for N-bonding is strong.

The other interesting mode involves the pseudosymmetric stretching of the NCO unit. It has been shown[58] that the ν_{CO} for isocyanates are generally of weak-to-medium intensity, higher in frequency than those of the cyanates[57], and appear as a singlet at about 1330 cm^{-1}. In most transition metal tetraisocyanates the frequency range is between 1319 and 1337 cm^{-1}. The pseudosymmetric stretch is identified as being at 1385 (or 1387) cm^{-1} in $CrO_3(NCO)^-$. Because the $\nu_{sym}(NCO)$ is known to increase in the N-bonded cases and decrease in the O-bonded ones relative to NCO^-, the spectra in Table II.11 suggest N-bonding in the $CrO_3(NCO)^-$ ion.

The weak bands at 630 and 616 (or 638 and 605)cm^{-1} have been assigned to the bending modes δ(NCO) and δ(πNCO), by analogy with the 570 - 640 cm^{-1} absorption bands in the spectra of isocyanato complexes of other electropositive metals.[29,31]

Table II.11 The Vibrational Spectra of the $CrO_3(NCO)^-$ Anion.

$KCrO_3NCO$		Ph_4AsCrO_3NCO (infrared solid)	Tentative Assignment
Raman(solid)	(Infrared Solid)		
		2370w	
		2350w	
	2276vs,br		ν_{asy}(NCO)
	2204vs,sh	2206vs	
1392w	1387w,br	1385w,br	ν_{sym}(NCO)
970w	965vs,sh		
954w	951vs	951vs	$\nu_{asy}(CrO_3)$
940w		925w,sh	
915vs	910s	904s	$\nu_{sym}(CrO_3)$
	887w-m		
	638w-m	630vw,sh	δ (NCO)
	605m	616w	
	573w	570vw	δ (π-NCO)
516w	512s		ν_{Cr-N}
	500s,sh	485m,sh	
	420	420w	
	397	390w	
	386		
379s	376		
371m	353		
362w	326 very	330w	
	316 weak	307m	
	300		
	280	283m	
	266	268w	
	245	243w	
250-240m,br	226	229w	

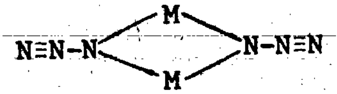
The strong 512 cm^{-1} band in $KCrO_3NCO$ (485m cm^{-1} in Ph_4AsCrO_3NCO) is assigned to the stretching of the Cr-N bond. The frequency of this band is consistent with the 495 cm^{-1} absorption in the compounds $CrO_3N_3^-$, CrO_2ClN_3[52] and $Ge(NCO)_4$[59] but higher than the Fe-N stretching fundamental at 410 cm^{-1} in $(Ph_4As)Fe(NCO)_4$[31].

The complexity of the far infrared spectra (400 - 200 cm^{-1}) discourage any efforts to make specific assignments for the deformation modes $\delta(CrO_3)$, $\delta(OCrN)$ or $\delta(CrNC)$.

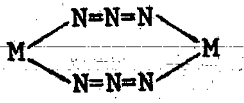
Tetraphenylarsonium Trioxoazidochromate

As is the case with cyanates and thiocyanates the presence of a coordinated azido group can be easily detected by the infrared bands at $\approx 2000 cm^{-1}$ ($\nu_{asy}(N_3)$), 1300 cm^{-1} ($\nu_{sym}(N_3)$) and between 500 and 700 cm^{-1} ($\delta(N_3)$).[60] The type of coordination of the azido group, ie monodentate or bridging, cannot generally be established solely by consideration of infrared data.[61] Consider, for instance, the complexes $[Cu_2(diphos)_3(N_3)_2]$,[62] $[(CO)_3Mn(N_3)_3Mn(CO)_3]$[63] and $[Cu(PPh_3)_2(N_3)]_2$[64] which represent, respectively, the three bonding modes known for azido

I



II



III

complexes. The solid state spectra (IR and Raman) of the $CrO_3N_3^-$ anion (Table 11.12) has absorptions.

Table II.12 The Vibrational Spectra of the $CrO_3N_3^-$ Ion in $Ph_4AsCro_3N_3$.

Raman (solid)	Infrared (KBr)	Assignments
	2380vw	
	2160vw 2073vs	$\nu_{asy}(N_3)$
	1280m	$\nu_{sym}(N_3)$
956w	953vs	$\nu_{asy}(CrO_3)$
936w	929s,sh	
899s	898s	$\nu_{sym}(CrO_3)$
674w	670m,sh	$\delta(N_3)$
	580w	δ (π-NNN)
490s,br	492s	ν(Cr-N)
	313w	$\delta(O\overset{Cr}{\frown}O)$
	235m	$\delta(O\overset{Cr}{\frown}O)$ or $\delta(O\overset{Cr}{\frown}N)$
	220	$\delta(O\overset{Cr}{\frown}N)$ or δ(Cr-N-N)

at 953, 929 and 898 cm^{-1} which are assignable to the CrO_3 stretching vibrations. The frequencies of the pseudoasymmetric (2073 cm^{-1}) and pseudosymmetric (1280 cm^{-1}) stretching vibrations of the N_3 group are also much in line with those of other transition metal azido complexes.[59-64] The stretching vibration $\nu_{asy}(N_3)$ has sometimes been used to detect the asymmetry of a coordinated azido group.[65] The structural data on transition metal azido complexes[68] indicate that the two N-N bond lengths are generally unequal, $\Delta d = r(N_I - N_{II}) - r(N_{II} - N_{III})$. In the N_3^- ion, each N-N bond is 1.54Å.[66]

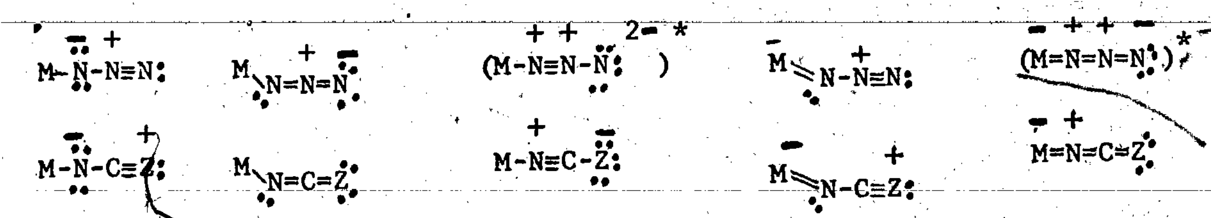
Agrell[65] has demonstrated that there is in fact a linear relationship between the degree of the asymmetry and the energy of $\nu_{asy}(N_3)$ (or $\nu_{sym}(N_3)$) by plotting $\nu_{asy}(N_3)$ against the Δd for a series of related or similar complexes. We can, therefore, compare the vibrational spectra of the complex ion $CrO_3N_3^-$ with that of the neutral solid complex CrO_2ClN_3. In the latter complex $\nu_{asy}(N_3)$ occurs at 2145 cm^{-1} while $\nu_{sym}(N_3)$ drops down to 1223 cm^{-1}.

In addition to the stretching modes, the spectrum of the $CrO_3N_3^-$ ion also has absorptions at 580 and 670 cm^{-1} (674 cm^{-1} in Raman) assignable to the $\delta(\pi NNN)$ and $\delta(NNN)$ modes. Although these have no diagnostic value, they compare well with the 702 and 622 cm^{-1} bands observed for GeH_3N_3,[43] the 637 cm^{-1} band observed in CrO_2ClN_3 and those of other azido complexes.

The M-N stretching vibrations are observed at 466 cm^{-1} in GeH_3N_3,[43] at 492 cm^{-1} in $CrO_3N_3^-$, and 495 cm^{-1} in CrO_2ClN_3.[52] In the CrO_3NCO^-, which is isoelectronic with and possibly isostructural with $CrO_3N_3^-$, the Cr-N stretching frequency is at 512 cm^{-1}. This increase is comparable to that from GeH_3N_3 (466 cm^{-1}) to GeH_3NCO (493 cm^{-1}).[44] Assignments of the lower frequency deformation modes are less certain.

(iii) The Structure of CrO_3Ps^- Complexes and the Nature of the Cr-Ps Bond

Except for the spectroscopic evidence suggesting Cr-N bonds in all CrO_3Ps^- complexes, the analyses, in terms of the expected and observed fundamentals assuming C_{3v} or Cs symmetry, have not been completely definitive. But structural possibilities developed by the inspection of a number of ground state structures of the N-bonded complexes could be envisaged. These structures represent the geometries of the MXYZ if steric constraints and/or crystal packing, caused by other ligands or counter ions, are absent.


a(~109°) b(~120°) c(~180°) d(~120°) e(~180°)

The M-N-C-Z and M-N-N-N structures also suggest that extensive π-bonding may be present.[67-69]

(d) The Effects of the Substituents on the ν_{sym} Cr-O.

In the ground state, the effects of substituents are reflected in the gradual shift of the ν_{sym}(Cr=O) as the substituent is changed from $L^- = F^-$ to $L^- = N_3^-$. It has been established [70,71] that the value of the M=O stretching frequencies in metal oxocations $M_xO_y^{n+}$, is dependent on the other ligands attached to the cation. McGlynn and co-workers [70,71] used the frequencies of the symmetric and asymmetric U-O stretching vibrations in the complexes $K_xUO_2L_y(NO_3)_2$ and established a

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* Unlikely due to the adjacent like formal charges.

ligand series which exhibits a striking parallelism to the spectrochemical series. It therefore seemed worthwhile to investigate shifts in ν_{sym}(Cr=O) as a function of the anionic ligand L in CrO_3L^{n-}. The Raman technique was used because ν_{sym}(Cr=O) has a particularly strong band[9,7] in the Raman, and accuracies of ± 1 cm^{-1} were obtainable. The results are collected together in Table II.13

To minimize solid state effects, e.g. crystal packing forces, in this study the vibrational (Raman) spectra of the freshly prepared Ph_4AsCrO_3L compounds were measured in DMSO (ϵ=46.6) and CH_2Cl_2 (ϵ=8.9). Other solvents (MeCN, acetone, $MeNO_2$) were unsuitable on the basis of solubility, stability or interfering solvent bands in the 800 - 950 cm^{-1} region.

Table II.13 The ν_{sym} Cr=O Frequencies (Raman) of CrO_3L^{n-} Compounds

	Raman (cm^{-1})	
Substituent (L)	DMSO	CH_2Cl_2
F	910	low solubility
Cl	904	905
NCO	903	904
Br	902	903
NO_3	898?(decomposes)	decomposes
N_3	897	898
NCS	884?	decomposes

One result of the study is that the order and relative magnitude of the substituent effects appear to be independent of solvent effects. The other important factors are the simple mass effects and mechanical coupling of the Cr=O stretch with the Cr-L vibrations. It is assumed, as in previous studies,[70,71] that the effect of the substituent (L) on $\nu_{Cr=O}$ is purely a bonding one. The coupling of the Cr=O modes with Cr-L modes is probably insignificant when L is a heavy atom or group, and may be neglibible even with lighter atoms, since the Cr-L vibrational frequencies (ν_{Cr-F}=637 cm^{-1}) are lower than $\nu_{Cr=O}$. In agreement with this, the shift in ν_{V-O} (995 cm^{-1} to 964 cm^{-1}) is much larger than would be expected (989 cm^{-1}) from mass effects alone[70]. So that for a series of ligands attached to the CrO_3 moiety, the order of the ligands based on the position of $\nu_{Cr=O}$ should be independent of mass effects, and almost completely dependent on ligand bonding effects. Since the vibration of a bond A-B is considerably influenced by the difference in the electronegativities of atoms A and B, the increase in $\nu_{Cr=O}$ is taken to be a reflection of the difference in the electronegativites of O and CrO_2L. The results are shown in Figure II.2. A shift of the $\nu_{sym}(CrO_3)$ to lower frequency is interpreted to mean a weakening of the Cr=O bond (c.f. the ν_{sym}Cr=O for the isoelectronic CrO_3NCO^- (903 cm^{-1}) and $CrO_3N_3^-$ (897 cm^{-1}), and the small shift from CrO_3Cl^- (904 cm^{-1}) to CrO_3Br^- (903 cm^{-1}) despite the large mass difference.)

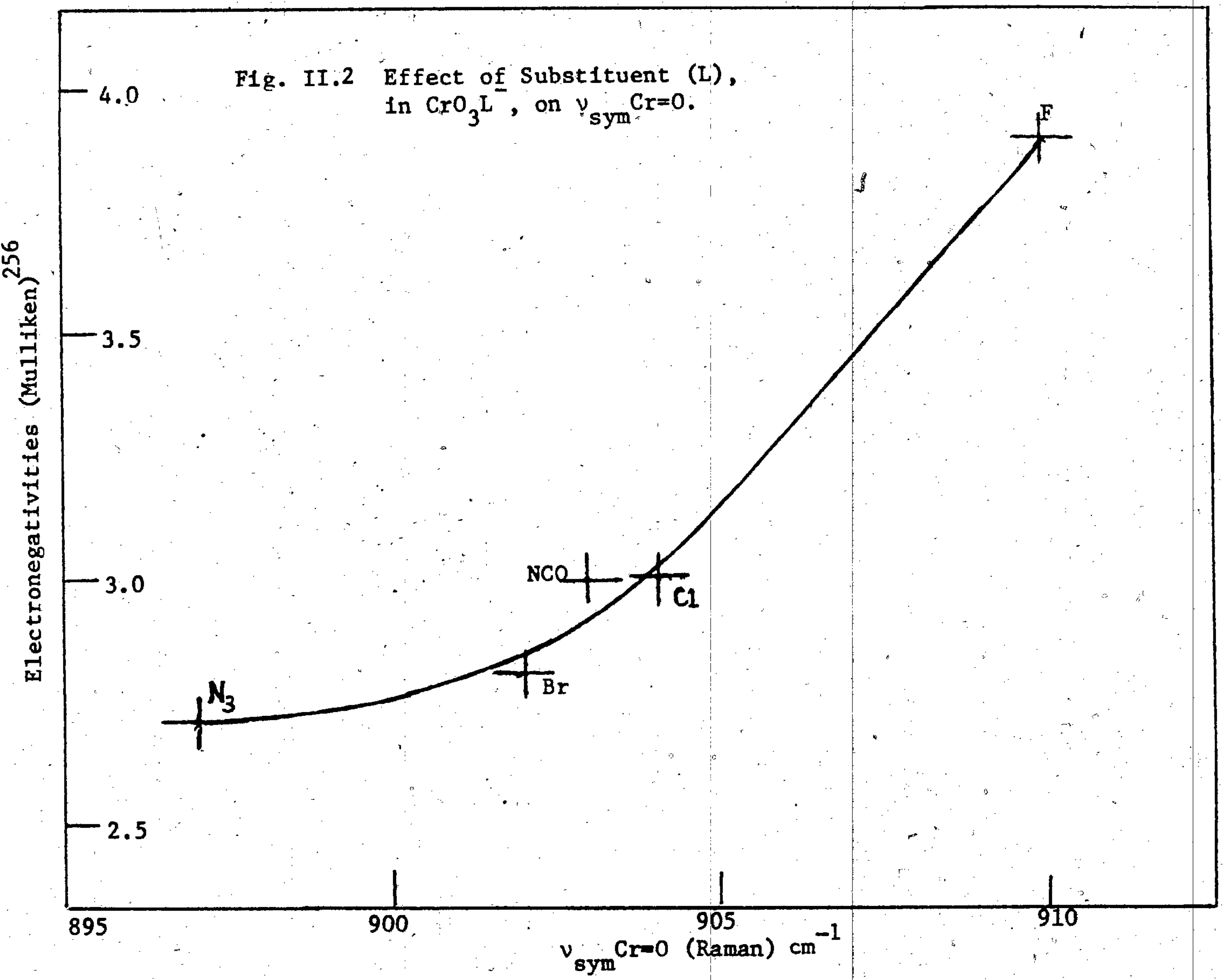
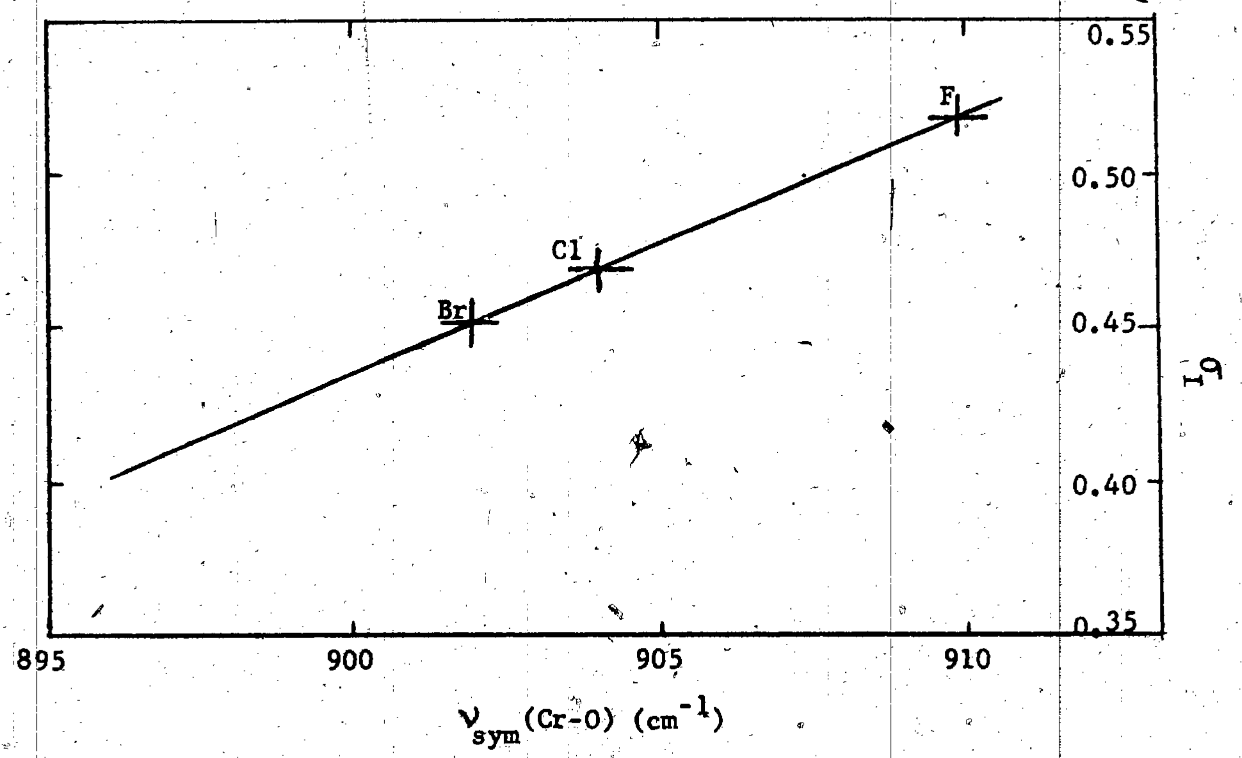


Fig. II.2 Effect of Substituent (L), in CrO_3L^-, on ν_{sym}Cr=O.

Analysed properly, sets of $\nu_{M=O}$ such as these can be used to estimate electronegativities of substrates. They can also be used to estimate the Hammett σ_I constants (the inductive substituent constant for aliphatic compounds). Figure II.3 shows that a plot of ν_{sym} (CrO_3) against σ_I for F(0.52), Cl(0.47), and Br (0.45)[72] gives a straight line. From this plot it is established that σ_I for NCO and N_3 are 0.46 and 0.41, respectively. The value of 0.41 for N_3 compares well with the 0.44 reported by Taft and Lewis[72a], who derived their value indirectly from the σ_{meta} and σ_{para} constants. The most important conclusion to be drawn from the present results is that ν_{sym}(Cr-O) in CrO_3L^- ion is indeed affected by the nature of the ligand L. This is reasonably explained in terms of a transmission of the charge in the Cr-L bond. We shall see below that the electronic spectra are also dependent on the ligand L, in a manner which is in keeping with the vibrational spectra.

Figure II.3 Plot of Hammett Inductive Substituent Constant σ_I Versus $\nu_{sym}(CrO_3)$ observed for CrO_3L^- Derivatives.



III.4 THE ELECTRONIC SPECTRA OF MONOSUBSTITUTED TRIOXO CHROMATES.

A large number of substitution and redox reactions have been reported between CrO_4^{2-}, $HCrO_4^-$ or $Cr_2O_7^{2-}$ and various donor ions and molecules.[73-81] In many instances the initial step in the reaction involves the formation of a Cr(VI)—substrate complex O_3Cr-L. The evidence for equilibria or reaction intermediate(s) is generally obtained directly from changes in the $HCrO_4^-$ absorption spectrum. In some cases[56] the change is very small and in others competing hydrolytic reactions e.g.

$$CrO_3L \; + \; H_2O \longrightarrow HCrO_4^- \; + \; HL \qquad [14]$$

have hindered drawing definite conclusions.[75] It is generally agreed, however that since Cr(VI) is d^0, the absorption must be a charge-transfer, electric-dipole allowed ($g \rightarrow u$ in O_h symmetry), transition occuring from non-bonding orbitals on the oxygens (or a π-bonding MO consisting of oxygen atomic orbitals) to the Cr π^*-orbital, in effect reducing the Cr(VI) in the excited state. Charge-transfer bands are usually very intense ($\varepsilon \geq 10^3$) and occur in the UV (or near visible) region of the spectrum.

The original semiempirical molecular orbital calculations of Helmholz and coworkers[82] on the CrO_4^{2-} and MnO_4^- ions started a debate when they reported an energy level scheme in which the lowest unoccupied orbital was the t_2 instead of the e level expected from crystal field theory; with the ground state configuration

$$(1a_1)^2(1t_2)^6(1e)^4\,(2t_2)^6\,(2a_1)^2\,(3t_2)^6(t_1)^6(4t_2)^0(2e)^0$$

having symmetry A_1. The first promotion, $t_1 \rightarrow t_2$ is expected to give rise to four symmetry states, A_1, E, T_1 and T_2 (both singlet and triplet states are possible though there is no spectral evidence for triplet states), of which only the ${}^1A_1 \rightarrow {}^1T_2$ transitions are symmetry (orbital) allowed;

transition to other levels being forbidden in the absence of perturbing effects. The second excitation was predicted to occur from the $3t_2$ orbital to the $4t_2$ orbital (symmetry states A_1, E, T_1 and T_2), with only the ${}^1A_1 \rightarrow {}^1T_2$ being allowed. Unfortunately, the experimental results did not agree very well with the observed energies or intensities of either transition.

In 1958, Ballhausen and Liehr[83] proposed an alternative scheme consistent with the crystal field theory and assigned the first transition to $t_1({}^1A_1) \rightarrow e({}^1T_2)$ and the second to $t_1({}^1A_1) \rightarrow t_2({}^1T_2)$. The first transition gives T_1 and T_2 states, the second A_1, E, T_1 and T_2 states.

So that, in addition to the two possible allowed ${}^1A_1 \rightarrow {}^1T_2$ transitions, there are at least four orbitally forbidden transitions concealed, plus singlet → triplet transitions. The latter scheme was supported by other molecular orbital calculations[83-89] and the single crystal electron spin resonance spectra of certain d^1 and d^2 ions.[90] More recent and extensive MO calculations[89,91] (Fig. II.4) on the MnO_4^- ion appear to have arrived at reasonable agreement but the same have failed to produce a consistent energy level scheme or spectral assignments for the CrO_4^{2-} ion.

