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STUDIES OF MONOSUBSTITUTED TRIOXO- AND OXODIPEROXOCHROMIUM(VI) COMPLEXES

by

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B.Sc., University of Washington, 1968

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

in the Department of Chemistry

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Title of Thesis/Dissertation:

STUDIES OF MONOSUBSTITUTED TRIOXO- AND OXODIPEROXOCHROMIUM(VI) COMPLEXES

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February 28, 1975.

(date)
New monosubstituted trioxo- and oxodiperoxochromium(VI) complexes CrO₃L⁻, (for L = Br⁻, NCO⁻, N₃⁻, NCS⁻ and NO₃⁻) and CrO(O₂)₂L (for L = F⁻, NCO⁻, NCS⁻, N₃⁻, NO₃⁻ and OP(C₆H₅)₃), prepared by metathetical reactions in acetonitrile, have been characterized.

The vibrational spectra of the CrO₃L⁻ (infrared and Raman) and CrO(O₂)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 ~ 900 cm⁻¹, generally assigned to ν_{sym} (Cr-O) (A₁), were studied closely. There was a gradual but regular decrease in the frequency as the substituent L was changed from F⁻, Cl⁻, NCO⁻, Br⁻, NO₃⁻, N₃⁻, to NCS⁻, demonstrating that ν_{sym}(Cr-O) could be used as a probe for substituent effects in CrO₃L⁻ ions.

The electronic charge-transfer spectra of the two sets of complexes CrO₃L⁻ and CrO(O₂)₂L in the UV-visible region were also recorded. In the case of the CrO₃L⁻ ions, the spectra showed three absorption bands, one of which (in the 360 nm 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 charge-transfer spectra were discussed in terms of the Cr-O²⁻ and Cr-O²⁻₂ bonding interactions in CrO₃L⁻ and CrO(O₂)₂L, respectively.
Attempts were made to measure the equilibrium constant for the substitution processes of the type

\[ \text{CrO}_3\text{L}^- + \text{L'}^- \rightleftharpoons \text{CrO}_3\text{L'}^- + \text{L}^- \]

and

\[ \text{CrO(O}_2\text{)}_2\text{L} + \text{L'} \rightleftharpoons \text{CrO(O}_2\text{)}_2\text{L'} + \text{L} \]

in non-aqueous (dimethylsulphoxide or acetonitrile) solutions, conditions chosen to eliminate competing hydrolytic process which generally occur in aqueous solutions. While the $^{19}\text{F}$ NMR studies showed very slow exchange in the $\text{CrO}_3\text{F}^-/\text{F}^-$ and $\text{CrO}_3\text{F}^-/\text{Cl}^-$ systems, the substitution reactions in $\text{CrO}_3\text{L}^-/\text{F}^-$ for $\text{L}^- = \text{Br}^-$, $\text{N}_3^-$, $\text{NCO}^-$, $\text{NCS}^-$ and $\text{NO}_3^-$ were very fast. Attempts to synthesize $\text{CrO(O}_2\text{)}_2\text{F}^-$ or affect exchange in $\text{CrO(O}_2\text{)}_2\text{L}/\text{F}^-$ and $\text{CrO(O}_2\text{)}_2\text{NC}_5\text{H}_5/\text{NC}_5\text{H}_5$ (and $\text{d}_5$) 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
ACKNOWLEDGEMENT

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.

I have also incurred debts of gratitude, which I am delighted to acknowledge: to AAI-University of Washington Scholarships for financial support during the period 1964 - 1968; to Mr. M. K. Yang for analysing the carbon, nitrogen and hydrogen contents of the compounds expeditiously; to Val, Kirk and Diane Michaelian for being the people they are and finally to the Chemistry Department for providing the facilities for the research work.

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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ν = stretching; δ = deformation; ρ = rocking; $f_{M-X} = \frac{M-X}{\lambda}$ (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(VI)
1.1 