Except for the one attempt made on the CrO_3F^- and CrO_3Cl^- ions[92] no extensive theoretical analysis of changes in orbital energy levels and the spectral changes that occur when one passes from CrO_4^{2-} (T_d) to $CrO_3X(C_{3v})$ exists. A study[93] of the dichroism of the $KCrO_3Cl$ complex has, however, established that the electronic ground state

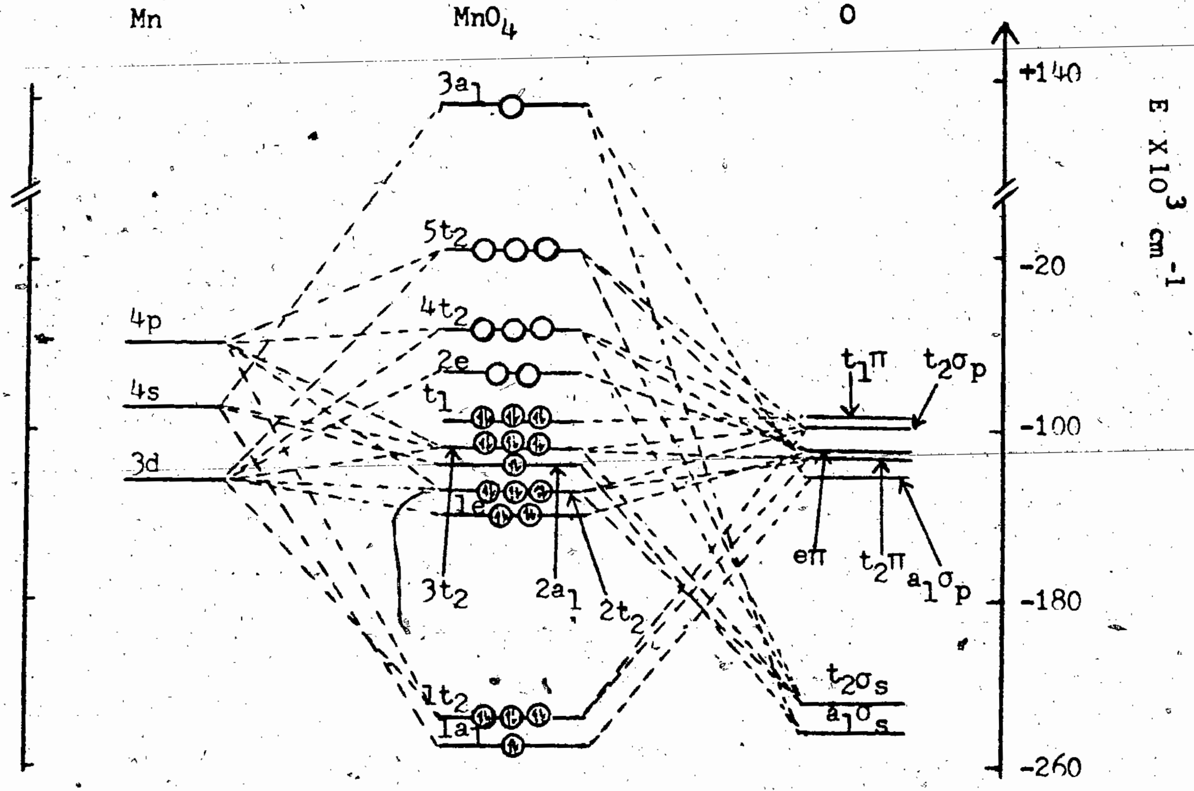


Figure II. 4 MO Energy Level Diagram for MnO_4^-

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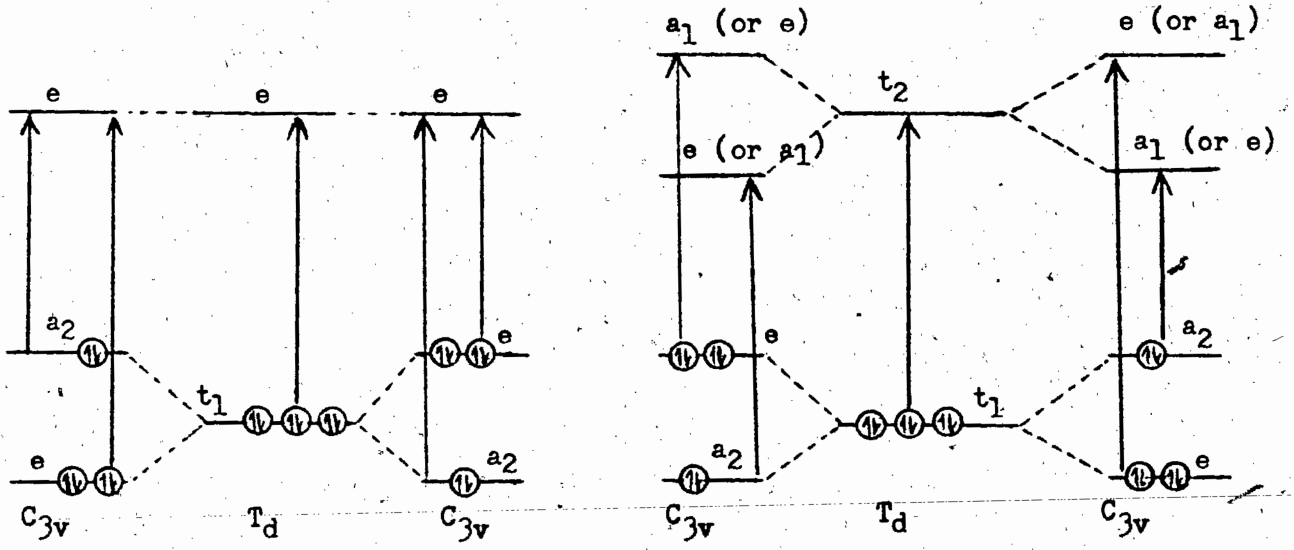


Figure II. 5 Effect of $T_d \rightarrow C_{3v}$ Symmetry Reduction on the Assignment of the First Excitation .

of the CrO_3Cl^- ion is also $^1A_1$, the same as the CrO_4^{2-} ion. The symmetry reduction $T_d \rightarrow C_{3v}$ would be expected to split all orbital triplets into a singlet (a) and a doublet (e), $t_1 \rightarrow (e + a_2)$ and $t_2 \rightarrow (e + a_1)$. While the degeneracy of the doublet levels may remain unchanged, the molecular form and energy, relative to that in CrO_4^{2-}, may alter. Because the selection rules for C_{3v} symmetry would allow all $A_1 \rightarrow A_1$ and $A_1 \rightarrow E$ transitions, the possibilities ($a_2 \rightarrow a_1$, $a_2 \rightarrow e$, $e \rightarrow a_1$, $e \rightarrow e$, $a_1 \rightarrow a_1$ and $a_1 \rightarrow e$) arising from these excitations make assignment difficult, see Fig. II.4 and 5. Furthermore, the problem of how the non-bonding electrons (in the a_2 and e orbitals)[92, 94] are distributed between the oxygen(s) and substrate donor atom, makes only tentative assignment, based on comparisons with the CrO_4^{2-} and MnO_4^- spectra, possible.

The absorption spectra of the anion, CrO_3L^{n-} (for L = F^-, Cl^-, Br^-, NO_3^-, NCO^-, NCS^-, N_3^- and acetate), have been investigated and found (Figures II.6 to II.8) to have a minimum of three bands located in the regions 450 mμ, 360 mμ and 270 mμ.

(a) The Absorption Band Centered at 450mμ.

The lowest energy band (≈ 450 mμ) is relatively weak (ε = 100 - 300), insensitive to the nature of the substituent L and sometimes partly overlapping with the stronger second band. It exhibits distinct, though poorly resolved, vibrational peaks spaced by ≈ 700 cm^{-1}, Fig. II.6. Similar low intensity, poorly structured bands have been observed in the polarized spectra of the CrO_4^{2-} and MnO_4^- ions in low symmetry sites of various host crystalline lattices. It has been

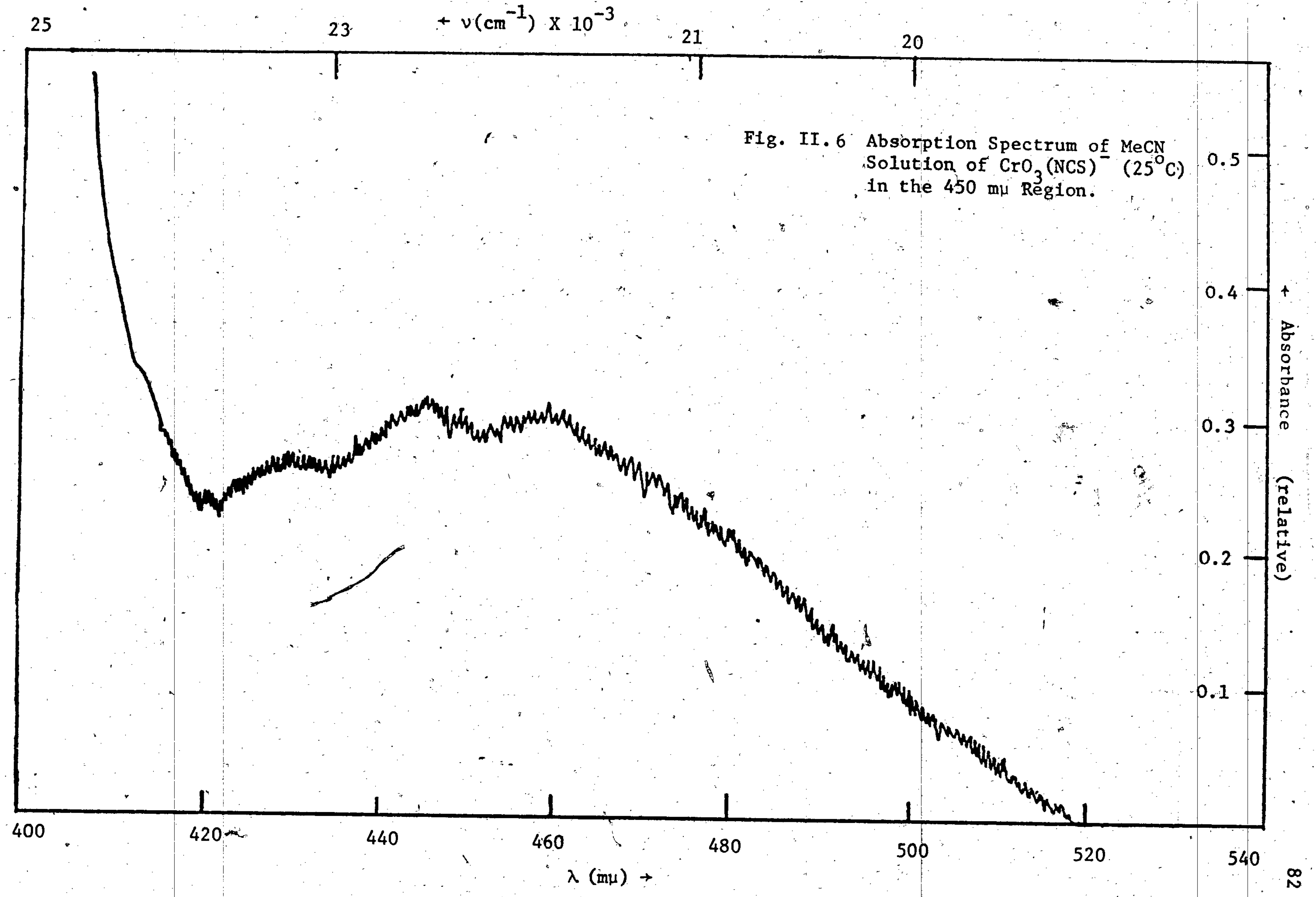


Fig. II.6 Absorption Spectrum of MeCN Solution of $CrO_3(NCS)^-$ (25^oC) in the 450 mμ Region.

suggested that this weak transition is a $^1A_1 \rightarrow {}^1T_1$, corresponding to $(t_1^5e^1)$,[92,95,96] which is electric-dipole forbidden in the T_d point group.

In the C_{3v} ($LiClO_4 \cdot 3H_2O/LiMnO_4 \cdot 3H_2O$[96] and $K_3Na(SO_4)_2/Na_2CrO_4$[95]) and the C_3 ($Ba(ClO_4)_2 \cdot 3H_2O/Ba(MnO_4)_2 \cdot 3H_2O$[96] and $LiKSO_4/K_2CrO_4$[95]) site symmetries, however, the $\perp$ component ($A_1 \rightarrow E$) and both the $\perp$ component ($A_1 \rightarrow E$) and the $||$ component ($A_1 \rightarrow A_1$) transitions respectively, have been observed and shown to be electric-dipole allowed. Because these observations are supposed to reflect the site effects,[97] they provide further support for the assignment $^1A_1 \rightarrow {}^1T_1$ for the parent T_d ion. Collingwood and coworkers,[98] who also support the assignment, have shown, from the dipole strengths and site splittings, that the intensity of this band arises from the mixing of the $^1T_1$ with the $^1T_2$ states induced by the trigonal field.[96,99]

Comparing the low intensity, low energy absorption spectra of CrO_4^{2-}, MnO_4^-, CrO_3F^-, CrO_3Cl^-, CrO_3OR^-[94] and CrO_3L^{n-} (for L^{n-} = Br^-, NCO^-, NCS^-, N_3^-, acetate and NO_3^-), it becomes attractive to think of the substituted ions, CrO_3L^{n-}, in the same way as a slightly perturbed CrO_4^{2-} ion. The perturbation does not seem to have an effect on the energy of this first band regardless of the nature of the substituent. By comparison, this is most probably the $^1A_1 \rightarrow {}^1T_1$ component of the parent T_d ion.

(b) The Absorption Band Centered at 360mμ.

The intense band in the 360 mμ region (400 mμ to 320 mμ)

Table II.14. Electronic Spectra and Vibrational Structure in the 360 mμ (and the 270mμ) Absorption Band of CrO_3L^-. **

	$\bar{\lambda}$, mμ	ν (approx) (cm^{-1})	Splitting $\Delta\bar{\nu}$ (cm^{-1})	ε_{max} (X 10^{-3})
Ph_4AsCrO_3F	435	23,000	-	0.12
	395	25,320	-	
	282	26,180	860	
	371	26,950	770	
	361	27,700	750	
	*352	28,410	710	0.79
	343	29,150	740	
	336	29,760	610	
	329	30,400	640	
	320	31,250	850	
	Average		740	
Ph_4AsCrO_3Cl	435	23,000		0.14
	406?			
	397	25,190	-	
	384.5	26,010	820	
	373.5	26,770	760	
	*363	27,550	780	1.43
	353.5	28,290	740	
	345	28,990	700	
	337	29,670	680	
	328	30,490	820	
	Average		760	
	282(max)			
$KCrO_3NCO$	435	23,000	-	0.13
	407	24,570	-	
	395	25,320	750	
	384.5	26,010	690	
	373.5	26,770	760	
	*363.3	27,530	760	1.32
	354	28,250	720	
	346	28,900	650	
	336.5	29,720	820	
	328	30,490	770	
	Average		740	
	271(max)			
	266sh			
	260sh			
	248			
	237sh			

	$\bar{\lambda}$, mμ	$\bar{\nu}$ (approx) (cm^{-1})	Splitting $\Delta\bar{\nu}$ (cm^{-1})	ε_{max} (X 10^{-3})
Ph_4AsCrO_3NCS	460			
	445			0.19
	430			
	397	25,190	-	
	386.5	25,890	700	
	376	26,600	710	
	*366	27,320	720	1.81
	356	28,090	770	
	347.5	28,770	680	
	338	29,590	820	
		Average	750	
	287 (max)			
$Ph_4AsCrO_3NO_3$				
	435	23,000	-	0.22
	406 ?			
	393	25,500	-	
	382.5	26,100	600	
	371.5	26,900	800	
	*360	27,770	800	1.11
	352	28,400	700	
	342	29,200	800	
		Average	740	
	275 (max)			
$Ph_4AsCrO_3N_3$				
	435	23,000	-	0.26
	407	24,500	-	
	395.5	25,280	710	
	385	25,970	690	
	*375	26,670	700	
	*365	27,400	730	2.16
	356	28,090	690	
	347	28,820	730	
	338	29,590	770	
		Average	720	

	$\bar{\lambda}$, mμ	$\bar{\nu}$(approx), cm^{-1}	Splitting $\Delta\bar{\nu}$ cm^{-1}	ϵ_{max}(X 10^{-3})
Ph_4AsCrO_3Br				
	435	23,000	-	0.23
	408	24,510	-	
	397	25,190	680	
	385.5	25,940	720	
	374.5	26,700	760	
	*365	27,400	700	1.68
	354.5	28,210	740	
	345.5	28,940	730	
	337.5	29,630	690	
	328	30,490	860	
		Average	740	

* The maximum absorption

** All numbers are averages of four determinations.

Acetonitrile solution of Ph_4AsCl has electronic absorption bands at 271, 264, 258 and 253sh mμ.

Allowance was made for overlap between the bands. It was assumed that the first and second bands are symmetrical, that the third band contributes little at the peak of the second, that the first band has a maximum at approximately 440 mμ in all cases, and that the overlap of this with the second band does not extend above 450 mμ.

The uv-visible spectra were also recorded in CH_2Cl_2 at -10°C to try to improve spectral resolution and possibly locate the 0→0 bands, but without success.

Attempts to locate the 0→0 bands (in MeCN or CH_2Cl_2 solutions) by fluorescence spectroscopy were also unsuccessful. The fluorescence band(s) obtained, by employing highest sensitivity, was too weak to allow any unambiguous conclusions to be drawn. (Dr. Steve Lower's help in running the spectra is greatly appreciated.)

exhibits strong distinct progressions of vibrational fine structure (Table II.14). The extinction coefficient at the maximum absorption range between 790 and 2200. The spectra of the CrO_3L^{n-} complexes are similar except for the gradual shift to the red with changes in the electronegativity of the substituent L. Studies of the polarized absorption spectra of mixed crystal systems of CrO_4^{2-} and MnO_4^- (C_{3v} and C_3 site symmetries)[95] assigned the structured high intensity absorption to electric dipole allowed transition $^1A_1 \rightarrow {}^1T_2$. The data on the dichroism of $KCrO_3Cl$ and calculations[92] on $KCrO_3F$ and $KCrO_3Cl$ indicate that the transition in CrO_3L^{n-} ions (C_{3v} symmetry) involves a transition from the $^1A_1$ ground state to an excited E state. The fact that only $^1A_1 \rightarrow {}^1E$, and not both $^1A_1 \rightarrow {}^1E$ and $^1A_1 \rightarrow {}^1A_1$ transitions, is observed is not well understood. Some difficulties have been encountered[96,99] in resolving these peaks in the spectra of the MnO_4^- and CrO_4^{2-} ions.

The vibrational fine structure in the 360 mμ band is ascribed to the coupling of the electronic transition with the $\nu_{sym}CrO_3$ since all Cr-L vibrations are below 650 cm^{-1} and the $\nu_{sym}(CrO_3)$ transforms as the totally symmetric representation A_1. By analogy with assignments of the vibrational progression in CrO_4^{2-}[100] and MnO_4^-[96] the fine structure, which exhibit an average interval of between 720 and 760 cm^{-1} in CrO_3L^{n-} complexes, has been assigned to the totally symmetric stretching frequency of the CrO_3 group in the excited state. In the ground state of the CrO_3L^{n-} anion, the frequency of this mode ranges from 884 - 910 cm^{-1} (see Table II.13). The 16% reduction is therefore ascribable to the fact that a non-bonding electron is transferred to an antibonding orbital. The

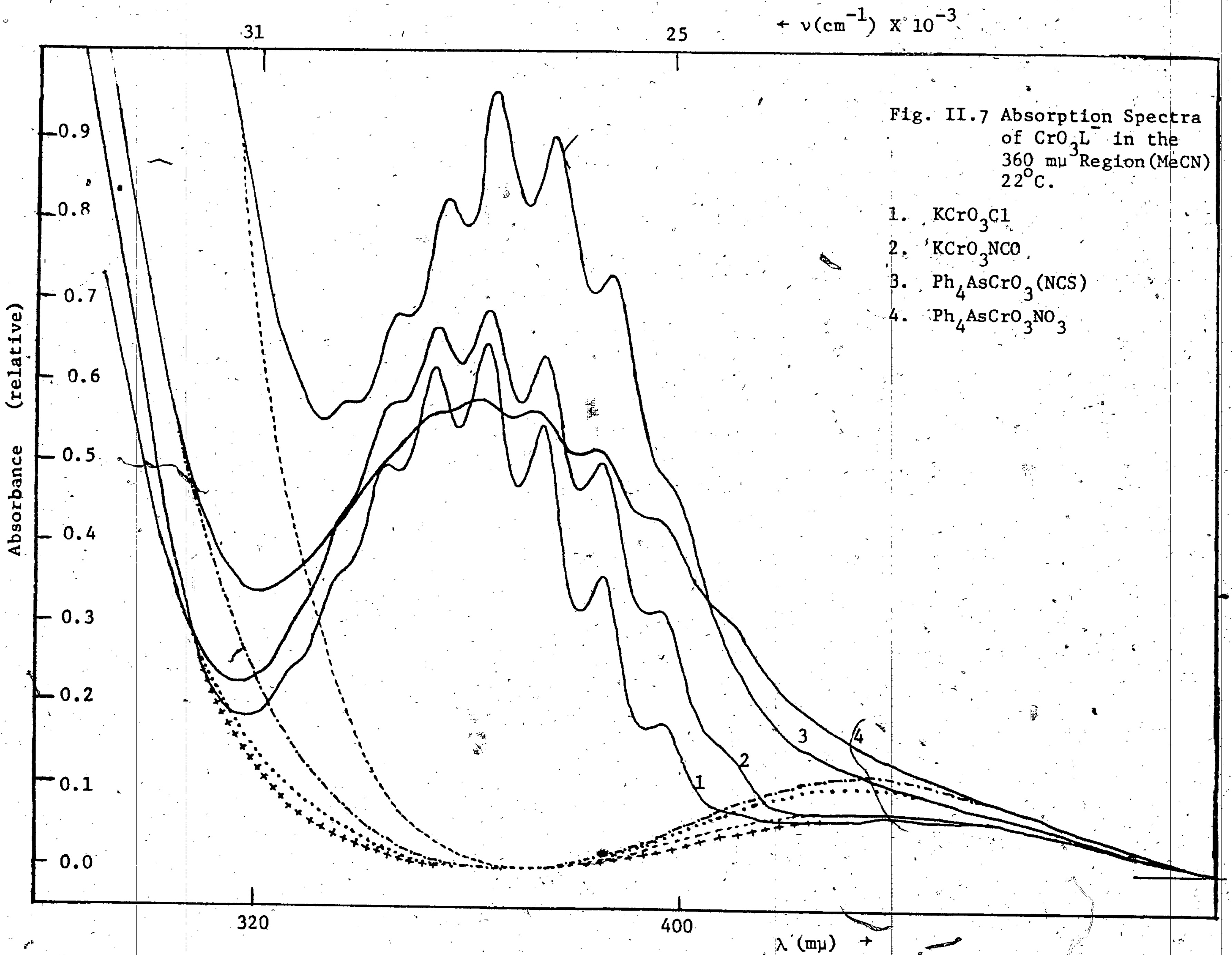


Fig. II.7 Absorption Spectra of CrO_3L^- in the 360 mμ Region (MeCN) 22°C.

1. $KCrO_3Cl$
2. $KCrO_3NCO$
3. $Ph_4AsCrO_3(NCS)$
4. $Ph_4AsCrO_3NO_3$

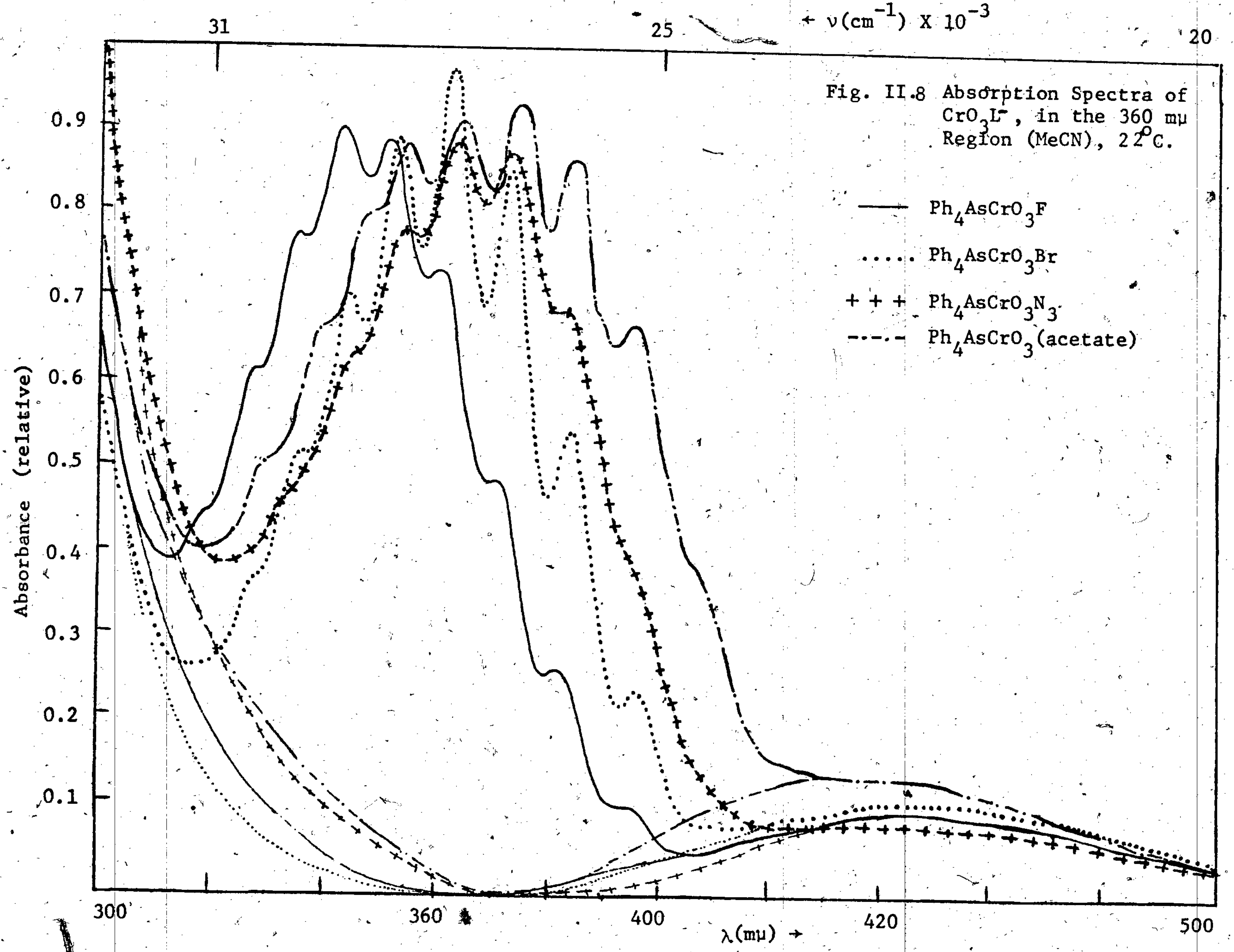


Fig. II.8 Absorption Spectra of CrO_3L^-, in the 360 mμ Region (MeCN), 22°C.

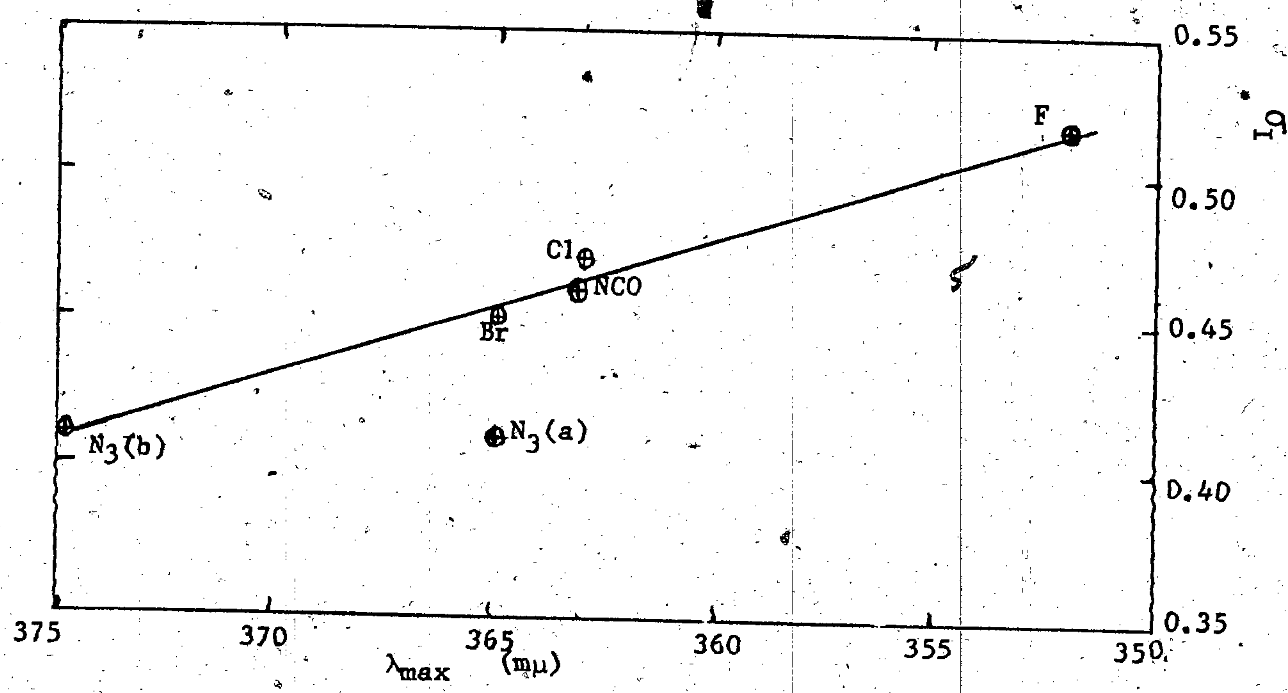
CrO_4^{2-} ion is reported[100] to show a comparable decrease, with a change from the ground state $\nu_{sym}(CrO_3)$ value of 847 cm^{-1} to 780 cm^{-1} in the excited state.

Vibrational fine structure in solution spectra is only rarely observed; gas phase or more special techniques are required for its detection. It is noteworthy that such vibrational detail has been observed here, in view of solvent broadening effects and the low quality of resolution attainable in solution at 22°C. Our attempts to improve spectral resolution or obtain the fluorescence spectra of CrO_3L^- species failed to give information on the energy of the 0 → 0 bands.

While the position (ν_{max}, or λ_{max}) of each absorption maximum may not be important, the magnitude of shifts, due to changes in the character of the substituent donor atom have been correlated[101] with the electronic properties of the ligands. For instance, the band at 350mμ in CrO_3OH^-, $CrO_3PO_4^{3-}$, and $CrO_3SO_4^{2-}$[73] (all of which have Cr-O bonds) is shifted to 360mμ in CrO_3Cl^- (with a Cr-Cl bond), 380mμ in $CrO_3(NCS)^-$ (with either a Cr-N or Cr-S bond) and to 390mμ in $CrO_3S_2O_3^{2-}$[2] (assumed to have a Cr-S bond). In the case of CrO_3L^{n-}, for L = NCS^-, NO_3^-, N_3^- and $S_2O_3^{2-}$, intraligand transitions may influence the positions of band maxima.

One of the established trends[102] for the energy of a charge-transfer band is that for a given metal, the energy increases with the negative charge on the central atom. So that the red shift in the CrO_3L^{n-} spectra probably suggests a decrease in the formal negative charge on the Cr. In terms of bonding, these effects may be correlated with the inability of Cr to accept more charge. A correlation of λ_{max} with Hammett σ_I constant (inductive substitient constant for alphatics) - Fig.11.9 gives a straight line.

Figure II.9 Plot of Hammett Inductive Substituent Constant σ_I Versus λmax observed for CrO_3L^- Derivatives



Thus one effect of the substituent L, in CrO_3L^- may be to decrease the chromium-oxygen dπ-pπ interaction by making Cr less able to accommodate more charge from O pπ-electrons. This can be accomplished if L bonds to Cr mainly by σ-electron pair donation. This could explain why the shifts in the present spectra are larger than those reported for the complexes $CrO_3.OR^{n-}$ for R =alkoxide,[94] PO_3, SO_3, NO_2, CrO_3, ... etc.[73], where the electronic properties of the donor atom (O) do not alter much. Figure II.10 shows that a linear relationship exists between the electronegativities of the substrates: F(3.9), Cl (3.0), Br (2.8)[104], iso-NCO(3.0), iso-NCS(2.6) and N_3(2.7)[105], and the absorption maxima (ν_{max} or λ_{max}). This supports the proposal by Jörgensen [106] that the energy of a charge-transfer band is directly proportional to the electronegativity difference between the ligand and the central atom.

Because these are charge-transfer transitions in which the central metal could be considered "reduced" and the donating ligand "oxidized" in the excited state,[103] the shifts in the absorption spectra would be expected to parallel the ease of oxidation of the ligand system. The participation of substituent non-bonding orbitals in the $e(^1A_1)$ donor level has been suggested,[94] so that for the substrates whose oxidation products and redox potentials are known,[107]

$$2L^- = L_2 + 2e^- \text{ (for L = F, Cl, Br and NCS)} \qquad [15]$$

the relationship given in Fig.11.11, can be drawn.

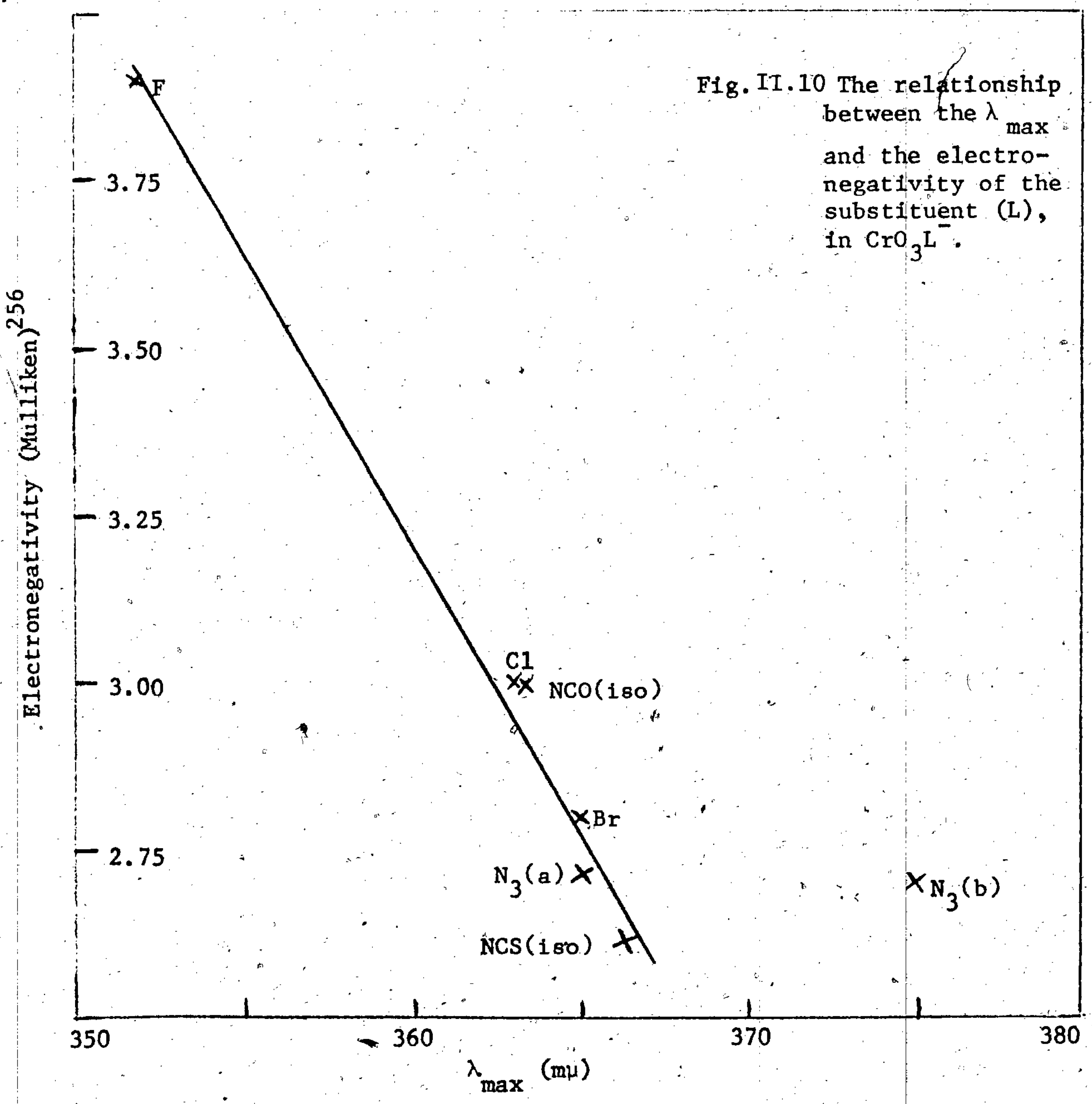


Fig. II.10 The relationship between the λ_{max} and the electronegativity of the substituent (L), in CrO_3L^-.

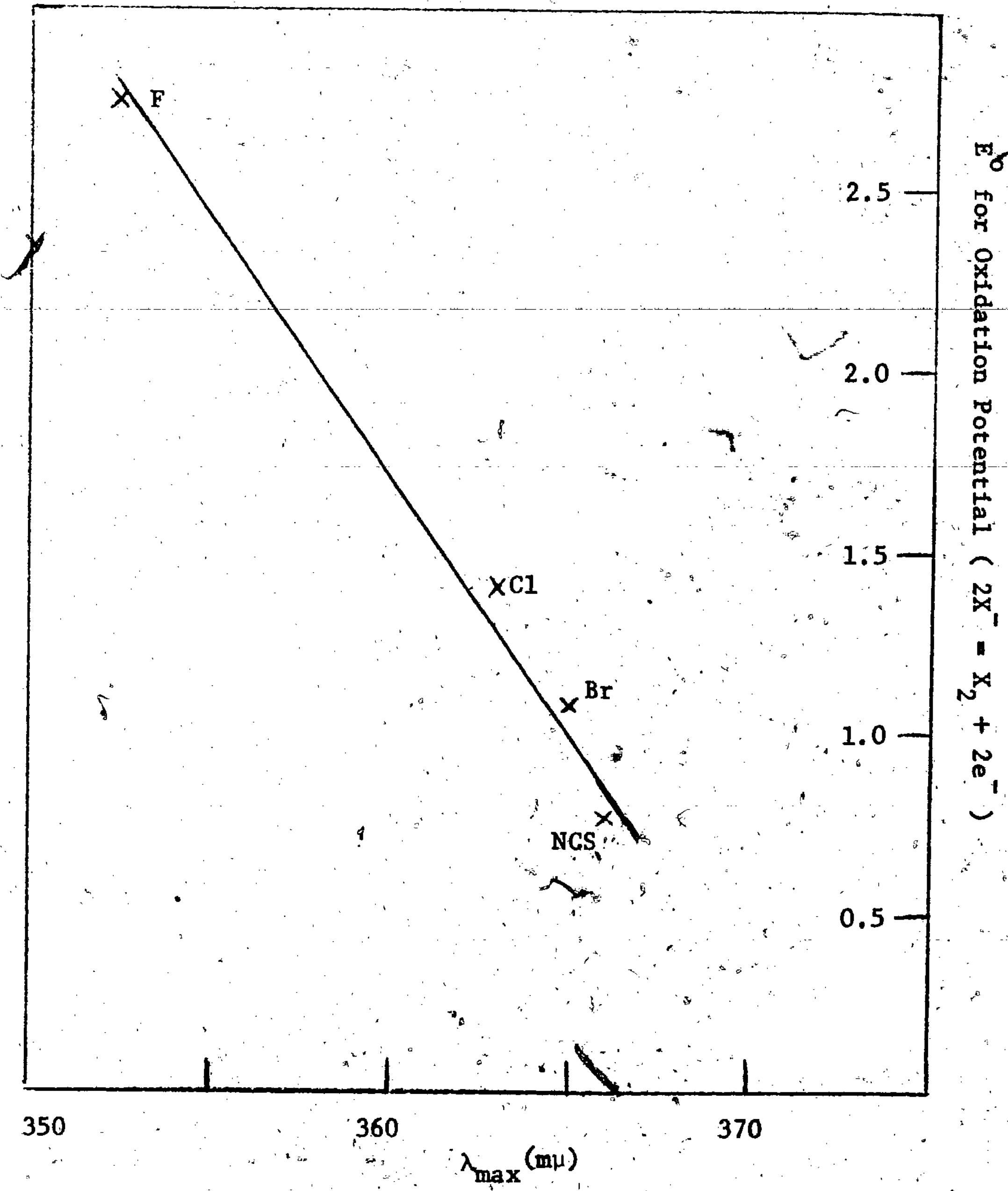


Fig . II.II Dependence of Absorption maxima (λ_{max}) on the Oxidation Potentials of the the substituents ($2X^- = X_2 + 2e^-$)

(c) The Absorption Band Centered at 270mμ.

The third set of bands (the 270mμ region) are weakly structured, very intense and appear in the UV end of the spectum (36,000 - 41,000 cm^{-1}) where they are generally overlaid by cation and intraligand absorptions (especially where L^{n-} = NO_3^- [108], NCS^- [109], $S_2O_3^{2-}$ [109] and NCO^- [110]). Subtracting out the cation absorptions suggests that this band is probably split into three or four components; the split could be due to lowered symmetry or more than one transition in the CrO_3L^{n-} complexes. By comparison with studies on the MnO_4^- and CrO_4^{2-}, the most probable assignment is a $^1A_1 \rightarrow {}^1T_2$ transition, in the T_d ion which splits into $^1A_1 \rightarrow {}^1A_1$ and $^1A_1 \rightarrow {}^1E$ components in the C_{3v} symmetry. Another strong band with no vibrational structure is observed in the 240mμ region. The corresponding band in the spectrum of CrO_4^{2-} has been assigned to a $^1A_1 \rightarrow {}^1T_1$ transition, in T_d symmetry, which splits into an allowed $^1A_1 \rightarrow {}^1E$ ($\perp$ component) and a forbidden $^1A_1 \rightarrow {}^1A_2$ ($\parallel$ component) transitions in C_{3v} symmetry.

Summary

Methathetical procedures were used to synthesize a series of new anionic monosubstituted trioxochromium(VI) complexes, CrO_3L^{n-}. The compounds were characterized by chemical analysis, vibrational and electronic spectroscopy. Evidence for substituent-dependent Cr-O bonding interactions was found in the ground (IR and Raman) and excited (electronic spectra) states of these ions, suggesting that the amount of Cr–O bonding increases with decreasing Cr – L bonding (σ- or π-) interaction, at least for the series where L^{n-} = F^-, Cl^- and Br^-.

CHAPTER THREE

PREPARATION AND CHARACTERIZATION OF SUBSTITUTED OXODIPEROXOCHROMIUM(V1) COMPLEXES

III.I INTRODUCTION

The best characterized peroxo complexes of chromium form three series of derivatives in aqueous solution depending on the pH conditions. The preparation and structural properties of the solid compounds $M^{I}_3Cr^{V}(O_2)_4$, $Cr^{IV}(O_2)_2L_3$ and $Cr^{VI}O(O_2)_2L$ were discussed in Chapter 1. In light of the complexity of the aqueous solution chemistry of chromium, the structural studies of chromium(VI) peroxo complexes require the elimination or stringent control of hydrolytic reactions. It is also apparent from preceeding accounts that certain donor molecules or ions may stabilize the $CrO(O_2)_2$ moiety. In the absence of water, for instance, substitution in oxodiperoxochromium(VI) complexes, $CrO(O_2)_2\cdot$donor, appears to follow the sequence.

$$H_2O < \text{ether} < \text{py, bipy, phen, } OH^-, Cl^-.$$

The kinetics of these substitution reactions have not received much attention, probably due to the instability of perchromic acid in aqueous solution, and to the extremely rapid formation of adducts.

Since solutions of these adducts in non-aqueous donor solvents are relatively stable, it appeared possible to study substitution reactions under these conditions. The use of solvents such as $CHCl_3$ or MeCN has the added advantage that these solvent are easily purified, have lower melting temperatures and, because of their low polarity, ionic products can be isolated by cooling or by precipitating with hydrocarbons. The following new oxodiperoxochromium(VI) complexes $CrO(O_2)_2.L$ for $L = NCO^-$, NCS^-, NO_3^-, N_3^-, F^- and $OPPh_3$ have now been synthesized, and studied spectroscopically.

III.2 EXPERIMENTAL

(a) Apparatus and Materials

In addition to the apparatus and materials described in the preceeding chapter, reagent grade pyridine used was first dried with KOH, redistilled and stored over molecular sieves. Nitromethane was spectroquality. Ph_4AsNO_3 was prepared by either precipitating out the chloride in Ph_4AsCl, as AgCl, with $AgNO_3$ dissolved in dilute HNO_3 and then evaporating the solution, or by acidifying the PhAsOH solution with 1M HNO_3 and evaporating. $OPPh_3$ was purified by dissolving in hot benzene and adding petroleum ether until the first appearance of turbidity, then slowly cooling in ice. The other phosphine oxides, $OPCl_3$ and $OPPhCl_2$ were reagent grade.

(b) Syntheses of Substituted Oxodiperoxochromium(VI) Complexes

Because most of the oxodiperoxochromate(VI) complexes prepared in this study were obtained by substituting the chloride in $Ph_4AsCrO(O_2)_2Cl$, it is appropriate to describe a new and convenient method used in the preparation of the $Ph_4AsCrO(O_2)_2Cl$. The new method uses $CrO(O_2)_2py$, instead of Ph_4AsCrO_3Cl[4], as the starting material.

(i) Oxodiperoxopyridinochromium(VI) Complex, $CrO(O_2)_2py$,

The solid $CrO(O_2)_2py$ was prepared by established methods.[113] The blue needle-like crystals of $CrO(O_2)_2py$ formed in aqueous solution were then washed three times with cold (10°C) distilled water and the excess water pumped off on the aspirator. The slightly wet $CrO(O_2)_2py$ precipitate was extracted with $CHCl_3$ and reprecipitated by using dry low boiling petroleum ether. If not exposed to light, shock or higher than 0°C temperatures, the pyridine adduct can be kept for longer than two weeks.

Analysis (%), calculated for $CrO(O_2)_2py$: Cr, 24.6; C, 28.4; H, 2.4 and N, 6.6. Found: Cr, 24.3; C, 28.2; H, 2.4 and N, 6.3.

(ii) Tetraphenylarsonium Oxodiperoxochlorochromate(VI) Complex, $Ph_4AsCrO(O_2)_2Cl$

The $Ph_4AsCrO(O_2)_2Cl$ can be conveniently prepared at room temperature by adding a stoichiometric amount of reagent grade Ph_4AsCl, dissolved in chloroform, to the chloroform solution of freshly prepared $CrO(O_2)_2py$.

$$CrO(O_2)_2py + Ph_4AsCl \longrightarrow Ph_4AsCrO(O_2)_2Cl + \text{pyridine} \quad [1]$$

The reaction is fast and clean. The blue needle-like crystals were washed with dry low boiling petroleum ether and air dried.

Analysis (%), calculated for $Ph_4AsCrO(O_2)_2Cl$: Cr, 9.7; C, 52.2; H, 3.8 and Cl, 6.4. Found: Cr, 9.5; C, 52.3; H, 3.6 and Cl, 6.5.

Magnetic susceptibility measurement showed that the compound has a similar magnetism (χ_m=4.20 x 10^{-4} cm^3 $mole^{-1}$) to other Cr(VI) compounds.[111,112] The electrolytic conductivity, measured in nitromethane, was 108.6 ohm^{-1} cm^2, and corresponds to a 1:1 electrolyte since values of 70 - 120, 250 and 300 ohm^{-1} cm^2 have been reported for 1:1, 1:2 and 1:3 electrolytes respectively.[115]

(iii) Tetraphenylarsonium Oxodiperoxocyanatochromate(VI) Complex, $Ph_4AsCrO(O_2)_2NCO$

$Ph_4AsCrO(O_2)_2Cl$ (1.002 gm) dissolved in 10 ml acetonitrile reacts with a slurry of AgNCO (0.272 gm), also in 10 ml acetonitrile, to form

$$Ph_4AsCrO(O_2)_2Cl + AgNCO \xrightarrow{-10^oC} Ph_4AsCrO(O_2)_2NCO + AgCl \quad [2]$$

a white precipitate of silver chloride (0.0645 gm of Cl was found compared to 0.0644 gm, expected) and a royal blue solution of $Ph_4AsCrO(O_2)_2NCO$. The AgCl was filtered off and the $Ph_4AsCrO(O_2)_2NCO$ in the filtrate precipitated using ice-cold 1:2 benzene-hexane mixture. The crystals were filtered, washed with more benzene-hexane solution and dried by pumping on the vacuum line. The compound can be recrystallized from chloroform by addition of cyclohexane or petroleum ether.

Analysis (%), calculated for $Ph_4AsCrO(O_2)_2NCO$: Cr, 9.3; C, 53.9; H, 3.6 and N, 2.5. Found: Cr, 9.6; C, 54.1; H, 3.5 and N, 2.5.

This blue crystalline compound decomposed slowly in the dark at room temperature to a greenish gray (mixture of yellow and royal blue) powder within approximately three months, and eventually turned completely yellow.

(iv) Tetraphenylarsonium Oxodiperoxoazidochromium(VI) Complex, $Ph_4AsCrO(O_2)_2N_3$.

$Ph_4AsCrO(O_2)_2Cl$ (0.750 gm) dissolved in 10 ml of MeCN was treated, at -10°C, with an acetonitrile solution of sodium azide (0.124 gm, finely ground).

$$Ph_4AsCrO(O_2)_2Cl + NaN_3 \longrightarrow Ph_4AsCrO(O_2)_2N_3 + NaCl \qquad [3]$$

The mixture was allowed to stir for 5 hr. The white precipitate containing NaCl was filtered off and the filtrate treated with 1:2 benzene-hexane mixture to precipitate out the blue crystals containing $Ph_4AsCrO(O_2)_2N_3$.

Analysis (%), calculated for $Ph_4AsCrO(O_2)_2N_3$: Cr, 9.3; C, 51.7; H, 3.6 and N, 7.5. Found: Cr, 9.0; C, 52.0; H, 3.6 and N, 7.6.

(v) Tetraphenylarsonium Oxodiperoxothiocyanatochromium(VI) Complex, $Ph_4AsCrO(O_2)_2NCS$.

When a solution of $Ph_4AsCrO(O_2)_2Cl$ (0.6061 gm) in 10 ml of acetonitrile was stirred, at -10°C, with NH_4NCS (0.0835 gm, finely ground) dissolved in a minimum amount of MeCN, the mixture slowly (in minutes) produced white crystalline precipitate and pale sky-blue solution. After about an hour, the ammonium chloride precipitate was filtered off

$$Ph_4AsCrO(O_2)_2Cl + NH_4NCS \longrightarrow Ph_4AsCrO(O_2)_2NCS + NH_4Cl \quad [4]$$

and the $Ph_4AsCrO(O_2)_2NCS$ precipitated from the solution by adding ice-cold 1:2 benzene-hexane mixture. It is important that both solvents be pure and dry.

Analysis (%), calculated for $Ph_4AsCrO(O_2)_2NCS$: Cr, 9.0; C, 52.4; H, 3.5; and N, 2.5. Found Cr, 8.8; C, 52.3; H, 3.5 and N, 2.6.

Because the $Ph_4AsCrO(O_2)_2NCS$ compound decomposes so easily when in contact with most solvents, it was necessary to precipitate in the cold, and pump dry as soon as the reaction was complete. The analytical results and spectral studies were obtained from freshly prepared samples. The reaction of MeCN solutions of either $Ph_4AsH(NCS)_2$[114] with $CrO(O_2)_2.py$, or AgNCS with $Ph_4AsCrO(O_2)_2Cl$, failed to produce $Ph_4AsCrO(O_2)_2NCS$, and no precipitate of AgCl was detected.

(vi) Tetraphenylarsonium Oxodiperoxonitratochromium(VI) Complex, $Ph_4AsCrO(O_2)_2NO_3$.

Numerous analyses of the Cl content of $Ph_4AsCrO(O_2)_2Cl$ have been conducted by reacting with solutions of $AgNO_3$ in MeCN. 0.0643 gm of Cl, as AgCl, was obtained from 1gm of $Ph_4AsCrO(O_2)_2Cl$ - 0.0644 gm was expected. The $Ph_4AsCrO(O_2)_2NO_3$ solution in MeCN is stable for up to 24 hr without much apparent decomposition, when kept in the dark at $<-10^\circ C$. The metathetical reaction is given below.

$$Ph_4AsCrO(O_2)_2Cl + AgNO_3 \longrightarrow Ph_4AsCrO(O_2)_2NO_3 + AgCl \quad [5]$$

When the silver chloride precipitation was carried out at room temperature, the solution of $Ph_4AsCrO(O_2)_2NO_3$ gradually turned yellow. Attempts to precipitate the $Ph_4AsCrO(O_2)_2NO_3$ by adding CCl_4, petroleum ether and mixed solvents have also failed. But when the freshly prepared $Ph_4AsCrO(O_2)_2NO_3$

P

solution (at -20°C) was treated with chilled dry diethyl ether, sky blue fluffy precipitate forms. The precipitate was washed twice with more ether and filtered under nitrogen. The ^{1}H NMR spectra of this compound redissolved in $CDCl_3$ (-20°C) showed no other resonances except for the one assignable to phenyl hydrogens. This weakens the possibility of having formed $CrO(O_2)_2.OEt_2$ or $CrO(O_2)_2.NCMe$, in stead of $CrO(O_2)_2NO_3^-$. $CrO(O_2)_2.OMe_2$ is known and reported[116] to be stable at -50°C and explode above -30°C.

The blue solid is slightly more stable (at 25°C) than the solution in MeCN or $CHCl_3$ which readily decomposes, with effervescence, to an orangish-yellow solution. These results suggest the possibility of the reactions

$$Ph_4AsCrO(O_2)_2NO_3 + \text{solvent} \longrightarrow Ph_4AsCrO(O_2)_2NO_3 \leftarrow \text{solvent}. \quad [6]$$

$$Ph_4AsCrO(O_2)_2NO_3 \leftarrow \text{solvent} \longrightarrow Ph_4AsCrO_3NO_3 + (\text{solvent} + O_2) \quad [7]$$

occuring (where solvent = MeCN or OEt_2) in solution instead of

$$Ph_4AsCrO(O_2)_2NO_3 + \text{solvent} \longrightarrow Ph_4AsNO_3 + CrO(O_2)_2.\text{solvent}. \quad [8]$$

The freshly prepared solid gave C, 51.3; H, 3.6; N, 2.0; compared to C, 50.0; H, 3.46; N, 2.4 expected for $Ph_4AsCrO(O_2)_2NO_3$.

Other attempts at preparing the $CrO(O_2)_2NO_3^-$ anion involved treating $CHCl_3$ solutions of the pyridine adduct, $CrO(O_2)_2py$, with Ph_4AsNO_3; but this was inconclusive.

Analysis (%), calculated for $Ph_4AsCrO(O_2)_2NO_3$: C, 50.0; H, 3.46; N, 2.4.
Found: C, 52.4; H, 3.8 and N, 0.5.

Unfortunately, the infrared spectra of the $CrO(O_2)_2NO_3^-$ anion in either product was unobtainable because of decomposition.

Treating a MeCN solution of $CrO(O_2)_2py$ with $AgNO_3$, also in MeCN, produced red-brown precipitate found to contain Ag_2CrO_4.

(vii) Oxodiperoxo(triphenylphosphine oxide)chromium(VI) Adduct, $CrO(O_2)_2.OP(C_6H_5)_3$.

The initial interest in preparing the oxodiperoxochromium(VI)-phosphine oxide adducts, $CrO(O_2)_2.OPL_3$, was to study the effects of coordination on the phosphorus-oxygen stretching frequency and on the ^{31}P nuclear magnetic resonance frequency.

100 ml of ether was added to 100 ml of aqueous CrO_3 (5.0 gm). When the mixture had acquired the temperature of the salt-ice bath, 25ml of 5% H_2O_2 solution was added dropwise with stirring. The blue colour of $CrO(O_2)_2.OEt_2$ developed in the ether layer. When the reaction was complete, the ether layer was extracted and washed twice with 50 ml portions of chilled distilled water. The $OPPh_3$ solution in 1:2 chloroform-ethyl ether mixture was added with stirring to the ether solution. The use of less than stoichiometric amount of $OPPh_3$ safeguards against excess ligand. The mixture was allowed to react in the cold (≈0°C) for about three minutes.

$$CrO(O_2)_2.OEt_2 + OPPh_3 \longrightarrow CrO(O_2)_2.OPPh_3 + Et_2O \qquad [9]$$

The solid $CrO(O_2)_2.OPPh_3$ was then isolated by adding chilled low boiling petroleum ether and collecting only the first crop of crystals. The crystals which were washed with more petroleum ether, could be kept for months at -20°C. Analysis (%), calculated for $CrO(O_2)_2.OPPh_3$: Cr, 12.7; C, 52.7; H, 3.7. Found: Cr, 12.7; C, 52.5 and H, 3.7.

Attempts to prepare $CrO(O_2)_2.OPPh_3$ by reacting $CrO(O_2)_2py$ in chloroform with $OPPh_3$ also dissolved in chloroform failed, probably, because the pyridine is more strongly coordinated than the $OPPh_3$ would be. The ^{31}P NMR could not be investigated because of the low solubility and stability of $CrO(O_2)_2.OPPh_3$ in most non-coordinating solvents, e.g. chloroform, ether, benzene or dichloromethane.

(viii) Tetraphenylarsonium Oxodiperoxofluorochromium(VI) Complex. $Ph_4AsCrO(O_2)_2F$

When the freshly prepared equal molar mixtures (at -20°C) of $Ph_4AsCrO(O_2)_2Cl$ - Et_4NF or $Ph_4AsCrO(O_2)_2NO_3$ - Et_4NF were immediately treated with chilled low boiling pet ether, blue crystals fell out. The fluorine, carbon, hydrogen and nitrogen analyses (%) gave C, 55.3, F, 3.3, H. 3.9 and N, 0.0 for the first mixture, and C, 54.6, F, 3.0, H, 4.0 and N, 0.0 for the second mixture. $Ph_4AsCrO(O_2)_2F$ requires C, 53.8, F, 3.56. H, 3.8; $Ph_4AsCrO(O_2)_2Cl$ requires, C, 52.4, H, 3.6; and $Ph_4AsCrO(O_2)_2NO_3$ requires C, 50.0, H, 3.5 and N, 2.4. Because the room temperature infrared spectra showed no solvent, NO_3 or Cr-Cl (435 cm^{-1}) vibrations, these analytical results support the formulation, $Ph_4AsCrO(O_2)_2F$. From these observations, it is concluded that $Ph_4AsCrO(O_2)_2F$ is unstable but can probably be prepared and studied at < -20°C.

(ix) Other Attempts to Prepare $CrO(O_2)_2.L$ Complexes.

Other Phosphine Oxides.

Attempts to prepare $CrO(O_2)_2.OPCl_3$ via the method used for $CrO(O_2)_2.OPPh_3$ failed. Adding $OPCl_3$ to $CrO(O_2)_2py$ dissolved in chloroform and allowing the mixture to sit for 3 minutes, at 0°C, gave a solution which was blue for about five minutes; when low boiling petroleum ether was added to the mixture at 2 minutes, immediate decomposition to a greenish-yellow powder resulted. A similar reaction occurred between $OPCl_3$ and $CrO(O_2)_2 \cdot OEt_2$, producing an olive green ether-insoluble oil. The same reaction and colour were observed when $OPPhCl_2$ was used. Allowing the oil to sit in air yields water-insoluble green crystals. The analytical results (28.78%C and 3.82%H) suggest that the compound, probably a Cr(III) complex, has other ligands containing carbon and/or hydrogen atoms in addition to $OPPhCl_2$.

Trifluoro β-diketones

Attempts to prepare $CrO(O_2)_2L$, for L = TAA, TTA, BTA, and NTA, failed. When ethereal solutions of $CrO(O_2)_2 \cdot OEt_2$ or $CrO(O_2)_2py$ were treated with solutions of the ligand (L) in ether, the mixtures underwent gradual decomposition.

Monosubstituted Pyridines (NC_5H_4X, for X = F, Cl, Br and NH_2)

Using the procedure for the preparation of $CrO(O_2)_2py$ to prepare the 2-fluoropyridine analog failed. The initially blue solution formed in the aqueous solution readily decomposed, with effervescence, to a brown solution. When freshly prepared 2-fluoropyridine was added to an ether solution of $CrO(O_2)_2 \cdot OEt_2$, the blue solution was stable for about 1 hr but the ^{19}F NMR spectra of the mixture was identical to that of fresh 2-fluoropyridine. Similar decomposition reaction occured when attempts were made to prepare the $CrO(O_2)_2 \cdot L$ adducts with 2- and 3- monosubstituted pyridines, NC_5H_4X for X = Cl, Br or NH_2, using the methods above.

Bromide, $CrO(O_2)_2Br^-$.

Treating a chloroform solution of $CrO(O_2)_2py$ with Ph_4AsBr or reagent grade n-$BuPh_3PBr$ failed to produce $CrO(O_2)_2Br^-$ because of competing decomposition reactions. But the visible spectra of $Ph_4AsCrO(O_2)_2NCS$ in MeCN is similar to that of a solution containing 1:1 $Ph_4AsCrO(O_2)_2NCS$ and Et_4NBr, indicating that the $CrO(O_2)_2Br^-$ anion probably exists. The pale blue color of $Ph_4AsCrO(O_2)_2NCS$ went noticeably darker, although the shift in the visible spectrum was only from 569 to 563 mμ.

Acetate, $CrO(O_2)_2(OAc)^-$

When an acetonitrile solution of $Ph_4AsCrO(O_2)_2Cl$ was treated with a slurry of silver acetate, in MeCN at 22°C, a quantitative yield of AgCl was obtained. But the $Ph_4AsCrO(O_2)_2(OAc)$ solution gradually turned grayish blue and finally yellow.

$$Ag(OAc) + Ph_4AsCrO(O_2)_2Cl \longrightarrow AgCl + \underset{\text{(decomposes)}}{Ph_4AsCrO(O_2)_2(OAc)} \qquad [9]$$

Attempts to precipitate out the freshly prepared complex $Ph_4AsCrO(O_2)_2(OAc)$ failed.

III.3 INFRARED SPECTRA OF SUBSTITUTED OXODIPEROXOCHROMIUM(VI) COMPLEXES

$CrO(O_2)_2L$

The infrared and Raman spectra of numerous complexes containing the dioxygen group have been studied in the hope of making structural assignments. Generally a persistent band observed in the region 800 - 900 cm^{-1} has been considered "characteristic" of the O-O stretch.[117] In the present study, however, only a few of the peroxo complexes appear to have infrared absorptions in the 800 - 900 cm^{-1} region. Considering the assignments in the literature, it is obvious that earlier interpretations of the IR spectra of peroxo complexes have not been totally conclusive.

(a) Oxodiperoxopyridinochromium(VI) Complex

The IR spectra of pyridine[118] and pyridino complexes[119, 120] have been extensively studied and assignments made for most of the observed bands. As was the case in the other studies,[119] the vibrational spectrum of the coordinated pyridine in $CrO(O_2)_2py$ (Fig. III.2) is qualitatively different from that of the free ligand (Fig. III.1) by

- the presence of a weak band, assigned to an overtone or a combination, between 1235 and 1250 cm^{-1},
- a shift in the strong band at ≈1580 cm^{-1} to near 1610 cm^{-1},
- and shifts of the 601 and 403 cm^{-1} bands to near 632 and 450(?) cm^{-1},

respectively. The complete spectrum, 200 - 4000 cm^{-1}, of the $CrO(O_2)_2py$ complex is given below Fig. III.2. The spectrum is consistent with that reported,[121] within the region 5000 - 600 cm^{-1}, by Stomberg. The discussion of the spectra will be limited to the identification and assignment of the diagnostic bands.

Fig. III.1 Pyridine(smear).

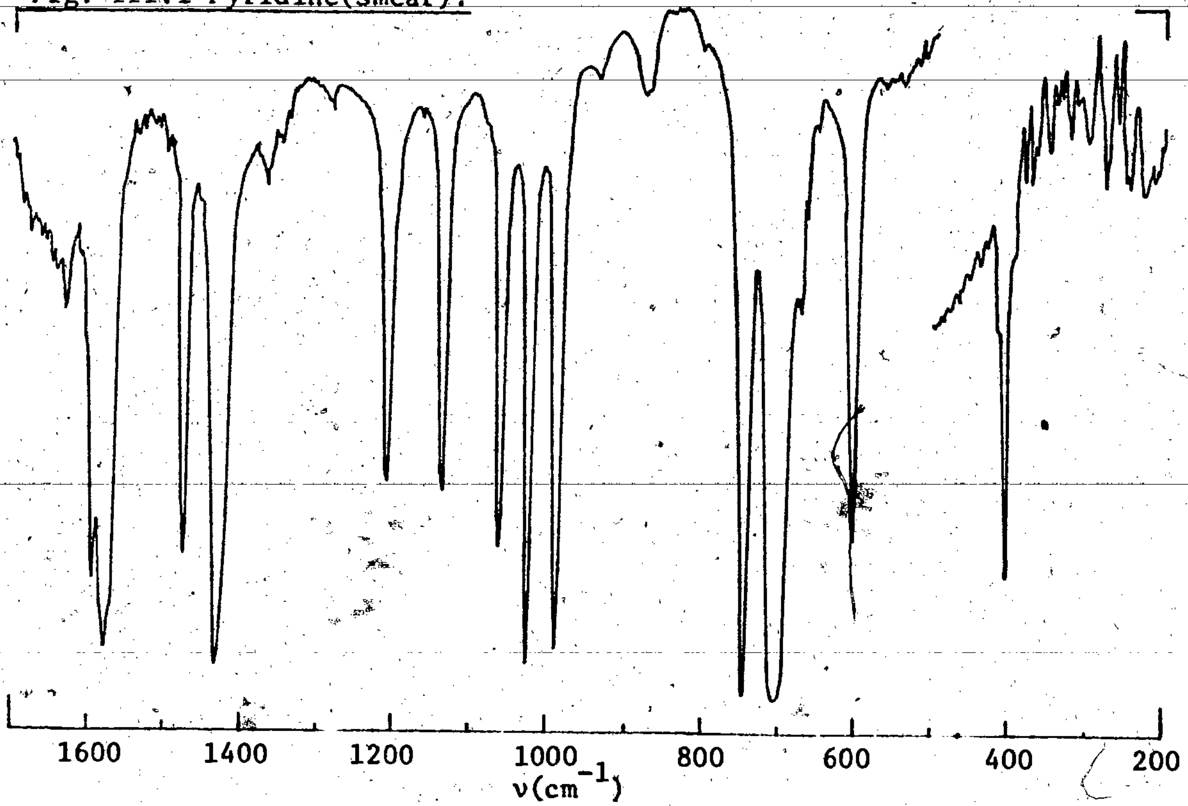
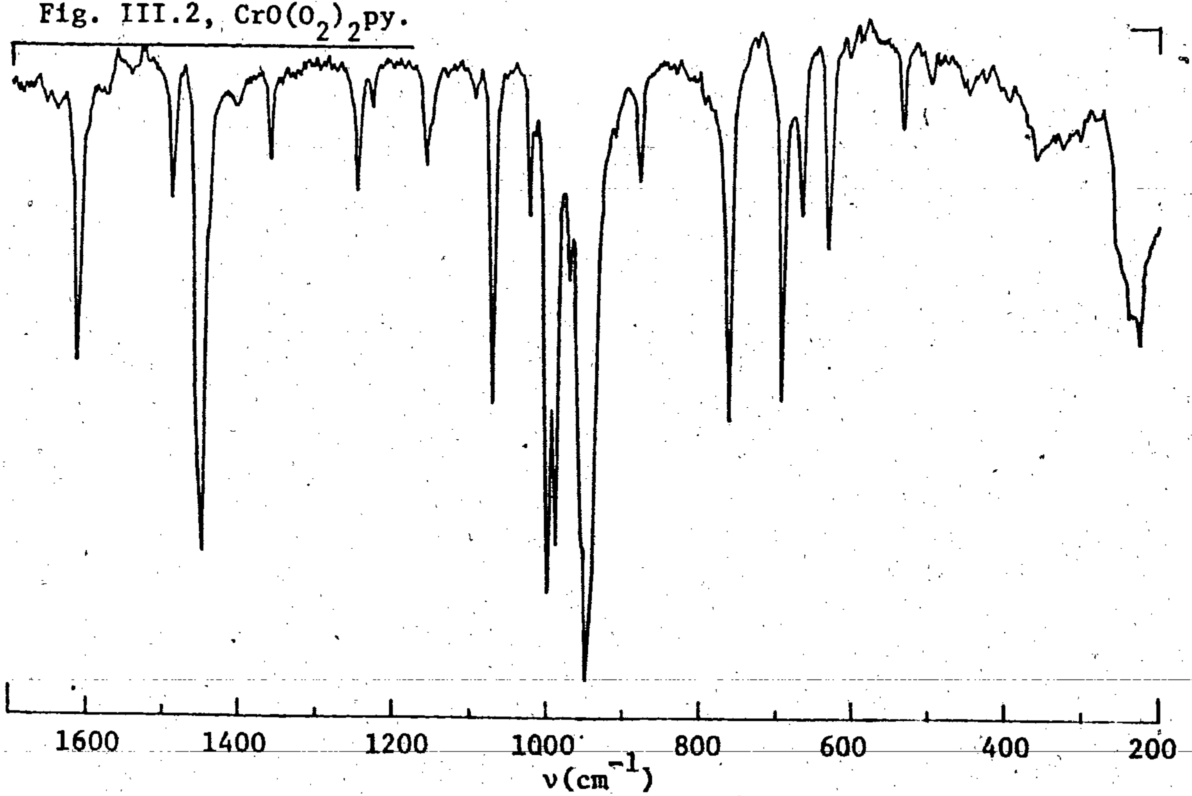


Fig. III.2, $CrO(O_2)_2py$.



$CrO(O_2)_2py$, IR(KBr): 223s, 230s,br, 300vw, 327vw, 361w, 431vw, 453vw, 460vw,sh, 500vw, 539w, 606vw, 632m, 666m, 692s, 763s, 881w, 914vw,sh, 946vs, 970m,sh, 986s, 996s, 1023w-m, 1100vw, 1150w-m, 1229w, 1248w-m, 1360w-m, 1450vs, 1489m, 1610s.

The spectrum has weak absorptions at 1229 and 1248 cm^{-1} assignable to the overtone or combination bands. The strong absorption occuring at ≈1580 cm^{-1} in the free ligand becomes weaker and moves up to 1610 cm^{-1} in the complex. In the free ligand, the 601 cm^{-1} band is strong and assigned to an in-plane ring deformation while the 403 cm^{-1}, also strong, is an out-of-plane ring deformation. The rather large shift in the 601 cm^{-1} band to 632 cm^{-1} on complexing may have stereochemical significance; Gill[119] and coworkers observed +41 cm^{-1} shift for tetrahedral $Co(py)_2Cl_2$ (monomeric) and a +30 cm^{-1} for octahedral $Co(py)_2Cl_2$ (polymeric) and a +58 cm^{-1} shift for monomeric cis-$Pt(py)_2Br_2$. The out-of-plane ring deformation occuring at 403 cm^{-1} in the free ligand is rather hard to identify in the complex. The lower intensity is probably due to solid state effect. The assignment of the 881 cm^{-1} band to "O-O stretch" is consistent with other reports, Table III.1.

Table III.1, Vibrational Spectral Assignments for $CrO(O_2)_2py$

"O-O Stretch" (cm^{-1})	Cr=O Stretch (cm^{-1})	Ref.
875m	937s	122
880m	910 - 960vs	121
---(?)	934s, 942w, 950w	123
881w	946vs, (914w,sh, 970m,sh)	This work

There was, however, no peak assignable to the Cr-N stretching vibration. Such a peak would be useful for the purpose of comparison with other peroxo complexes.

(b) Oxodiperoxo(triphenylphosphine oxide)chromium(VI) Complex.

The infrared spectra of the triphenylphosphine oxide adduct of the oxodiperoxochromium(VI) complex, $CrO(O_2)_2.OPPh_3$, has also been examined. Several authors[124-126] have studied adduct formation of phosphine oxides with metal halides and metal-halide complexes, and established the effectiveness, as a donor, of the phosphoryl oxygen. The present study is interested in observing the effect of coordination on the stretching frequency of the O-P bond in phosphine oxides. The O-P vibration in $OPPh_3$ occurs at 1195 cm^{-1} (in nujol) compared to the higher (1200 - 1400 cm^{-1}) absorptions in phosphoryl halides[127-129]. IR studies[124] of numerous $OPPh_3$ adducts show that except for splitting and shifting in the O-P band, the spectra of all the complexes are virtually identical with that of the free ligand. In this study the major point of difference between the spectrum of $OPPh_3$ and that of $CrO(O_2)_2.OPPh_3$ is in the region 1100 - 1200 cm^{-1}. The band at 1120 cm^{-1} is assigned to ν(O-P) in keeping with previous studies[124, 125] Fig. III(a) and (b).

(c) Tetraphenylarsonium Oxodiperoxochlorochromate

the IR, the $Ph_4AsCrO(O_2)_2Cl$ complex shows the following absorptions in addition to the bands assignable to the Ph_4As^+ cation.

Table III.2. The Vibrational (IR) Spectrum of $Ph_4AsCrO(O_2)_2Cl$

Frequency(cm^{-1})	Tentative Assignments
950vs 935vs	$\nu_{Cr=O}$
907m 900w,sh	ν_{O-O}
615m,br	ν_{Cr-O_2}
435m	ν_{Cr-Cl}

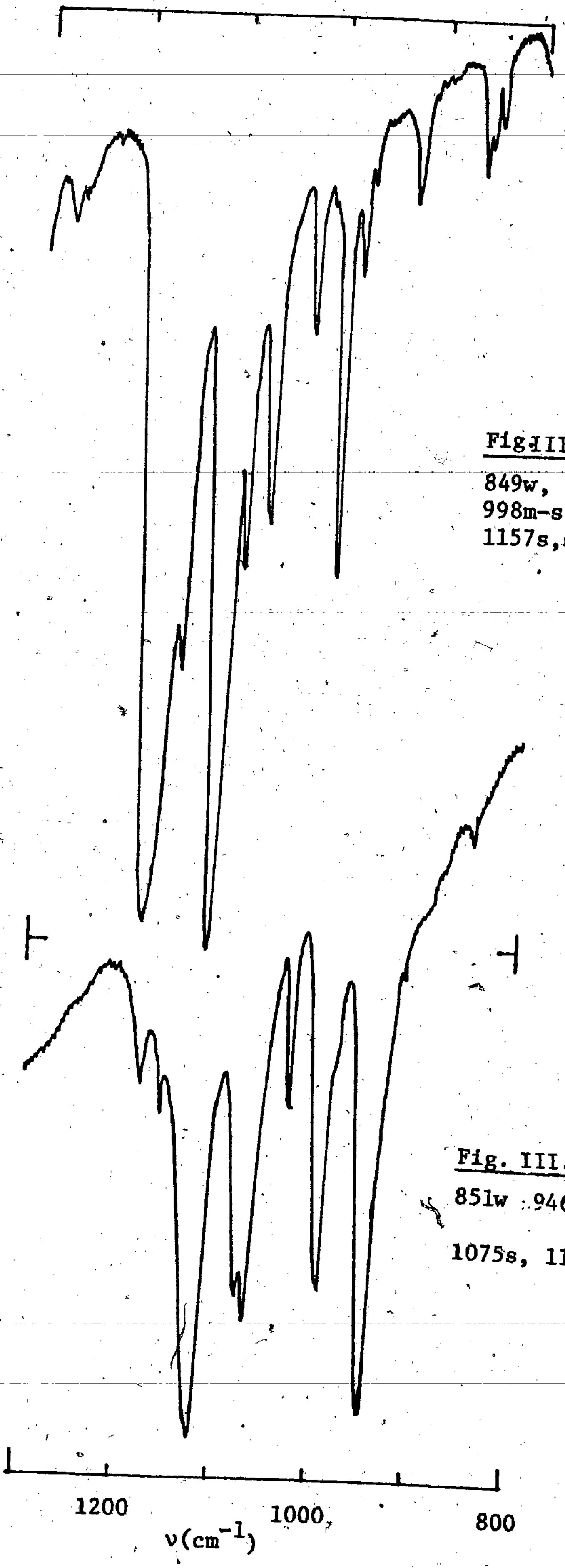


Fig. III.3a OPPh$_3$, IR (KBr)
849w, 858w, 864w, 939w, 974vw, 983w, 998m-s, 1031w, 1070m, 1094m, 1121vs, 1157s,sh, 1187vs,br.

Fig. III.3b; CrO(O$_2$)$_2$OPPh$_3$, IR (KBr)
851w 946s ν(Cr=O), 994s, 1028m, 1068s, 1075s, 1124s (ν_{O-P}), 1165w, 1185w.

The spectrum is relatively simple and consistent with that previously reported[4] and will not be discussed further.

(d) Tetraphenylarsonium Oxodiperoxoazidochromate

The spectrum of the azido complex, $CrO(O_2)_2N_3^-$, is also rather straightforward, partly because the azide ion is N-N-N not N-X-Y and the vibrational absorptions characteristic of the complex $CrO(O_2)_2N_3^-$ are not masked by the cation bands, Table III.3.

The strong high frequency band at 2030 cm^{-1} (with a splitting at 2070 cm^{-1}) is assigned to $\nu_{asy}(N_3)$. Splittings have also been observed in the IR spectra of $SnCl_3(N_3)$ and $TiCl_3(N_3)$,[130,131] and are probably caused by descending symmetry, cation or lattice effects. The broad medium intensity composite occuring at 1275 cm^{-1} is assigned to $\nu_{sy}(N_3)$. It is interesting to note that while the pseudoasymmetric ligand vibration in $CrO(O_2)_2N_3^-$ is of much lower energy than the corresponding vibration in $SnCl_3(N_3)$, $TiCl_3(N_3)$, $VOCl_2(N_3)$, $CrO_2Cl(N_3)$, $MoCl_4(N_3)_2$,[131] $VCl_4(N_3)$[129] and $GeH_n(N_3)_{4-n}$,[132] the pseudosymmetric mode is comparable to that of $GeH_n(N_3)_{4-n}$ but much higher than those of the other complexes cited above. This may have some bearing on the degree of asymmetry in the complexed azido group (see page 70).

The vibrations at 950 (possibly 935 cm^{-1}) have, by comparison to other oxochromium(VI) complexes, been assigned to the stretching modes of Cr=O bond. The assignments of the 905m and 898w,sh cm^{-1} bands are less certain because both the ν_{O-O} and the $\nu(Cr=O)$ (for CrO_3L^{n-} complexes) have been observed in this region. It is also possible that the two bands have characters of both modes.

Because the bending modes of the free azide (as salts of alkali metals) have been observed between 620 and 650 cm^{-1} [133] and at 683 and 614 cm^{-1} for the complex, $MoCl_4(N_3)_2$,[129] some of the bands (at 615, 595, 560 and 525 cm^{-1}) observed in the spectrum of the $Ph_4AsCrO(O_2)_2N_3$ complex could be assigned to the bending modes of the azido group, except that these same bands occur rather consistently through the oxodiperoxopseudohalogenochromium(VI) complexes $CrO(O_2)_2Ps^-$ for $Ps^- = N_3^-$, NCO^- and NCS^-. Because of this and the fact that Griffith's[117,134-136] peroxo complexes exhibit absorptions in the same region, it is very likely that these are vibrations of the $M\text{-}O_2$ group.

(e) <u>Tetraphenylarsonium Oxodiperoxocyanatochromate</u>

On the basis of the arguments used for $KCrO_3(NCO)$, the following features are recognizable, Table III.3. The sharp unsplit 2195 cm^{-1} absorption, assigned to ν_{CN}, is significantly shifted to higher frequency from the free ligand value of 2165 cm^{-1} (broad). The guide-lines established in Chapter II also suggest that shifts to higher frequency occur in either bonding mode, although larger increases in ν_{CN} have been observed in the isocyanato complexes of Foster and Goodgame[56] and Bailey and Kozak.[57] The problem in spectral assignments is further complicated by the fact that the more diagnostic ligand vibration, ν_{CO} which is normally weak was not observed anywhere between 1420 and 1050 cm^{-1}. The N-bonded cyanate would be expected to show a single band shifted to higher energy ($\approx$1300 cm^{-1})[56] from the free ligand value of 1254 cm^{-1}. Such increases have been observed in the vibrational spectra of isocyanato complexes: $Si(NCO)_4$ (1482 cm^{-1}), $Ge(NCO)_4$ (1426 cm^{-1})[132] and of 3d transition metal tetraisocyanates (1319-1337 cm^{-1}).[129]

Table III.3 The Infrared Spectra of the $CrO(O_2)_2(NYZ)^-$ Anions in $Ph_4AsCrO(O_2)_2(NYZ)$, (cm^{-1}).

$CrO(O_2)_2N_3^-$	$CrO(O_2)_2(NCO)^-$	$CrO(O_2)_2(NCS)^-$	Assignment
2070m	2195s	2080vs, broad base	$\nu_{asy}(NYZ)$
2030vs, broad base			
1275m,br			$\nu_{sym}(N_3)$
		985m,shr	$\nu(Cr=O)$
950s	948s	955sh	
935vs	942s,shr	940s,shr	$\nu(Cr=O)$
		920s,sh	ν_{O-O} or ν_{CS}
905m	906w	910m,sh	
898vw,sh		880w,sh	
		740s,sh(?)	ν_{CS}
615m	620m	625m,br	$\nu_{(M-O_2)}$ or $\delta(NYZ)$
595w	590m	610m	
560vw	555vw		
525w	525vw	530m	
490m,sh			
410w	415w	415w	$\nu_{Cr=N}$

The presence of a band in the 610 cm^{-1} region through the series of complexes $CrO(O_2)_2Ps$ for Ps = N_3^-, NCO^- and NCS^- again suggests that it may be more a characteristic of the M-O_2 system than the bending mode of the pseudohalide system. However, vibrational spectra of isocyanato complexes of other electropositive metals [29,137] also show the same rather consistent weak-to-medium absorption between 570 and 640 cm^{-1}. These absorptions have generally been assigned to the N-C-O bending modes. It is, therefore, possible that one or both of the 620 and 590 cm^{-1} bands are due to NCO deformations. The assignment would be consistent with those of unsubstituted transition metal isocyanates.[56,31]

The Cr-N stretching vibration, which occurs at ≈495 cm^{-1} in $KCrO_3NCO$ and $CrO_2Cl(N_3)$, would be expected to shift to lower energy if either a greater M-O_2 bonding or steric interactions with O_2 groups result in the weakening of the Cr-N bonding in $CrO(O_2)_2NCO^-$ compared to CrO_3NCO^-. What appears to be the ν_{Cr-N} in $CrO(O_2)_2NCO^-$ is observed as a weak band at 415 cm^{-1} as compared to the strong ν_{Cr-Cl} stretch in $CrO(O_2)_2Cl^-$ which occurs at 437 cm^{-1}. It is generally argued that the M-NCO stretch occurs above the ν_{M-Cl} of the analogous complex. The assignment of the 415 cm^{-1} band to ν_{Cr-N} is favoured because it compares with the assignment of the isoelectronic species $CrO(O_2)_2N_3^-$ and with metal-isocyanate vibrations of other complexes in which the metal is highly electropositive.[31] For instance, $Ph_4As[Fe(NCO)_4]$ is reported [56] to have the Fe-N stretch at 410 and the other ligand vibrations at 2208, 2171 (ν_{asy}(NCO)), 1307, 626 and 619 cm^{-1}.

(f) Tetraphenylarsonium Oxodiperoxothiocyanatochromate

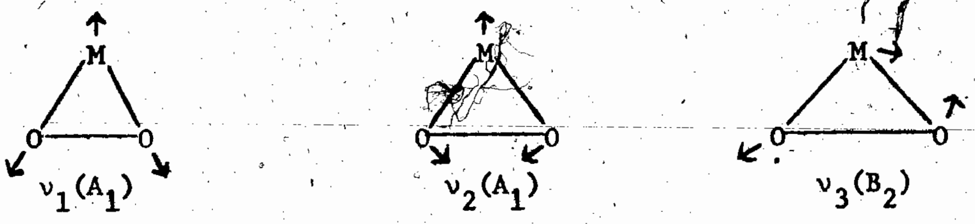
The spectrum of the anionic complex, $CrO(O_2)_2(NCS)^-$ (in nujol mull) is more complicated than the preceding ones. The arguments and assignments suggested for the other complexes, $CrO(O_2)_2Ps^-$ for $Ps^- = N_3^-$ and NCO^-, have been applied here especially with respect to the absorptions at 955m, 940vs, 920s, 910m, 880w, 625m, 610m, 530m and 415m cm^{-1}.

The observed frequencies and tentative assignments for $CrO(O_2)_2(NCS)^-$ are given in Table III.3. The characteristic pseudoasymmetric stretching mode, ν_{CN}, is assigned to the intense band at 2080 cm^{-1}. The small increase from the free ligand value of 2053 cm^{-1} is strong evidence for an N-bonded complex according to an analysis by Tramer.[48]

According to Sabatini and Bertini[49] and Lewis and coworkers,[138] the ligand pseudosymmetric stretch, ν_{CS}, would be expected to shift from 746 cm^{-1}, the "free" ligand value, to between 800 and 845 cm^{-1} for N-bonded complexes and to ≃700 cm^{-1} for S-bonded thiocyanates. Unfortunately, this band could not be identified in $Ph_4AsCrO(O_2)_2(NCS)$ as a result of masking absorptions arising from the Ph_4As^+ cation. But there are two strong absorptions, one at 985 cm^{-1} and the other at ≃740 cm^{-1} (shoulder), the origins of which are doubtful, though either could very well be the ligand C-S stretch. Knox and Brown[139] have reported a series of hexaisocyanato complexes, $Nb(NCS)_6^{n-}$ for n = 1 or 2, and $Ta(NCS)_6^-$ in which the C-S stretch is assigned to bands between 850 and 940 cm^{-1}. The vibrational spectra of the isothiocyanato(methyl)germanes, $Me_2HGe(NCS)$ and $MeGe(NCS)_3$,[132] gave the values of ν_{CS} at 968 and 948 cm^{-1}, respectively. These and preceding criteria make either of the absorptions (985 or 740 cm^{-1}) a likely representative for ν_{CS} in the complex $CrO(O_2)_2(NCS)^-$.

III.4 DISCUSSION OF THE VIBRATIONAL SPECTRA OF COORDINATED DIOXYGEN -- THE "O–O" MODES.

Assuming a triangular geometry, local symmetry C_{2v}, for complexes in which the dioxygen groups are bonded "side-on" to the central metal, the vibrational spectra of the MO_2 (M=metal) species would be expected to give rise to three normal vibrations of symmetry species $2A_1 + B_2$;[140]



all of which should be active in both the infrared and Raman. The A_1 modes would be polarized in the Raman while the B_2 mode is depolarized. Unfortunately, most transition metal peroxo complexes are so highly coloured that Raman data have been unavailable or, at best, very scarce. Griffith[135] and Griffith and Wickins[117, 136] have reported the infrared (and some Raman) spectra of a large number of such complexes, but have positively identified only the $\nu_1(A_1)$ vibration which they attribute to the O–O stretching. Low frequency modes (500 - 700 cm^{-1}) have also been observed in the infrared spectra of several peroxo compounds, but no definite assignments to either $\nu_2(A_1)$ or $\nu_3(B_2)$ has been made.

The infrared spectra of the potassium salts of unsubstituted tetraperoxo anions $M(O_2)_4^{3-}$ show characteristically strong absorptions at 875, 853, 814 and 814 cm^{-1} for M = Cr, V, Nb, and Ta, respectively. Since peroxo groups are the only ligands these bands, by analogy to the 877 cm^{-1} band in H_2O_2 and the 870 - 900 cm^{-1} band in organic peroxides,[139] have been assigned to the O-O stretching vibrations of the coordinated peroxo groups with, maybe, some contribution from the O-M-O deformation vibration. In addition to the "ν_{O-O}" band in these complexes, weak high frequency absorptions also occur between ≈950 and 975 cm^{-1}. Other peroxo complexes, including the $Cr(O_2)_4^{3-}$, also show additional medium intensity bands between 670 and 674 cm^{-1}. Griffith and coworkers[135] have suggested that the later band is due to M-O stretches (symmetric or asymmetric) with some O-O stretch character to them.

Table III.4 Spectral Assignments for $CrO(O_2)_2OH^-$ and $CrO(O_2)_2L$, (cm^{-1})[120]

Complex	ν_{O-O}	$\nu_{Cr=O}$
$K[CrO(O_2)_2OH]$	876s	984m, 924s
$Tl[CrO(O_2)_2OH]$	870s	970w, 920s
$NH_4[CrO(O_2)_2OH]$	932s	980s
$CrO(O_2)_2$(in ethyl acetate)	864s	940s
$CrO(O_2)_2$.py	875m	937s
$CrO(O_2)_2$.bipy	890m	922s

Because opposing factors[142-144] result in minimal shifts in the "ν_{O-O}" band even when the character of the coordinating metal or substituents[145] is changed drastically, no positive correlation can be made between the ν_{O-O} frequency and the O-O bond length or the donor (σ or π) properties of the substituent. Furthermore, vibrational coupling with

M=O modes in the case of oxoperoxo complexes, are probably inevitable. This would tend to raise the frequency of ν_{0-0}. It is no surprise that some of the oxodiperoxochromium(VI) complexes reported in this study do not give absorptions between 800 and 900 cm^{-1} assignable to ν_{0-0}.

The use of the large cation Ph_4As^+ to stabilize the anionic complexes $CrO(O_2)_2L^{n-}$ has also meant that certain important vibrations ν(O-O, M-O_2, M-XYZ, and X-Y-Z) could not be unequivocally assigned.

III.5 THE VISIBLE SPECTRA OF OXODIPEROXOCHROMIUM(VI) COMPLEXES.

Until the early 1950's, no visible spectral studies had been reported for oxodiperoxochromium(VI) complexes. The present study complements reports [141] of the absorption spectra of $CrO(O_2)_2.OEt_2$, $CrO(O_2)_2py$, $CrO(O_2)_2.CH_3OH$ and $CrO(O_2)_2.phen$ in showing that the UV and visible spectra of these compounds (except $CrO(O_2)_2.phen$) have, as the main feature, a strong band at ≃ 360 mμ ($\epsilon \simeq 10^3 - 10^4$) and a doublet with the maxima at ≃ 580 (ϵ=700) and 750 mμ (ϵ=400). In the case of $CrO(O_2)_2.phen$, the intensities of the doublet absorption are reversed and much shifted to lower energy. Griffith[122] reported a peak at 530 mμ (ϵ=441) for methanolic and aqueous solutions of the $NH_4[CrO(O_2)_2OH]$ complex. It is noteworthy that the peroxides of other transition metals, in Groups IV, V and VI such as Ti, V, Nb and Mo, have absorption bands with molar extinction coefficients of the same order of magnitude (≃10^3). [30, 146] Tuck and Walters attribute the bands in the visible spectra to charge-transfer absorptions. It seems likely that appreciable charge-transfer (from the O_2 group to the metal atom) is involved, since for the peroxides of Group IV, V, and VI elements there is a fairly good correlation between the position of the absorption maximum and the formal oxidation state of the metal involved.

In the present study, the UV and visible absorption spectra of the anionic compounds $CrO(O_2)_2L^-$, for L = Cl^-, NCO^-, Br^-, N_3^-, NCS^- and NO_3^-, were investigated, Figure III.4. A solution of $CrO(O_2)_2OPPh_3$ in most non-donor solvents ($CHCl_3$, benzene) and even ethers was found to be very unstable, decomposing within five minutes. Except for small blue shifts, the spectra of the anionic complexes are almost identical to those of the neutral adducts previously reported by Evans. Similar shifts were observed in the spectra of $CrO(O_2)_2OH^-$.[141] The intense band occuring at ≈ 360 mμ is associated with the charge-transfer transition within the Cr=O system, as discussed in detail in Section II.4.

The more intense component of the doublet absorption has been followed through the complexes $CrO(O_2)_2L^-$, for L = N_3^-, Br^-, NCO^-, Cl^-, to NCS^-, and found to exhibit increasing shifts to the red in that order. On the other hand, the extinction coefficients of the maximum, which is always twice as large as that of the second component in the doublet, increased in the order L = NCO^-, Cl^-, NCS^-, Br^- and N_3^-, Table III.5. It is not possible at the moment to extract any significant information from the red shifts or increased intensities.

Table III.5 Absorption Spectra of Anionic Substituted Oxodiperoxochromium(VI) Complexes.

Substituent L^-	mμ	cm^{-1}	$\varepsilon (x\ 10^{-3})$	Ref
OH^-	531	18,800	0.44	141
N_3^-	554	18,100	5.15	this work
Br^-	563	17,800	4.35	"
NCO^-	565	17,700	3.76	"
Cl^-	568	17,600	4.02	"
NCS^-	569	17,500	4.28	"

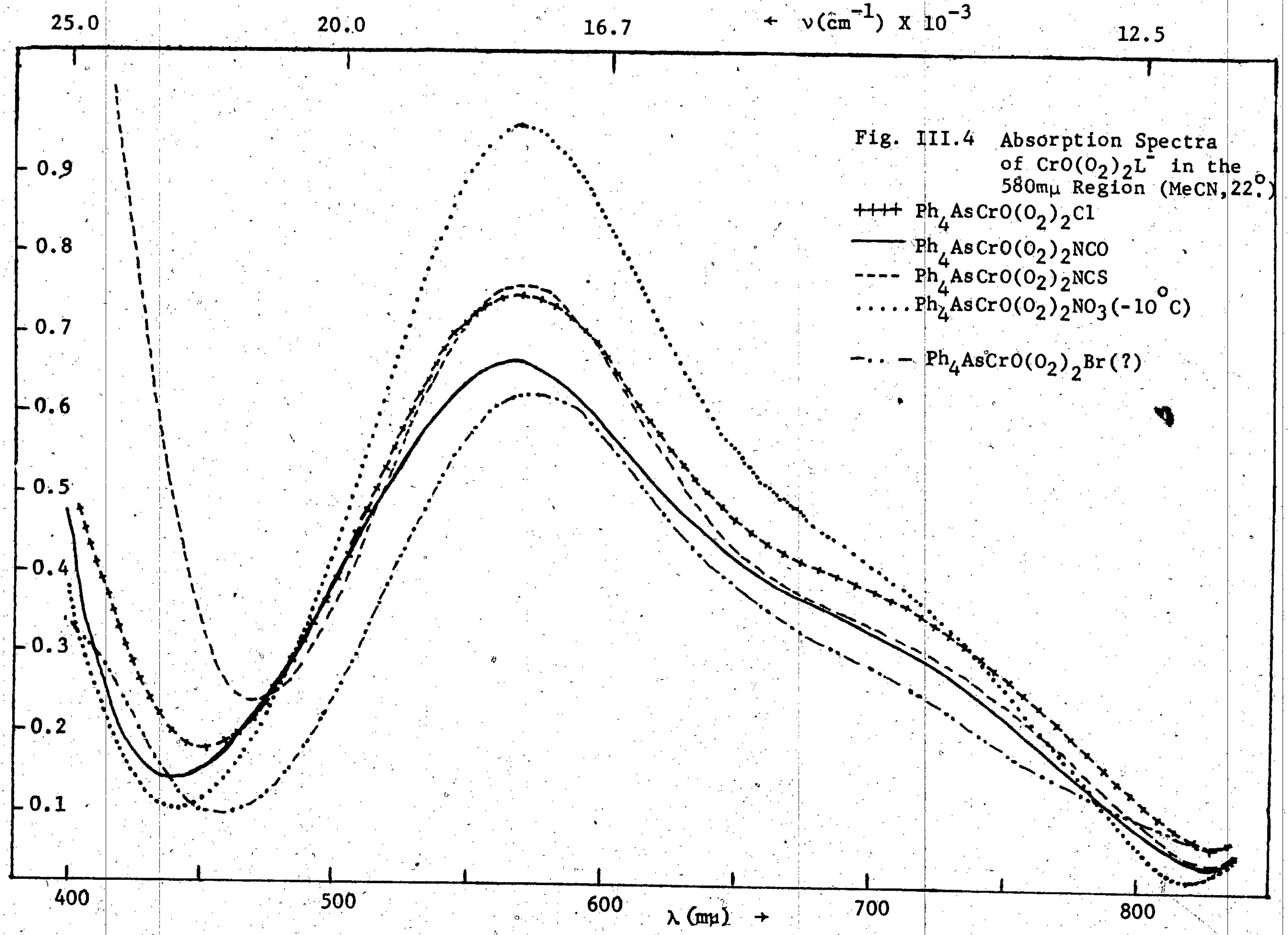


Fig. III.4 Absorption Spectra of $CrO(O_2)_2L^-$ in the 580mμ Region (MeCN, 22°)

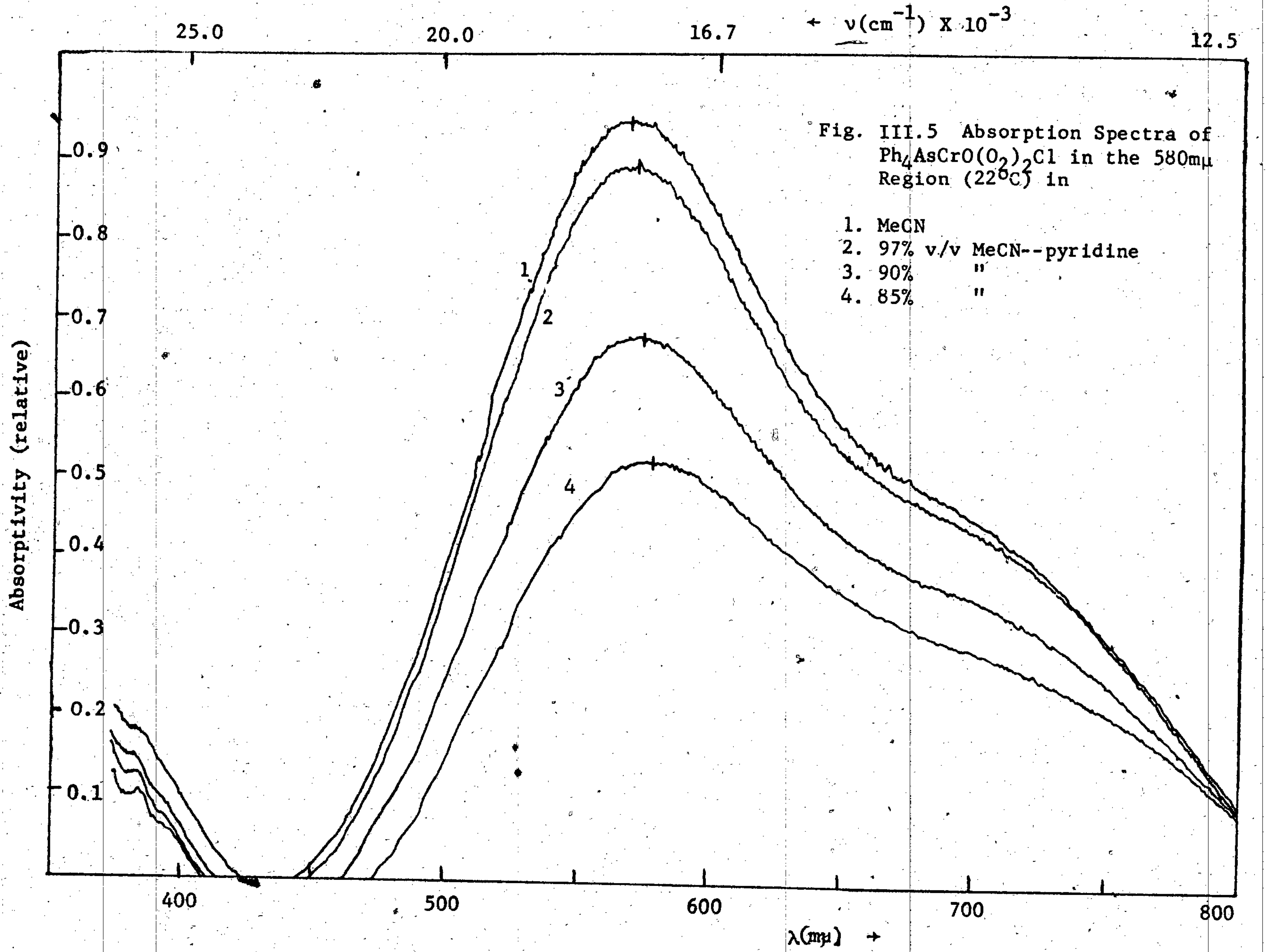


Fig. III.5 Absorption Spectra of $Ph_4AsCrO(O_2)_2Cl$ in the 580mμ Region (22°C) in

1. MeCN
2. 97% v/v MeCN--pyridine
3. 90% "
4. 85% "

It is conceivable that the substituent acts to lower or raise the energy of the change-transfer acceptor orbitals on the chromium. On the other hand, these shifts could be more a result of medium effects (second coördination sphere) than necessarily that of the coordinated substituent. This is reflected in the solvent studies on $CrO(O_2)_2Cl^-$, (Fig. III.5).

The absorption spectrum of $Ph_4AsCrO(O_2)_2NO_3$ (at -10°C), which, because of decomposition could not be obtained at room temperature, has the maximum absorption occurring at 587 mμ (17,000 cm^{-1}). This is a significant red shift but may be purely a temperature dependent shift, since Evans [141] showed that the spectrum of $CrO(O_2)_2CH_3OH$ was temperature-dependent. Because of the large variations in the temperatures and the media necessary to ensure the stability of the oxodiperoxochromium(VI) complexes, we have not made any attempts to derive quantitative correlations from all the spectral shifts.

We shall consider only the isothermal spectra in MeCN of $CrO(O_2)_2L^-$, for L = N_3^-, Br^-, NCO^-, Cl^- and NCS^-. As the electron density on the chromium is increased, the positive charge decreases and the chromium acceptor orbital levels are raised. The order of the energies of the absorption band in the 550 mμ (≃ 18,000 cm^{-1}) region can be readily compared with the absorption energies in the corresponding CrO_3L^{n-} anions, using the results from Chapter II.

Table III.6

A Trend in the Effect of the Ligand (L) Upon the Absorption Spectra of $CrO(O_2)_2L^-$ and CrO_3L^- Complexes

Ligands	$CrO(O_2)_2L^-$ (± 100) cm^{-1}	CrO_3L^- (± 50) cm^{-1}
N_3^-	18,100	26,670
Br^-	17,800	27,400
NCO^-	17,700	27,530
Cl^-	17,600	27,550
NCS^{-*}	17,500	27,320

* The thiocyanate complexes were rather unstable in most solvents (see experimental sections).

The effects (i.e. the magnitude of the shifts and the order) of these substituents (L) upon the absorption spectra are generally the same in both series. Note that the range of the differences in energy is 600 cm^{-1} (± 100) in $CrO(O_2)_2L^-$ and 880 cm^{-1} (± 50) in CrO_3L^- - with the estimated accuracy in the measurement of the energy given.

The results for L = N_3^-, Br^-, NCO^-, Cl^- are definitely compatible with the model that the electron releasing effects of the substituent L is one important factor affecting the energy of the particular transitions involved. In the neutral complexes $CrO(O_2)_2 \cdot L$, where L = py, and phen,[141] the absorption maximum is shifted to 17,200 and 12,500 cm^{-1}, respectively.

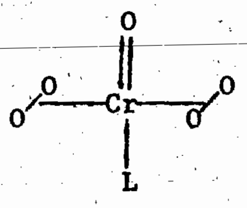
The subject of bonding in peroxochromium(VI) complexes is treated more fully in the next section.

III.6 THE STRUCTURE OF ANIONIC OXODIPEROXOCHROMIUM(VI) COMPLEXES.

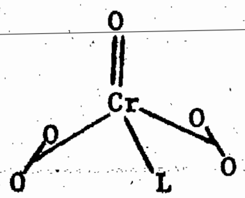
The survey of dioxo, trioxo and oxodiperoxo chromium complexes clearly indicates that geometries other than tetrahedral and coordination numbers higher than four are increasing. It has been shown that both mono- and bidentate ligands can coordinate to chromium in $CrO(O_2)_2L$. Of the oxodiperoxochromium(VI) complexes with established structures, probably $CrO(O_2)_2py$ most closely resembles the new monosubstituted complexes. The pyridine complex is described as a pentagonal pyramid with the peroxo groups and the pyridine nitrogen forming the basal plane,[147]

and the chromium being displaced some 0.51A° from the plane in the direction of the apical oxygen atom. One of the factors that might influence the geometry of the complex $CrO(O_2)_2.L$, for L = OH^-, Cl^-, Br^-, NCO^-, NCS^-, N_3^-, NO_3^- and $OPPh_3$ is the extent of mutual repulsions between the oxygens (O_2^{2-} or O^{2-}) and substituent group, resulting in C_{2v} (not very likely), C_s or no symmetry.

C_{2v}



C_s



The results of vibrational spectroscopy obtained in the present study and by Griffith[120,135] support the structure obtained by the x-ray methods on $CrO(O_2)_2py$; but it has not been possible to get any detailed information about unknown structures or to propose probable structures. Because vibrational spectroscopy has not generally proved reliable, the great need is for crystallographic studies to determine the molecular structures.

III.7 BONDING IN PEROXO CHROMIUM COMPLEXES.

In order to present the electronic structure of peroxo complexes it is necessary to discuss the structure of the dioxygen species. O_2, O_2^-, and $O_2^{=}$. The electronic configuration of molecular oxygen, O_2, as described by MO theory[148,149] is either

$$(\sigma_1)^2(\sigma_2^*)^2(\sigma_3)^2(\pi_1)^4(\pi_2^*)^2 \quad \text{or} \quad (\sigma_1)^2(\sigma_2^*)^2(\pi_1)^4(\sigma_3)^2(\pi_2^*)^2$$

In both cases the bond order is predicted to be 2.0 and the molecule is paramagnetic, with two unpaired electrons ($^3\Sigma$, ground state). The addition of a single electron to the unfilled antibonding (π_2^*) orbital on O_2 leads to the superoxide O_2^-. And, as expected, the removal of this electron from the π^* orbitals strengthens the O-O bond while addition of one more electron weakens the bond.[150]

Table III.7 The Structure of Common Dioxygen Species[a]

Species	Example Compound	No. Unpaired Electrons	O-O Bond Length (A°)	Bond Order	Bond Energy (kcal/mole)
O_2	O_2(gas)	2	1.2107 ± 0.0001	2	118[b]
O_2^-	KO_2(solid)	1	1.28 ± 0.02	1.5	69[c]
$O_2^{=}$	K_2O_2(solid)	0	1.49 ± 0.01	1	≃-125

a. Ref. 150, b. Ref. 149, c. Ref. 148.

Table III.7, above summarizes the information on bond lengths, bond orders, number of electrons in the (π^*) orbital and the dissociation energies of the $(O_2)^{n-}$ system, where n = 0, 1 or 2.

The nature of bonding of the peroxo group to metals especially in transition metal peroxo complexes has been the subject of a lot of speculation The controversy arose in part because the bonded peroxide ion exists in such diverse environments as $Ir(O_2)Cl(CO)(PPh_3)_2$, $Cr(O_2)_2 \cdot L_3$ and $Cr(O_2)_4^{3-}$. The biographical review of structural studies (Section I.3) has established that the peroxo groups in the complexes discussed are laterally coordinated and that the O-O bond length and the ∠O-M-O in $CrO(O_2)_2L$, for L = py, bipy or phen, average 1.40A° and 45°, respectively.

Fergusson,[123] Duffey[151] and Cartmell and Fowles[153] have argued that the ability for transition metals in their high oxidation states to form peroxo compounds is associated with their ability to provide d^4sp^3 or d^3sp^3 hybrid orbitals. This explanation presupposes that each of the oxygen atoms of an O_2^{2-} ligand donates a pair of σ-bonding electrons and, for the O-Cr-O angles to be small, the hybrid orbitals must subtend small angles. Griffith [135] supported the above σ-bonding scheme and went on and postulated a "bent bond" hypothesis, similar to that used for cyclopropane [154] and ethylene oxide, [155] as a mechanism by which the molecule relieves some of the strain otherwise expected from a three-membered ring system.

The different bonding scheme is that of Tuck and Walters [146], who suggest a donation of peroxide π electrons to the empty d-orbitals on the metal atom in a manner anologous to that suggested for the olefin and ethylene complexes of transition metals.[156] Because chromium(VI) is a d^0 system and the antibonding orbitals on the O_2^{2-} ion are already filled, back-donation from filled metal orbitals into empty ethylenic-type $\pi^*(2p)$ orbitals would be impossible. The scheme, therefore, proposed[157] two alternate π-bonding interactions in association with the σ-type. The first one involves electron donation from the peroxo-$\pi^*(2p)$ antibonding orbitals if the chromium d-orbitals are of suitable symmetry; and the second involves a shift of electron density from the π^* to the π orbitals on O_2^{2-}, as a result of σ-donation, such that backbonding to π^* orbital can occur, alleviating the build-up of charge on the chromium. In the broadest terms, the effect of coordination on the O-O bond would depend on the relative strengths of the two interactions - in other words, on whether donation was principally from the π- or π^*- orbitals of the peroxo group. Force constant calculations[143] have also noted interdependence in M-O and O-O interactions. Also see section III.4.

Because the above scheme involves, in part, the removal of π(2p) electron density from the O_2^{2-}, erroneous interpretation of this bonding mode has led others [135] to expect a slight increase in the O-O bond length on coordination or a decrease in the O-O stretching frequency if the central metal was made more electronegative by attaching fluoride ligands. Griffith[135] reported increases in the O-O stretching frequencies in his fluorinated peroxo compounds and most structural studies of early transition metal peroxo complexes report no major changes in the O-O bond length. But even in the case of $CrO(O_2)_2L$ complexes, or $Cr(O_2)_4^{3-}$, where the O-O bond length average 1.40(± 0.02) and 1.405 ± 0.03A°,[121] respectively, the shortening of the O-O bond distance is easily attributable to the possibility that the electrons in the O-O π^*-antibonding orbitals are more strongly involved in the Cr-O(peroxide) bonding than the π-bonding electrons. Because donation of electrons by either π- or π^* orbitals may not be totally independent of each other it is difficult to assess the effect of the substituent L in $CrO(O_2)_2 \cdot L$ on the O-O bond length.

Quantitative support for the Tuck and Walter's scheme comes from the SCF-MO-LCAO calculations of Dacre and Elder,[144] who showed that in the peroxo complex ion $Cr(O_2)_4^{3-}$ the O-O π-bonding orbitals (in the CrO_2 plane) make the largest contributions to the Cr-O σ-bonds. Another large part comes from the overlap of the Cr π-orbitals ($3d_{z^2}$, $3d_{xz}$ and 4_{p_x}) with O_2^{2-} π^* molecular orbitals (in the plane of CrO_2). The electrons in the O-O π bonding orbitals above the CrO_2 plane were also shown to be partially delocalized toward the chromium by way of the $Cr(4_{p_x})$ and $Cr(3d_{xz})$ orbitals. The fact that no appreciable changes in the O-O bond length occurs on coordination can be explained by the results of these SCF-MO-LCAO calculations which show that there is in fact a considerable degree of mixing between the σ-orbitals involved in O-O σ-bonding and the O_2^{2-} π-orbitals, which are of the same symmetry. Furthermore, these same σ-orbitals also make small contributions to the Cr-O σ- and

π-bonding. Finally, these authors postulated "bent bonds", i.e. the overlap density of the Cr $\pi(3d_{z^2}, d_{xz},$ and $4p_x)$ orbitals with O_2^{2-} $\pi^*(2p)$ orbitals (in the plane of CrO_2) to form Cr-O σ bonds which lie outside of the CrO_2 triangle. The slight bending was attributed to the directional character of O-O π^*-orbitals.

Although the MO calculations were on the unsubstituted complex $Cr(O_2)_4^{3-}$, it is probable that the bonding in oxodiperoxochromate(VI) complexes follow the same basic scheme. The factors determining whether any significant bond is formed are (i) that orbitals of the same symmetry exist on the chromium and the O_2^{2-} ion, (ii) that significant overlap of the orbitals occurs and (iii) that the energies of the donor and acceptor orbitals are similar. Unfortunately, at the moment the values of these orbital energies are not available.

Concluding Remarks

The new peroxochromium(VI) compounds have substituents in which the character of the donor atom is significantly varied. This should provide a good testing ground for postulated bonding schemes. For instance, there may be changes in the Cr–O and O–O bond lengths as a result of differing σ- and π-bonding interactions. From the chemical studies it is apparent that chromium(VI) peroxo complexes containing substituents which have oxygen and fluorine as the donor atom [$CrO(O_2)_2L$, for L=H_2O, Me_2O, Et_2O, ROH, $OPPh_3$, $OP(OBu^n)_3$, OPX_3, OAc^-, NO_3^-, OH^-, and F^-] are more unstable than those which have nitrogen or chlorine [$CrO(O_2)_2L$, for L=py, bipy, phen, NCS^-, N_3^-, NCO^-, Cl^-]. Of all these $Ph_4AsCrO(O_2)_2Cl$ has so far displayed the highest stability to decomposition in the solid state; $Ph_4AsCrO(O_2)_2Cl$ has been kept at room temperature for over 9 months without decomposition, while $Ph_4AsCr(O_2)_2NCO$ was stable for about 3 months under similar conditions.

CHAPTER FOUR

SUBSTITUTION REACTIONS IN CHROMIUM(VI) TRIOXO AND OXODIPEROXO COMPLEXES

IV.I INTRODUCTION

Recent studies have provided detailed information on the redox reactions, kinetics and substitution equilibria involving chromium(VI) species in aqueous solutions. The oxidation of various substrates by chromium(VI) have recently been reviewed [158-160]. The interconversion of $HCrO_4^-$ and $Cr_2O_7^{2-}$ which accomplishes oxygen exchange between chromium(VI) and water has been shown [78,79] to proceed in acidic, neutral and basic solutions. It has been suggested [161] that the hydrogen ion catalysed condensation of $HCrO_4^-$ with the inorganic anions

$$HPO_4^{2-},\ H_2PO_4^-,\ S_2O_3^{2-},\ SO_4^{2-},\ NCS^-,\ C_2O_4^{2-}\ \text{etc.}^{162}$$

proceed by a mechanism similar to the dimerization reaction. The observed hydrogen ion dependent forward rate constants ($k_f^{H+} \simeq 5 \times 10^5\ M^{-2}\ sec^{-1}$) [76,169] in these systems are almost identical, but independent of the basicity of the substrates and the stability of the complex formed. The suggested rate determining step in the condensation reactions is the proton transfer (H^+ in solution or from the weakly associated acidic species) to the hydroxyl ligand, on $HOCrO_3^-$, to form the departing water molecule. Unfortunately, however, the observed rates, for instance, in the dimerization reaction [1]

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^{2} + H_2O \qquad [1]$$

only fixes a lower limit on the rate of the oxygen exchange since in aqueous solutions one or more additional pathways may be in operation.

In a non-aqueous study Flesch and Svec [166] reported observing chromylfluorochloride, CrO_2ClF, in the solvent-free mixture of the parent chromyl halides, CrO_2F_2 and CrO_2Cl_2. There have, however, been no reports of substitution studies of trioxo- and oxodiperoxochromium(VI) species in non-aqueous media. Holyer and Baldwin[80], who investigated the rate of exchange of ^{18}O between chromium(VI) oxo-anions and bulk water as a function of pH and total chromium(VI) concentration, found that at high pH (>10), the exchange was slow ($k_1' = k_1/H_2O = 7 \times 10^{-7}\ sec^{-1}$) and pH independent, suggesting that the main process was probably

$$*OCrO_3^{2-} + H_2O \rightleftharpoons CrO_4^{2-} + H_2O^* \qquad [2]$$

For pH between 8.4 and 10.0 the process was first order in $[H^+]$ and second order in $[Cr(VI)]$ suggesting

$$HCrO_4^- + CrO_4^{2-} \rightleftharpoons Cr_2O_7^{2-} + OH^- \qquad [3]$$

and, for pH between 6.7 and 8.4, the increasing dependence in H^+ was intepreted as supporting

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O \qquad [4]$$

These authors also noted an alternative path, involving a symmetrical

$$HOCrO_3^- + *OH^- \rightleftharpoons [HO \cdots CrO_3 \cdots \overset{*}{O}H] \rightleftharpoons O_3Cr\overset{*}{O}H^- + OH^- \qquad [5]$$

transition state and reported $k_f = 70\ l\ mol^{-1}\ s^{-1}$ for this process.

It became interesting therefore to perform exchange studies involving other chromium(VI) oxo species, for instance, the exchange of fluorine between the trioxofluorochromate anion and the fluoride ion; F^- and CrO_3F^- are isoelectronic with OH^- and CrO_3OH^- ions, respectively. The study of the exchange processes was also extended to include pseudo-isoelectronic systems CrO_3L^{n-} / L'^{n-} and $CrO(O_2)_2L^{n-}/L'^{n-}$ for n = 0 or 1 and L a donor species. It is hoped that such studies may help in the understanding of the equilibria and relative stabilities of trioxo- and oxodiperoxochromium(VI) species in solution, although a quantitive comparison with aqueous systems would not be reliable. In the attempt to measure the equilibrium constants for the exchange processes non-aqueous solvents were used, in order to eliminate the competing hydrolytic equilibrium e.g.

$$CrO_3F^- + H_2O \rightleftharpoons HCrO_4^- + HF \qquad [6]$$

which must occur in the aqueous solution. The number of possible solvents for this work was restricted. The requirement for reasonable resistance to chromium(VI) oxidations was met by DMSO and MeCN and, for the NMR studies of CrO_3F^-/F^- and CrO_3F^-/Cl^- systems, the requirement for high solute concentration was met only by DMSO. The solubility was enhanced by using tetraphenylarsonium or tetraalkylammonium salts throughout; and, where necessary, by working at temperatures above ambient. Attempts were also made to follow the exchange processes by ultraviolet spectroscopy. Acetonitrile proved satisfactory for the purpose because it does not have absorptions which obscure the anion bands or the fine structure of these bands. But the shifts in λ_{max} and changes in the ϵ_{max} of these complexes, for the series of processes, except for

$$CrO_3L^{n-} + F^- \rightleftharpoons CrO_3F^- + L^{n-} \qquad [7]$$

were not large enough to allow the use of UV - visible technique in the study of the exchange reactions in CrO_3L^{n-}/L'^{n-} or $CrO(O_2)_2L^{n-}/L'^{n-}$. This limited the investigation of the kinetics of the substitution processes to those in which ^{19}F and ^{1}H can be used as probes.

IV.2 EXPERIMENTAL

The preparation and and analysis of starting materials were described in previous chapters. Because solutions of monosubstituted chromate complexes were found to undergo decomposition on exposure to light, they were handled in the dark as far as possible. The stock solutions for UV-visible spectra were thermostated in polyethylene bottles at 22.0 ± 0.5° C.

The ^{19}F NMR spectra were run on a Varian A 56/60 spectrometer, operating at an oscillator frequency of 56.4 MHz. Unless otherwise stated, the sample temperature was 35°C. Chemical shifts for ^{19}F, defined as

$$\delta = -\frac{\nu_{sample} - \nu_{ref}}{\nu_{ref}}$$

were measured relative to $CFCl_3$ as an external standard. The ^1H chemical shifts were read directly from the chart paper.

IV.3 RESULTS AND DISCUSSION

(a) Preparative Studies:

The metathetical procedures used in the synthesis of the monosubstituted chromium(VI) complexes were probably aided by the rapid formation of stable precipitates, such as AgCl, NaCl, and NH_4Cl in the reactions;

$$Cr^{VI}\text{—}Cl + AgNCO \longrightarrow Cr^{VI}\text{—}(NCO) + AgCl \quad [8]$$
$$Cr^{VI}\text{—}Cl + NaN_3 \longrightarrow Cr^{VI}\text{—}N_3 + NaCl \quad [9]$$
$$Cr^{VI}\text{—}Cl + NH_4NCS \longrightarrow Cr^{VI}\text{—}(NCS) + NH_4Cl \quad [10]$$
$$Cr^{VI}\text{—}Cl + AgNO_3 \longrightarrow Cr^{VI}\text{—}(NO_3) + AgCl \quad [11]$$
$$Cr^{VI}\text{—}Cl + Ag(CH_3CO_2) \longrightarrow Cr^{VI}\text{—}(CH_3CO_2)+AgCl \quad [12]$$

wherein all the chromium(VI) carrying species are either the CrO_3 or $CrO(O_2)_2$ moiety.

Ligand substitution was not always the only reaction observed, as is demonstrated by reactions [13] - [17] (see Chapter III).

$$KCrO_3X + AgNO_3 \longrightarrow KCrO_3NO_3 + AgX \text{ (for X = Br or Cl)} \qquad [13]$$

$$KCrO_3Cl + NH_4NO_3 \longrightarrow NH_4CrO_3Cl + KNO_3 \qquad [14]$$

$$KCrO_3Cl + Ph_4AsNO_3 \longrightarrow Ph_4AsCrO_3Cl + KNO_3 \qquad [15]$$

$$\begin{tikzcd} KCrO_3Cl + Et_4NClO_4 \arrow[r] & Et_4NCrO_3Cl + KClO_4 \arrow[d, "AgNO_3"] \\ & Et_4NCrO_3NO_3 + AgCl \end{tikzcd} \qquad [16]$$

$$KCrO_3NO_3 + Ph_4AsBr \longrightarrow Ph_4AsCrO_3Br + KNO_3 \qquad [17]$$

which occur in acetonitrile.

The stability of certain Cr-ligand bonds have sometimes been infered from chemical reactions. For instance, the trioxochlorochromate anion reacts with ice cold 30% H_2O_2 to form $CrO(O_2)_2Cl^{-4}$, and undergoes the reduction reaction

$$CrO_3Cl^- \longrightarrow Cr(H_2O)_5Cl^{++} \qquad [18]$$

in which the oxidation state of chromium is changed from VI to III [42]. In both cases the coordination number of the chromium changes but the Cr-Cl bond persists in the products. Though the mechanisms are not known, these observations seem to suggest that the Cr-Cl bond in CrO_3Cl^- is more stable in aqueous solutions than the Cr-oxygen bond. Consequently, the reaction producing the blue perchromate compound, $(NH_4)_2Cr_2O_{12}\cdot 2H_2O$, [123] from aqueous NH_4Cl, $(NH_4)_2Cr_2O_7$, acetic acid and 30% H_2O_2 at -10°C probably proceeds by a different mechanism.

(b) Substitution Reactions of $CrO(O_2)_2py$

The present study investigated the proton NMR spectrum of $CrO(O_2)_2py$ in the hope of using the ^1H resonance in following the substitution reaction $CrO(O_2)_2py/L$, for L= pyridine (d_5), F^-, Cl^-, Br^-, NCO^-, NCS^-, N_3^-

or I^-. Figure IV.1 shows that the room temperature ^1H NMR spectra of free pyridine and the pyridine complex, both dissolved in $CDCl_3$, are almost identical except for the downfield shift of about 0.5 ppm compared to the free ligand spectrum. The assignments in Figure IV.1 were made by direct comparison with those reported [163] for pyridine. The downfield shift probably means all the protons in the complex are slightly less shielded than the free ligand ones as a result of the py — $CrO(O_2)_2$ electron donation. But the internal chemical shift may not be free from intramolecular effects such as temperature independent paramagnetism and anisotropic effects [164]. Intermolecular effects (e.g. contact shift due to paramagnetic impurities) can be neglected since large contact interactions would cause very broad NMR lines) (c.f. the results on the $CrO(O_2)_2py/py$ (and py-d_5) exchange studies - see next two pages).

Attempts were made to follow the substitution reaction $CrO(O_2)_2$pyridine/pyridine (and pyridine - d_5) in acetonitrile and in chloroform (both deuterated). The acetonitrile solution of $CrO(O_2)_2py$ does not seem to undergo any apparent decomposition within 30 minutes, while the chloroform solution decomposes in less than 20 minutes and the DMSO one within 2 minutes.

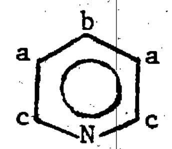
The proton NMR spectrum of the freshly prepared mixtures, containing equimolar amounts of $CrO(O_2)_2py$ and pyridine were found to be identical to that obtained by superimposing Figure IV.1(A) on Figure IV.1(B). There was no line broadening or apparent exchange.

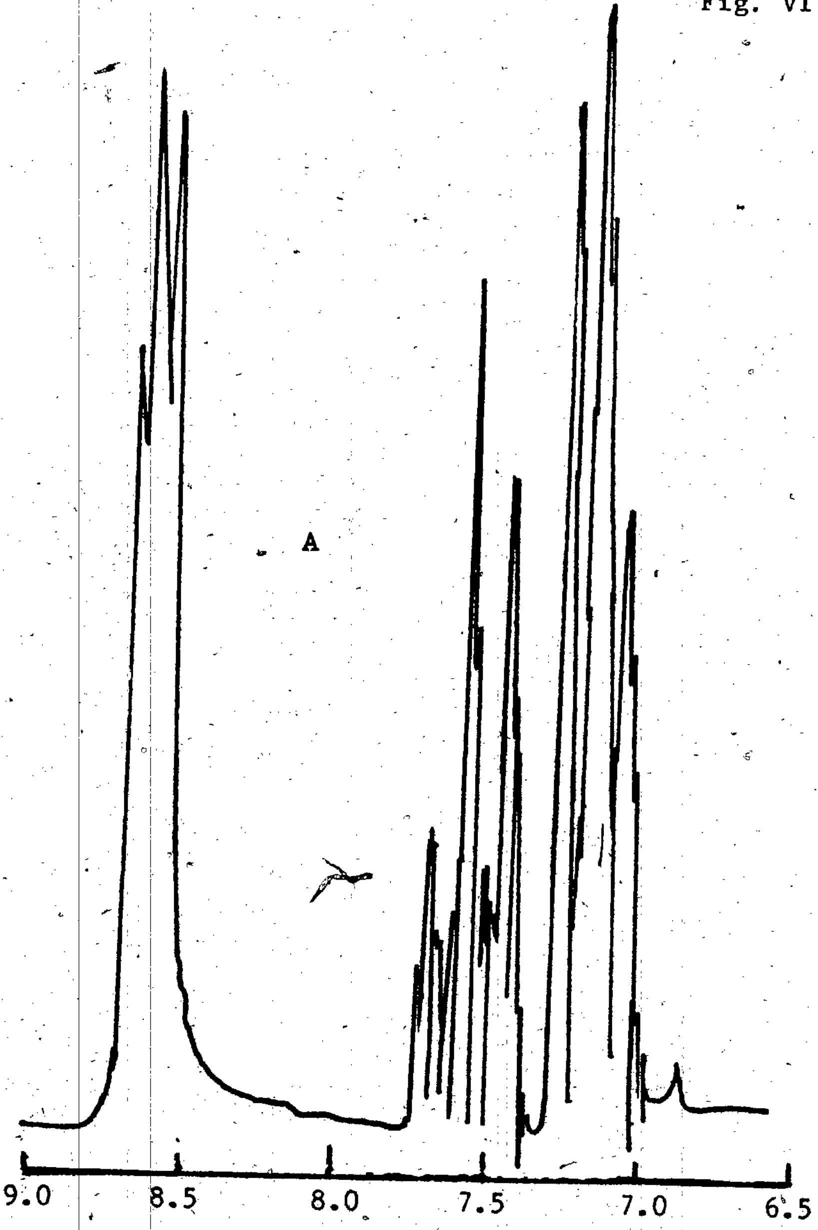
$$CrO(O_2)_2NC_5H_5 + NC_5D_5 \not\longrightarrow CrO(O_2)_2NC_5D_5 + NC_5H_5 \quad [19]$$

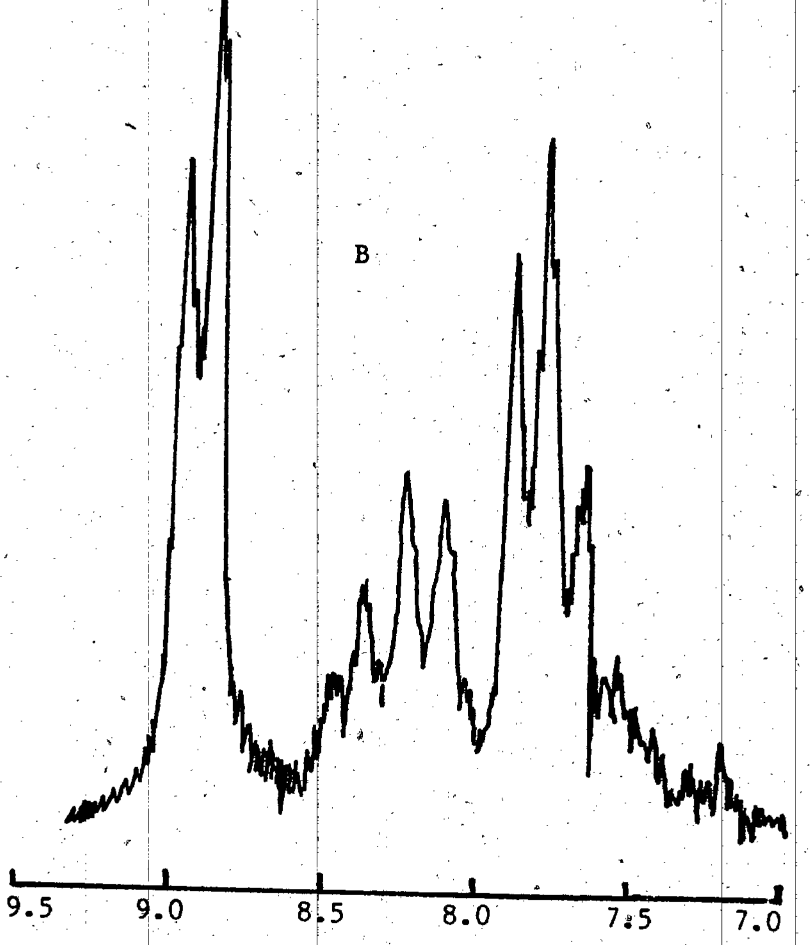
In the $CrO(O_2)_2NC_5H_5/NC_5D_5$ case the spectrum was unquestionably that of the undeuterated pyridine complex. Unfortunately, in both cases the reaction could not be followed for longer than five minutes because of the accelerated decomposition to a green Cr(III) compound. Within these five minutes

Fig. V1.1 The NMR Spectra and Chemical Shifts(± 0.05) ppm; Assignment of Pyridine(A) and $CrO(O_2)_2py$ (B) in $CDCl_3$ (TMS internal standard).

Pyridine	$CrO(O_2)_2py$	Assignment
8.60	9.00	c
7.50	8.30	b
7.15	7.80	a







there was, however, no apparent exchange. It is possible that uncoordinated pyridine catalyses the decomposition of the peroxo complexes.

The oxodiperoxopyridinechromium(VI) complex, $CrO(O_2)_2py$, reacts with Ph_4AsCl in chloroform to form blue, air stable crystals of the chloro derivative, $Ph_4AsCrO(O_2)_2Cl$. The visible spectrum of a MeCN solution containing stoichiometric amounts of $CrO(O_2)_2py$ and Ph_4AsCl or $Ph_4AsCrO(O_2)_2Cl$ and pyridine were found to be identical to that of $Ph_4AsCrO(O_2)2Cl$ ($\lambda max = 568$) in MeCN; suggesting that the displacement of pyridine by the Cl^- is fast and irreversible. The ^1H NMR spectra, which show resonances assignable to uncoordinated pyridine, further supports the above conclusion. The visible spectrum of freshly prepared MeCN solutions containing 1:1 mixture of Et_4NBr and $CrO(O_2)_2py$ at -10°C has maximum absorption at 573 mμ (the absorption, λ_{max}, for $CrO(O_2)_2py$ is 575 mμ) [141]; that for "$Ph_4AsCrO(O_2)_2Br$" is at 563 mμ (see page 106), suggesting that Br^- does not displace pyridine. Unfortunately, this mixture, like mixtures of $CrO(O_2)py$ and Et_4NX (X=F or I), $Ph_4AsH(NCS)_2$, Ph_4AsNO_3, AgNCO, NaN_3 or $AgNO_3$, evolves molecular oxygen and decomposes within minutes.

All together, the ease of substitution, $CrO(O_2)_2L/L'$, observed in the non-precipitating reactions seem to follow the order

$$H_2O > \text{ethers, acetates} > OPPh_3 > \text{pyridine} > Cl^-$$

(c) Substitution Reactions Involving Chromium(VI) - Fluorine Species:

(i) The Fluorochromate(VI) - Chloride System

The absorption spectrum of a millimolar solution of Ph_4AsCrO_3F in MeCN was unaffected over a time span of three days by the addition of an equimolar quantity of Ph_4AsCl. When ten-fold molar excess of the chloride salt was added, a small change in the fluorochromate spectrum was produced, but the rate of change was too slow to allow any significant rate measurements to be made. Oxidation of the solvent imposes limitations on such a study.

The above reaction was also followed for 1 hour by NMR methods. The ^{19}F resonance spectrum of Ph_4AsCrO_3F solution in dry DMSO (50°C) is at $\delta = 163.0 \pm 0.5$ ppm from (external), $CFCl_3$. The resonance in recrystallized Et_4NF dissolved in DMSO occurs at $\delta = 142.7$ ppm, but because the latter signal was very broad, the substitution reactions CrO_3L^{n-}/L'^{n-} were studied by following the development or disappearance of the more easily detectable ^{19}F resonance in CrO_3F^-.

The addition of 0.25M solution of either Ph_4AsCl or Et_4NCl in DMSO to equimolar quantities of Ph_4AsCrO_3F also in DMSO had no effect on either the frequency or the intensity of the ^{19}F resonance. When the solutions where mixed and stored in the dark for 12 hours, the ^{19}F peak was found to be slightly broadened.

Although no exact rate constants for reaction [20]

$$CrO_3F^- + Cl^- \underset{kr}{\overset{kf}{\rightleftharpoons}} CrO_3Cl^- + F^- \qquad [20]$$

can be obtained from these results, I estimate that the minimum change which could have escaped detection in the UV-visible spectroscopic measurements is ~5%. From the stoichiometry of the exchange reaction [20] and if we let $[CrO_3F^-]_o$ and $[Cl^-]_o$ represent the initial concentrations and $[CrO_3F^-]_t$ and $[Cl^-]_t$ denote the concentrations at time t, then the rate of the reaction is expressed by equation [21]

$$\frac{d\left\{\left[(CrO_3F^-\right]_o - \left[CrO_3F^-\right]_t\right\}}{dt} = k_f \left[CrO_3F^-\right]_t \left[Cl^-\right]_t \qquad [21]$$

The initial concentrations are $[CrO_3F^-]_o = [Cl^-]_o = 0.0005$ molar, and because they are equimolar the rate expression becomes

$$\frac{d\left\{\left[CrO_3F^-\right]_o - \left[CrO_3F^-\right]_t\right\}}{dt} = k_f \left[CrO_3F^-\right]_t^2 \qquad [22]$$

and the integrated expression

$$-\frac{1}{\left[CrO_3F^-\right]_t} = k_f t + C \qquad [23]$$

From this equation [23], the constant, C, was evaluated by setting $[CrO_3F^-]_o - [CrO_3F^-]_t = 0$ at $t = 0$. Therefore, the new rate expression becomes

$$k_f = \frac{1}{t} \cdot \frac{\left[CrO_3F^-\right]_o - \left[CrO_3F^-\right]_t}{\left[CrO_3F^-\right]_o \left[CrO_3F^-\right]_t}$$

Since the reaction is estimated to be no more than 5% complete in 3 days, the upper limit for k_f in acetonitrite is 2×10^{-4} l mol^{-1} sec^{-1}. Similarly, analysis of the NMR results shows that the decrease in CrO_3F^- concentration over 1 hour could not have exceeded 5%. The rate constant in DMSO is then less than 5×10^{-5} l mol^{-1} sec^{-1}.

(ii) The Fluorochromate - Fluoride System

When equal volumes of 0.25M solutions of Ph_4AsCrO_3F and Et_4NF in DMSO were mixed at 50°C, no appreciable change in the ^{19}F peak intensity or width was observed. The CrO_3F^- ^{19}F resonance, which was recorded over 2 hours, indicated the absence of significant fluorine exchange in the CrO_3F^-/F^- system at this temperature. In order for the two separate peaks to be observed at the frequencies −9.17 Kc and −8.05Kc, the lifetimes of each of the species CrO_3F^- and F^- must be greater than $1/(\upsilon_{F^-} - \upsilon_{CrO_3F^-})$[165]; i.e. $> 10^{-3}$ seconds, corresponding to a gross upper limit for the rate constant in dry DMSO for the fluorine exchange of 10^3 l mol^{-1} sec^{-1}.

$$CrO_3F^- + F^- \rightleftharpoons CrO_3F^- + F^- \qquad [25]$$

When the experiment was repeated with the water content deliberately increased above the 0.03% found in dry redistilled DMSO, the ^{19}F resonance peak of the CrO_3F^- anion collapsed at a readily measurable rate. For instance, using reagent grade Et_4NF (Eastman Kodak Co) which was very slightly wet the peak height decreased by approximately 60% within 100 minutes from the time of mixing. Some broadening was also observed. Plotting the ln(intensity) versus time and 1/(intensity) versus time gave straight lines. In mixtures in which the water content was deliberately increased to $> 10\%$ the ^{19}F peak collapsing instantaneously. The reaction in these systems may include, in addition to reaction [25], the equilibria

$$CrO_3F^- + H_2O \rightleftharpoons CrO_3(OH)^- + HF \qquad [26]$$

$$HF + F^- \rightleftharpoons HF_2^- \qquad [27]$$

In addition, the formation of the Cr(III) complexes $[Cr(H_2O)_5Cl]^{2+}$ (broad absorptions at 24,700 and 16,250 cm^{-1}) and $[Cr(H_2O)_5F]^{2+}$ (absorption at 25,300 cm^{-1})[167] was detected spectroscopically, in solutions of CrO_3Cl^- and CrO_3F^- left for longer periods - up to 24 hours. For that reason no attempt was made to follow the hydrolysis process.

(iii) Systems Involving CrO_3L^{n-}/F^- and $CrO(O_2)_2L^{n-}/F^-$

When 0.5M solutions of CrO_3L^-, for L = NCO^-, NCS^-, N_3^-, Br^-

and NO_3^-, are mixed with equal volumes of equimolar Et_4NF, in DMSO,

$$CrO_3L^{n-} + F^- \rightleftharpoons CrO_3F^- + L^{n-} \qquad [7]$$

the reactions followed by NMR were found to be very fast relative to the 0.5 min required to mix the solutions and scan. In each case the ^{19}F chemical shift, $\delta = 160$ ppm, and the UV-visible spectrum were consistent with that of the CrO_3F^- anion. Attempts to slow down the process by cooling failed because DMSO freezes at 18°C.

Treating solutions of $Ph_4AsCrO(O_2)_2L$, for $L = Cl^-$, NCO^-, NCS^-, NO_3^- and N_3^- in MeCN at room temperature, with stoichiometric amounts of Et_4NF, also dissolved in MeCN, caused the blue peroxo complexes to decompose with effervescence. $CrO(O_2)_2py$ reacts similarily with Et_4NF. The yellow solution produced, after the decomposition has stopped, has an absorption maximum at $\simeq$ 353 mµ and a ^{19}F resonance at $\delta = 162$ ppm characteristic of the CrO_3F^- anion.

Attempts to control the decomposition reaction by adding chilled (-10°C) reactants dropwise were only moderately successful. When freshly prepared 0.5M MeCN solution of $Ph_4AsCrO(O_2)_2Cl$ or $Ph_4AsCrO(O_2)_2NO_3$ was treated with equimolar Et_4NF in an equal volume of MeCN, and the mixture maintained at -10°C, the blue colour first turns blue-brown then gradually yellow. The blue-brown solutions had a sharp resonance at $\delta = 127.5$ ppm for the $Ph_4AsCrO(O_2)_2Cl - Et_4NF$ system. and $\delta = 127.0$ ppm for the $Ph_4AsCrO(O_2)_2NO_3 - Et_4NF$ system. Allowing these mixtures to warm up to 25°C over a period of 24 hours, completes the decomposition and the new NMR peaks appear at $\delta = 128.0$ ppm and $\delta = 147.5$ ppm (broad), respectively. The ^{19}F resonance for Et_4NF in dry MeCN is at $\delta = 115$ ppm. (Also see Chapter III Experimental Section).

The blue-brown intermediate in the decomposition is

$$CrO(O_2)F^- \longrightarrow \; ? \; \longrightarrow CrO_3F^- \qquad [28]$$

probably a monoperoxochromium species.

IV.4 POSSIBLE MECHANISMS FOR SUBSTITUTION REACTIONS IN NON-AQUEOUS CrO_xL^{n-} SYSTEMS

The mechanisms of substitution reactions of tetrahedral metal complexes in non-aqueous solvents have been little studied. Both S_N1 and S_N2 type reactions occur in the prototype organic carbon compounds. The larger size of the transition metals compared to carbon would be expected to favour a displacement-type mechanism, in that a fifth group can be held without steric crowding.

We are interested in the nature of the intermediate, i.e. whether the mechanism approaches the limiting S_N1 or S_N2. The kinetics of the chromium VI oxidations of I^-, NCS^- [54], $HS_2O_3^-$ and HSO_3^- [162] have been reported with terms in the rate law which are second order in reducing agent and discussed in terms of a six coordinate chromium (VI) in the activated state.

Although Cr(VI) compounds exhibiting coordination numbers 4 - 7 are known, our study of substitution reactions in non-aqueous media did not produce any evidence for or against five, six of seven coordinate intermediate in CrO_3L^{n-}/L'^{n-} or $CrO(O_2)_2L^{n-}/L'^{n}$. A dissociative mechanism involving the formation of CrO_3 or $CrO(O_2)_2$ species would probably require too high an energy to be consistent with the generally high rates observed for $CrO_3L^{n-}/F-$ (except for $L^{n-} = F^-$ and Cl^-) and $CrO(O_2)_2L^{n-}/L^{n-}$. While a transition state involving an increase in the net charge should be favoured in the more polar solvents, the use of solvents of lower dielectric constants like DMSO (C=46.6)[170] and MeCN (C=36.2)[171] will favour singly charged anions.

Without necessarily involving solvent or steric effects in the exchange process, the faster substitution reactions in CrO_3L^{n-}/F^- where L= Br^-, NCO^-, NCS^-, N_3^- compared to when L= F^- or Cl^- also suggests electronic factors. The mechanisms mentioned above emphasize the significance of bond breaking, of formation of the leaving group, in the activation process.[169] One possible explanation involves the formal charge on the chromium(VI) center. From the results and arguments developed on page 90, the formal positive charge on the chromium(VI) centre would be expected to increase in going from F^- to H_2O (through the series F^-, OH^- *, NO_3^-, Cl^-, NCO^-, Br^-, NCS^-, N_3^-, H_2O where the λ_{max} are at 352, ≃350, 360, 363, 363, 365, 366, 365 and 372 mμ, respectively). This means increasing electron acceptor power to the Cr(VI) center or, alternatively, decreasing coulombic repulsion and faster rate (k_f) in the substitution reaction - c.f. $CrO_3N_3^-/F^-$ to CrO_3F^-/F^- and O_3CrO^{2-}/O^{2-}. In the case of aqueous substitution reactions O_3CrOH^-/L^{n-}, the available evidence points to H_2O (a σ-donor) as the leaving group in the rate determining step and therefore argues in favour of this postulate. Thus in non-aqueous medium the attachment of a donor species in the transition state is all around more

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*OH^-, like the O^{2-} and F^-, is considered to be a strong electron donor not only through the σ-bond but also through HO-M π-bonding.

favoured in systems where there is relatively less electron density at the chromium(VI) site - and may or may not depend on steric hinderences by the leaving group.

In terms of bonding, the anions, CrO_3L^{n-} are pseudotetrahedral and therefore have relatively high molecular symmetry. It seems probable that the symmetrical σ- and π-bonding system would resist rearrangement to five, six or seven coordinate configuration. Consequently, where there is extensive Cr-O π-bonding, e.g. CrO_3F^-, this means higher resistance and decreased availability of Cr d-orbitals with which to form a chromium-substrate bond. Decreased π-bonding would relax the resistence to rearrangement and make the Cr orbitals available to the fifth ligand.

From these discussions it is clear that a general statement cannot be made about the structure of the activated complex or the timing of bond making and bond breaking in chromium(VI) substitution reactions. But electronic (and to some undetermined degree, steric and solvent) effects are obviously very significant in the activation and equilibria of the exchange processes $CrO(O_2)_2L/L'$ and CrO_3L^{n-}/F^- where $L = F^-$, OH^-, NO_3^-, Cl^-, NCO^-, Br^-, NCS^-, N_3^- and H_2O. These effects had not been demonstrated by studies in aqueous solutions.

CHAPTER FIVE

FURTHER ASPECTS: COMPOUNDS CONTAINING CHROMIUM-NITROGEN MULTIPLE BONDS

V.I INTRODUCTION

The coordination chemistry of chromium(VI) is dominated by oxo complexes, and as has been demonstrated, the pseudoisoelectronic O_2^{2-} group substitutes for the oxide ligand in a series of complexes. As an extension of the preceding discussions, this chapter is concerned with attempts to prepare compounds in which chromium(VI) is bonded to a nitrido (N^{3-}) or imido (NR^{2-}) group. It was established that in the complexes $CrO(O_2)_2py$, $CrO(O_2)_2 \cdot bipy$, $CrO(O_2)_2 \cdot phen$, CrO_2ClN_3, $CrO_3N_3^-$ and most probably in CrO_3NCO^- and CrO_3NCS^- as well, the chromium(VI) is bonded directly to a nitrogen. It is surprising, however, that so far no compounds containing chromium(VI)-nitrogen multiple bonds have been established. Other transition metals with no established nitride chemistry include Zr, Hf, Mn, Tc, Rh, Pd and Pt.[173]

The nitride and oxide ligands are isoelectronic and their chemistries are in many respects quite similar. Monomeric nitrido species are formed by transition metals in their higher oxidation states, especially in d^0 and d^2 electronic configurations, but unlike the oxo complexes, most nitrido species are formed with 2nd and 3rd row elements. This may be a reflection of the more effective π-donor capability of the N^{3-} ion, a factor which favours heavier elements in higher oxidation states. The greater π-bonding ability of the N^{3-} ion was demonstrated by force constant calculations on MO_3N^{n-} and MO_4^{n-} for $M=Re^{VIII}$[11] and Os^{VIII}[175].

The remarkable general chemical property is the stability of the metal-nitrogen bond to both addition and substitution. For instance, when the OsO_3N^- anion is attacked by mild reducing agents, e.g. HX (for X = F, Cl, Br, CN, ½ ox etc), it is the Os=O bond rather than the Os≡N, which is broken.[176] The derivatives $[Os^{VI}NX_5]^{n-}$ and trans-$[Os^{VI}N(H_2O)X_4]^{n-}$ have also been isolated. With stronger reducing agents (e.g. $SnCl_2$) the nitrido group is reduced to an amino group.[176] The M_2N groups in $[M_2N X_8(H_2O)_2]^{3-}$, for X = Cl, Br and I; and M = Os and Ru display the same stability.[313] Even in the iridium complexes, e.g. $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$, containing the coplanar Ir_3N unit, substitution, oxidation or reduction reactions have been carried out in aqueous solution without destroying the M-N triangle.[177]

V.2 REVIEW OF METHODS FOR THE PREPARATION OF NITRIDO COMPLEXES AND BASIS FOR EXPECTATION OF SUCCESS.

The relatively small number of imido and nitrido complexes is the result of a lack of preparative methods with wide range of applicability.

(a) The Hydrazine Salt Method:

$KReO_4$ or complexes of rhenium(V) halides containing tertiary phosphines, e.g. $ReOCl_3(PR_3)_2$ are reported to form the five- and six- coordinate nitrido complexes $ReNX_2(PR_3)_n$, for X = Cl, Br, I, R = alkyl or acyl and n = 2 or 3, from reactions with a hydrazine salt ($N_2H_4.Cl_2$ or $N_2H_4SO_4$) and the tertiary phosphine in ethanol.[178] Substitution and addition reactions yielding $ReNCl_4^-$, $ReNCl_5^{2-}$ [176], $K_3ReN(CN)_5$[179] and $(PEt_2Ph)_3X_2Re\equiv N\rightarrow L$ (for X = Cl or Br and L = BBr_3, BCl_3, $PtCl(PEt_3)$ etc)[180] have also been reported.

Unfortunately, the deprotonation of hydrazine to yield nitrido complexes has so far only worked for Re(V); products containing the NR^{2-} and N_2R^- groups as ligand have been observed in platinum chemistry.[176] Chromium(VI) is readily reduced by hydrazine to chromium(III).[181] For instance Cr(VI) in $HClO_4$ reacts with $N_2H_5^+$ in the presence of a wide variety of ligands (NO_3^-, Cl^-, $HBrO_3$, HSO_4^-,

$HSeO_4^-$, HN_3, SCN^-, H_3PO_2, H_3PO_3, H_3PO_4, $H_4P_2O_7$, H_3AsO_4, H_3CCO_2H, Cl_3CCO_2H and $H_2C_2O_4$ producing coordinated Cr(III) species.

(b) Reactions in Liquid Ammonia:

Two important reactions in liquid ammonia are the self ionization represented by the equilibrium

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^- \qquad [1]$$

and the generally slow reduction reaction

$$M + NH_3 \longrightarrow MNH_2 + \tfrac{1}{2}H_2 \,. \qquad [2]$$

Furthermore, with ammonia, the analogues of the oxo and hydroxo compounds in hydrolysis reactions are the compounds containing the groups, amide ($-NH_2$), imide ($=NH$), and nitride ($\equiv N$). The hydrolysis reactions of CrO_3, CrO_3L and $Cr_2O_7^{2-}$ are well established. Chapter 1, Section 1.2 also showed depolymerization-substitution reactions of CrO_3 producing the adducts $CrO_3.L$ and $CrO_3.2L$, for L a donor molecule or ion.

Liquid ammonia and solutions of potassium or potassium amide in liquid ammonia have been used to prepare the insoluble nitrido complexes, MO_3N^{3-} (for M = Mo and W)[182] and ReO_3N^{2-}; these products are probably results of the deprotonetion of the adducts $MO_3.NH_3$ or $MO_3.NH_2^-$. $MO_4.NH_3$, for M = Os and Ru[183] have been shown to contain the MO_3N^- anion. While the ruthenium analog explodes above -20°C, the OsO_3N^- anion gives rise to very extensive nitride chemistry involving osmium in the oxidation states VIII, VI and IV.[176]

To date, products of the reactions of chromium(VI) derivatives with liquid ammonia have not been positively characterized. Attempts have been made in the present study to identify these products. Reports of studies of the reaction of liquid ammonia with CrO_3, $KCrO_3Cl$ or $(NH_4)_2Cr_2O_7$ (with or without KNH_2) at -33°C indicate that some of the Cr(VI) is reduced to Cr(III).[184] In light of the fact that both NH_3 and NH_2^- have the ability to act (although slowly) as reducing agents and it has not been possible to prevent or control reduction reactions occuring in the analytical steps (c.f. the reaction of $KCrO_3(NCS)$ with dilute H_2SO_4 on page 44. We have repeated the earlier reactions and attempted varying the reaction time for the synthesis but without the attempt to determine the extent of Cr(VI) reduction in these or subsequent reactions.

(c) Decomposition of Azido complexes:

The thermal decomposition of the azido group to form a nitride ion and molecular nitrogen has been known for many years.[185] For instance, the complex $Re^{III}(PPhMe_2)_3Cl_3$ reacts very readily with sodium azide to give $Re^{V}(PPhMe_2)_3NCl_2$ and N_2, although the intermediate azido complex could not be isolated.[186] Attempts to obtain nitrido complexes by decomposition of $Os(N_3)_2(PMe_2Ph)_4$ and $OsCl_2(N_3)(PPhR_2)_3$(for R = Me, Et, n-Pr and n-Bu) have been unsuccessful.[187]

Applying the thermal decomposition technique to azido complexes of metals of the early transition series, e.g. MCl_5N_3 (for Mo and W)[130], VCl_4N_3 [188], $TiCl_3N_3$ and $VOCl_2N_3$[131], resulted in the formation of $(MCl_3N)_4$ $(Cl_3VNCl)_2$, TiNCl and VON, respectively. The addition compounds, $MNCl_5^{2-}$, $MNCl_3(PPh_3)$ and $MNCl_3 \cdot 3py$ for M = Mo and W, have also been reported.[189] RuO_4 reacts with HX (X = Cl or Br) and azide producing $RuNX_4^-$ and $RuNX_5^{2-}$.[176]

Dehnicke and Strahle[52] found, however, that when CrO_2ClN_3 is heated above 150°C, the whole molecule, not just the azido group, decomposed liberating nitrogen and oxygen. The new complexes, $CrO(O_2)_2N_3^-$ and $CrO_3N_3^-$ [($CrO_2(N_3)_2$ is very unstable)] seemed to be good candidates for the attempt to prepare nitrido chromium(VI) complexes by the decomposition method.

(d) Deprotonation of the Ammonium Ion

The deprotonation of the ammonium ion in the presence of certain osmium and ruthenium complexes have been shown to yield polynuclear nitrido species - e.g.

$$(NH_4)_2OsCl_6 \xrightarrow[Cl_2]{400^{\circ}C,} Os_2NCl_{5-7} \qquad [3]$$

$$K_2RuO_4 \xrightarrow{NH_4OH,\ OH^-} Ru_2N(OH)_5.nH_2O \qquad [4]$$

Numerous derivatives containing the M_2N unit have been reported.[176] Unfortunately, however, these reductive decomposition reactions would not work for chromium(VI). The product of a CrO_4^{2-} - NH_4OH - OH^- reaction is $(NH_4)_2CrO_4$. Upon heating, $(NH_4)_2Cr_2O_7$ decomposes according to the equation

$$(NH_4)_2Cr_2O_7 \longrightarrow Cr_2O_3 + N_2 + 4H_2O. \qquad [5]$$

(e) Miscellaneous Nitriding Reactions

Reduction reaction between $K_2Ru(NO)X_5$ (X = Cl or Br) complexes and formaldehyde or stannous choride have been reported [190] to yield the polynuclear complex $Ru^{IV}_2NX_8(H_2O)_2^{3-}$. It is also reported that ruthenium trichloride and sulphamide react to produce $RuN(OH)_5.nH_2O$.[190] These methods were discarded on the grounds that Cr(VI) compounds are highly oxidizing and these reactants are strongly reducing.

The ability of trifluoroacetonitrile to oxidize and/or complex with various metal chlorides has been demonstrated.[191] Both tungsten(V) and -(VI) chlorides yield the diamagnetic crystalline yellow solids, $WCl_6.2CCl_3CN$ and $WCl_6.CCl_3CN$, containing tungsten(VI). Analogous reactions with molybdenum(VI) and niobium(IV) yield mixed products consisting largely of $MoCl_5.2CCl_3CN$ and $NbCl_5.CCl_3CN$, respectively; these adducts have also been made directly from the corresponding metal(V) chlorides. Crystal structural analyses have established the presence of tungsten-nitrogen multiple bands in WCl_6CCl_3CN[192] and $WCl_6.2CCl_3CN$.[193] It looked promising to try to synthesize compounds containing chromium(VI) - nitrogen multiple bonds by either oxidative chlorination of chromium(V) compounds (though the most heavily chlorinated Cr(VI) compound is CrO_2Cl_2) or by complexation of the trifluoroacetonitrile with CrO_2Cl_2 and CrO_3, which are known to form 1:1 and 1:2 adducts with donor species.

V.3 EXPERIMENTAL

Much of the apparatus and materials used were the same as those described in the previous chapters.

The general method followed in these studies was to add 4 - 10ml of ammonia to a preweighed sample of the chromium(VI) compound, and to allow the mixture to react standing or in a soxhlet under reflux until no more reaction appeared to be occuring. The ammonia used was from a gas cylinder of reagent grade quality. Any moisture in the ammonia was first removed by condensing the ammonia into a flask containing chips of metallic sodium.

$$Na + NH_3\ (H_2O) \longrightarrow NaOH + NaNH_2 \qquad [6]$$

Caution: in washing up, the unreacted sodium and the sodium amide produced in this process were first deactivated by adding ethanol before washing with water.

The temperature of the reaction was controlled by using a dry ice-ethanol bath.

The diammine silver nitrate, $Ag(NH_3)_2NO_3$ was obtained by dissolving silver nitrate in liquid ammonia - analysis (%) calculated for $Ag(NH_3)_2NO_3$: Ag, 50.5; found: Ag, 51.5. The silver (or chloride) was analysed as AgCl. The chloride in Cl_3CCN reactions was determined as in ref. 194.

The nitrogen content was determined by the method of Akimoto et.al.[195] which is reported to work in the determination of nitrogen in the uranium nitrides, UN and U_2N_3.

Because of decompositions which occur when the compounds were excited with the Ne/He laser no Raman spectrum could be obtained for any of the compounds. Precautions were taken to keep both products and reactants out of contact with atmospheric moisture.

V.4 RESULTS AND DISCUSSIONS

(a) Reactions of Liquid Ammonia

The literature concerning the reactions of hexavalent chromium derivatives with liquid ammonia reveals little positive identification of the products. Sisler and coworkers[184, 196] investigated the reactions of CrO_3, $KCrO_3Cl$ and $(NH_4)_2Cr_2O_7$ with liquid ammonia (with or without KNH_2) at -33°C. These authors reported the formation of ammonium chromates, polymeric chromium(III) - chromate species of indefinite composition, but also noted that some of the nitrogen in the product could only be released by heating. This suggests that the nitrogen is coordinated in a form (probably nitride) which breaks down only under extreme conditions. At least one report[197] of chromium oxide - liquid ammonia reactions discounted the presence of nitrates, nitrites, hyponitrite, azide and oxides of nitrogen in the products.

(i) With Potassium chlorochromate, $KCrO_3Cl$.

Potassium chlorochromate, $KCrO_3Cl$, reacts with dry liquid ammonia in an enclosed system releasing gas (which has been identified [197] as nitrogen) and changing its colour from orange to light brown-yellow. The experiment was set up such that the $KCrO_3Cl$, in a soxhlet, was continuously being reacted and washed with liquid ammonia. A brown material remains in the thimble, while a predominantly white solid (shown by chemical analysis and IR spectroscopy to be NH_4Cl) is washed down from the $KCrO_3Cl$-NH_3 reaction. The chromium and chlorine analyses of the product gave

	1	2	3	4	5	6
%Cl	5.0	4.9	7.45	*	5.62	7.1
%Cr	22.3	*	25.7	26.2	27.3	*

and showed clearly that not all the chloride was removed as NH_4Cl. $KCrO_3Cl$ requires 20.3% Cl.

The light brown product obtained in the present study decomposed with evolution of ammonia when brought into contact with moist air. It dissolved in MeCN and only sparingly in DMSO. The uv-visible spectrum in these solvents resembles those of the trioxochlorochromate(VI) complex, but with less defined vibrational structure.

The infrared spectrum (KBr) is given in Table V-I. It is worth noting that the νCr-Cl band, normally occurring at 435cm^{-1}, is no longer detected, although the chloride still shows up in the analysis. There is evidence (N-H modes) in the infrared spectrum suggestive of the NH_4^+ (3200 and 1400 cm^{-1}) cation and possibly $K(NH_4)_2CrO_3N$ being formed.

Attempts to prepare the tripotassium salt K_3CrO_3N by treating potassium trioxochlorochromate and KCl in liquid ammonia did not work because KCl is insoluble.

This result and the absence of the ν_{Cr-Cl} band suggested that KCl is possibly formed in the $KCrO_3Cl$ - NH_3 reaction, and is analysed with the brown product. One remedial approach would be to use ammonium salts in the reaction. since NH_4Cl is soluble in liquid ammonia.

* Not analysed.

(ii) With Ammonium Trioxochlorochromate NH_4CrO_3Cl.

In other attempts to prepare the triammonium salt, $(NH_4)_3CrO_3N$, NH_4CrO_3Cl was used. The brownish-yellow product gave Cl, 0.2 and 0.3%; and Cr, 35.1 and 38.9% respectively. $(NH_4)_3CrO_3N$ requires 31.0% Cr, $(NH_4)_2HCrO_3N$ requires 34.4% Cr, and $(NH_4)H_2CrO_3N$ requires 38.8% Cr.

The infrared spectrum (KBr) is given in Table V.I. There was no Cr-Cl stretching vibration; and because the NH_4CrO_3Cl used has the following absorptions

3100 vs (br); 1600 vw(br); 1395 vs; 955 s, sh; 940 vs
905s; 880 w-m 770 m; 438 s; 385 vw and 364 vw

it can be established that the 3100, 1395, 955-905 and 438 cm^{-1} bands are due to N-H, NH_4^+, Cr=O and Cr-Cl modes, respectively. So that the medium-to-strong vibrations at 1600, 1260, 1105, 995 and 530 cm^{-1} probably arise from ammonia or its derivatives (NH_2, NO_2, NH or N) in the complex.

(iii) With Ammonium Dichromate, $(NH_4)_2Cr_2O_7$

When finely powdered ammonium dichromate was treated with liquid ammonia, it produced light yellow ammonia-insoluble powder. The analyis gave 33.3% Cr and 19.3% N; $(NH_4)_2Cr_2O_7$ requires 41.3% Cr and 11.1% N; $(NH_4)_2CrO_4$ requires 34.2% Cr and 18.4% N; $(NH_4)H_2CrO_3N$ requires 38.8% Cr and 20.9% N, and $(NH_4)_2HCrO_3N$ requires 34.4% Cr and 27.8% N. It is also possible that the product is a mixture of $(NH_4)_2CrO_4$ and a compound containing a $CrO_3NH_n^{n-3}$ species, because the CrO_4^{2-} ion, which could be formed in the depolymerization of $Cr_2O_7^{2-}$, is very unreactive toward NH_3.

The infrared data (KBr), given in Table V.1, shows that the product is definitely different from the starting material $(NH_4)_2Cr_2O_7$, which has the following absorptions; 3100vs, 1380vs, 900vs, 720vs, 550vs, 550m,sh and 350m

(cm^{-1}). Once again the 1610, 1270 and 1000 cm^{-1} bands suggest some sort of a reaction had occurred. Attempts to obtain a silver salt of this compound by dissolving the product in DMSO and treating the solution with three equivalents (based on Cr) of $AgNO_3$ gave reddish-brown precipitates. The precipitates were washed three times with chloroform. The compound turned yellow in the process of making KBr pellets for the infrared experiment. The IR spectrum of the decomposition product had bands at (cm^{-1}): 3400 vs, 1600 w, 1370 vs, 1010 m, 930-850 vs and 380 w. Except for the 3400cm^{-1} band, which is probably an N-H stretch, it was not possible to extract much information from these bands since N-O vibrations occur in the same regions.

The yellow product dissolves in 1M H_2SO_4 giving an orange solution and in NH_4OH giving a yellow solution, suggesting it is probably K_2CrO_4.

(iv) With chromic oxide, CrO_3

When red chromic oxide is treated with liquid ammonia, in the dark at -70°C for 30 hours, the colour gradually turns to a yellow-tan. The solid is insoluble in liquid ammonia and was isolated by evaporating the ammonia on the vacuum line. The analysis gave 32.0% Cr. $(NH_4)_3CrO_3N$ requires 31.0% Cr and $(NH_4)_2HCrO_3N$ ($\approx CrO_3.3NH_3$) requires 34.4% Cr. In the Sisler and Jirik[196] CrO_3-NH_3 reactions, an average of $\approx$26.0% of the chromium content was reportedly reduced to Cr(III). And when NH_4NO_3 was added to the reaction mixture, the percentage of chromium reduced rose to 28.5 - 44.8%.

The infrared data (KBr) obtained from the present study are provided in Table V.1.

The compound readily evolved ammonia when in contact with moist air but dissolved in DMSO without any apparent reaction. This suggested the possibility of carrying out the metathetical reaction

$$CrO_3 + 4NH_3 \xrightarrow{NH_3} (NH_4)_3CrO_3N \xrightarrow{3AgNO_3} Ag_3CrO_3N \quad [7]$$

in either liquid ammonia or in DMSO. Three equivalents of $AgNO_3$ per chromium were used, and for the reaction in liquid ammonia the complex salt $Ag(NH_3)_2NO_3$ was used instead of $AgNO_3$. The product, a very light brown powder was washed several times with ammonia. The elemental analyses gave 40.5 and 47.5% Ag and 16.8% Cr. Ag_3CrO_3N requires 73.7% Ag and 11.8% Cr, $Ag_2(NH_4)CrO_3N$ requires 62.0% Ag and 14.9% Cr, and $Ag(NH_4)_2CrO_3N$ requires 41.8% Ag and 20.1% Cr.

The infrared spectrum (KBr) showed absorptions at (cm^{-1}).

3200 m (broad); 1600 w-m (broad); 1380 m; 1260 w-m;
1000 w (broad); 880 vs (broad) and 380 vw.

specifically, the spectrum showed a decrease ($\approx$ 50%) in the intensity of the band (assignable to NH_4^+) near 1400cm^{-1} while the ones at 1600, 1260 and 1000 cm^{-1} remained unchanged. This implied that in addition to an ammonium ion, a NO_2, NH_3 or NH_2^- group is probably also present in the product. In one spectral run the initially brown product turned lighter and gave a more complicated spectrum.

3200 vs; 1610 m (broad); 1385 s; 1300 s; 1270 s; 1230 m;
1150 w-m; 1100 w-m, 1020 w, 980 s (shoulder) 930 vs (broad);
800 vs (broad); 560 m (broad); 400 m (shoulder); 385 m and 290

But the main features of the former spectrum were retained.

When the product of the chromic oxide-ammonia reaction was dissolved in DMSO and treated with three equivalents (based on Cr) of $AgNO_3$ and the dark brown precipitate washed with chloroform, the vibrational spectrum which has bands at (cm^{-1})

3300 s (very broad); 1360 vs; 1010 m-s; 930 vs; 800 m (broad) and
380 vw.

suggested that most of the vibrations characteristic of the product of the

Table V.1 The Infrared Spectra of the Products of Liquid Ammonia Reactions

$KCrO_3Cl-NH_3$(KBr)	$NH_4CrO_3Cl-NH_3$(KBr)	$(NH_4)_2Cr_2O_7-NH_3$(KBr)	CrO_3-NH_3(KBr)
3200vs,br		3160vs	3300s(vbr)
	3000 vs(br)		
1610s (br)	1600m(br)	1610m	
1400vs	1400s	1400s	
			1360vs
1290 m-s			
		1270w	
1260s	1260 m-s(br)		
1230			
	1105 w-m		
1080m(br)			
1000m(shoulder)	995m	1000w(shoulder)	1010m-s
980s			
		930s	930vs
950–700vs(br)	950–700vs(br)	900s	
		870vs(br)	
		770vs(br)	800m(br)
540m(vbr)	530w(br)	530w(br)	
380m	380w(br)		380vw
		370w(br)	
340vw			

Table V.I ... (continued)

$KCrO_3Cl-KNH_2-NH_3$(nujol)	$KCrO_3Cl-NaNH_2-NH_3$(KBr)	$CrO_3-KNH_2-NH_3$(Nujol)
	3200s(br)	3250s(br)
	1600m(b)	1600m
1580w(br)		
	1430s(br)	
1300w		
	1280(shoulder)	1290m
	1260(br)	
1240m		1240m
	1110w	
1000-700vs(br)	1010m(shoulder)	1000-700vs(br)
890(max); 780(max)	960-800s(br)	
570w	530w(br)	
435w		
390m	400(shoulder)	
380m	380m	380s
350w		
	340w	

CrO_3 - NH_3 reactions are not changed by the precipitation reaction in DMSO. And without considering N - O species, the vibrational spectra would seem to support the formation of CrO_3N^{3-}, CrO_3NH^{2-} and/or $CrO_3NH_2^-$ species.

(b) Reactions of KNH_2(or $NaNH_2$) with $KCrO_3Cl$ and CrO_3 in Liquid Ammonia

Potassium chlorochromate reacts rather slowly with potassium amide in liquid ammonia to give a dark brown product. The product was washed several times to remove any excess KNH_2. The elemental analyses gave 18.9, 17.8 and 17.7% Cr; 2.0% N and 11.4 and 10.1% Cl, K_3CrO_3N requires 22.5% Cr. Apparently not all the choride was washed through with the filtrate, since the 435 cm^{-1} band assignable to the Cr-Cl stretch appears in the infrared spectrum, Table V.1.

Tannebaum and coworkers[197] investigated the same reaction and observed that the amount of Cr(III) which was formed varied with the mole ratio of KNH_2 to Cr(VI); although there was no simple relationship between molar amide concentration in the ammonia solution and the reduction.

Because the analytical results from the reactions with potassium chlorochromate showed that the chloride persisted through these reactions; the alternative method using CrO_3 was attempted. The product was found to have 29.9% Cr, 2.2% N; K_3CrO_3N requires 22.5% Cr and 6.0% N; K_2HCrO_3N requires 27.0% Cr and 7.2% N; KH_2CrO_3N requires 33.8% Cr and 9.1% N. $K_3Cr_2O_6N$ (containing bridging nitride) requires 31.2% Cr and 4.2% N. The infrared data are given in Table V.1.

Tannebaum and coworkers observed a complex mole-ratio dependent reduction reaction in the CrO_3-KNH_2-NH_3 system; the presence of KNH_2 had little effect on the reactions of $K_2Cr_2O_7$ and K_2CrO_4 in liquid ammonia.

(c) Reactions of Trichloroacetonitrile

In the present investigation, the reactions of chromium(VI) compounds, CrO_3, CrO_2Cl_2 and $KCrO_3Cl$ with neat trichloroacetonitrile were studied in an all-glass vacuum line under air and moisture-free conditions.

(i) With CrO_3.

2.176 gm of chromic oxide was treated at room temperature with 5 ml (density 1.441 gm/ml) of trichloroacetonitrile. After two days, the unreacted ligand was pumped off. Elemental analyses of the product gave (%) C, 2.97; H, 0.44 and N 0.0; CrO_3NCCCl_3 requires (%) C, 9.8, N, 5.7.

The infrared spectrum contained a series of very broad bands from 1000 to 350 cm^{-1}.

(ii) With Chlorochromate, $KCrO_3Cl$ and Ph_4AsCrO_3Cl

When trichloroacetonitrile was left in contact with Ph_4AsCrO_3Cl for 3 days, there was no color change or apparent reaction. Ph_4AsCrO_3Cl did not dissolve in trichloroacetonitrile. The infrared spectrum of the product had vibrations assignable to C-Cl and C=C (or C=N) stretching modes in addition to normal Cr=O and Cr-Cl bands.

The experiment was repeated using $KCrO_3Cl$ (3.335 gm) and richloroacetonitrile (8 ml) under reflux at 85°C. The elemental analysis of the product, obtained after pumping off the excess ligand, gave (%) Cr; 27.7; C, 3.6, H, 0.5; Cl, 12.3 and N, 1.8. $KCrO_3Cl.NCCCl_3$ requires (%) Cr, 16.4; C, 7.55; Cl, 44.6 and N, 4.4; there are otherwise numerous possibilities.

The infrared spectrum of the product had no absorption assignable to the C≡N stretch. The only bands not present in the spectrum of the free ligand occurred at 1880w, 1850m, 1380m, 910vs($\nu(CrO_3)$), 435s($\nu(CrCl)$) and 350m(δ(O-Cr-O)) cm^{-1}.

(iii) With Chromyl Chloride

Leaving chromyl chloride in the dark in contact with trichloroacetonitrile for 24 hours, produced no observable reaction. But when the two reactants were mixed in dichloromethane and kept at -10°C for 24 hours, white crystals formed and the red solution turned green. The white solid melts at 144°C and from the mass spectral and chemical analyses (C, 15.0%, H, 1.2% and N 8.8%) the product is trichloroacetyl amide (Cl_3CCOHN_2 requires C, 14.8; H, 1.2 and N, 8.6). This reaction suggest that although Cl_3CCN may be strongly oxidizing in the presence of CrO_2Cl_2 and CH_2Cl_2 the Cl_3CCN is oxidized and the CrO_2Cl_2 reduced. Dichloromethane was used in the tungsten(V and VI) chloride - Cl_3CCN reactions but no hydrogen abstraction was reported.

(iv) With Cesium Pentachloro-oxo-chromium(V), Cs_2CrOCl_5

Because trichloroacetonitrile has been shown to oxidise [191] W(V), Mo(IV) and Nb(IV) to W(VI), Mo(V), and Nb(V), respectively, an attempt was made to prepare a chromium(VI) complex by oxidizing a chromium(V) chloride complex. The Cs_2CrOCl_5 used in the reaction was prepared by dissolving CrO_3(0.5gm) in 20 ml of glacial acetic acid (previously saturated with hydrogen chloride) and treating the solution with CsCl(1.0gm) dissolved in glacial acetic acid (with HCl). The reaction is reported to give Cs_2CrOCl_5.[198] But when the Cs_2CrOCl_5 was left in contact with trichloroacetonitrile at 65°C for two days, there was no observable reaction; Analysis (%): Cl, 34.0 Cs_2CrOCl_5 requires 34.8% Cl.

(d) Thermal Decomposition of $Ph_4AsCrO_3N_3$

It is established that certain azido complexes undergo thermal decomposition yielding nitrido complexes and molecular nitrogen. Attempts were, therefore made to synthesize nitrido chromium(VI) complexes from our azido complexes, $CrO(O_2)_2N_3^-$ and $CrO_3N_3^-$.

Heating $Ph_4AsCrO_5N_3$ resulted in spontaneous decomposition to a green solid.

When $Ph_4AsCrO_3N_3$ was heated under vacuum, for about 2 hours at 210^oC, it melted and turned dark brown. The dark brown product gave the analysis(%) C, 51.2; H, 3.6 and N, 3.0. $Ph_4AsCrO_3N_3$ requires C, 54.8, H, 3.8 and N, 8.0. The vibrational spectrum of the product had cation modes and other bands which are significantly different from those of the starting material. The $\nu_{asy}(N_3)$ and $\nu_{sym}(N_3)$ bands which occur at 2073 and $1280cm^{-1}$ in $Ph_4AsCrO_3N_3$ diminished to less than 10% of the original. New absorptions occur at 3400s (broad), 1620 m (broad), 965m (shoulder) 890s and 580m (broad) cm^{-1}. The ν_{Cr-N} vibration which occurs at $495cm^{-1}$ in $Ph_4AsCrO_3N_3$ disappeared after heating. The vibrational spectrum and the results of the elemental analysis, which show a proportionally larger drop in the nitrogen content compared to the carbon or hydrogen, suggest that decompostion of the azido group to a nitride might have occurred. But for a nitrogen clearage (equation [8]) to occur, this preparative method would require more cation to balance off the charges.

$$Ph_4AsCrO_3N_3 \xrightarrow{\text{heat}} \left[Ph_4AsCrO_3N\right]^{2-} + N_2 \qquad [8]$$

Other reactions might also have occured. Attempts to prepare $KCrO_3N_3$ from $KCrO_3Cl$ and NaN_3 (solutions in MeCN) for alternative reactions involving heating $KCrO_3N_3$ and K. failed.

(e) Analysis of the Vibrational Spectra

Because the analytical data obtained here and in previous studies [193,197] do not permit positive identification of the products, it was hoped that the data from vibrational spectoscopy compared with those of similar investigation on established compounds might shed some light.

The vibrational spectra of many nitrido complexes have been studied. The M≡N stretching mode in $(Me_4N)_2MoNCl_5$, $(Me_4N)_2WNCl_5$ [189] $MoNCl_3$ 4 and $WNCl_3$ [130] are assigned to the bands at 1023, 1035, 1045 and 1068cm^{-1}, respectively. Generally, the M≡N stretching mode falls in the comparatively narrow range of 1020-1150cm^{-1}.[311]

From the infrared spectra of amine complexes[198], the bands in the regions 3040-3400, 1570-1710, 1235-1400 and 590-890cm^{-1} can be assigned to the stretching and deformation modes ν(N-H), $\delta_{asy}(NH_3)$, $\delta_{sym}(NH_3)$ and NH_3 rocking (i.e. δ(M-N-H), $\rho(NH_3)$ respectively. Vibrational modes of coordinated nitro groups have also been observed in these same regions ($\nu_{asy}(NO_2)$, (1363-1497) cm^{-1}); $\nu_{sym}(NO_2)$, 1300-1373cm^{-1} $\delta(NO_2)$, (798-849cm^{-1}) and NO_2 wag (585-650))[198]. The infrared spectrum of $Cr(NH_3)_5.ONO\ Cl_2$ containing complexed nitrito group[198] Cr-ONO, has bands at 1460 ($\nu_{asy}(NO_2)$, 1048 ($\nu_{sym}(NO_2)$ and 839 ($\delta(NO_2)$). It is therefore not possible to make unequivical assignments of the bands we observed at 1250 and 1025 (or 1010)cm^{-1} to either $\nu_{Cr\equiv N}$, $\delta(NH_2)$[199], $\nu_{Cr=N}$ or ν_{sym}(ONO) vibrations. Drago and Sisler [184] assigned the bands at 1005 and 982cm^{-1}, to the skeletal vibrations of the chromium(III) - chromate polymers produced in the CrO_3-NH_3 reactions.

One possible drawback in synthesizing chromium(VI) nitrido complexes is the fact that chromium is a small atom, and, for oxo species there is already extensive Cr=O π-bonding; too extensive to allow, for instance, K_2CrO_4 to react with NH_3. It is therefore less likely that chromium(VI) would form the MO_3N^{n-} anion formed by Os^{VIII}, Re^{VII}, Mo^{VI} and W^{VI}. It may be possible to prepare chromium nitrido complexes by reacting $CrOF_4$ with either KNH_2, NH_3 or Cl_3CCN.

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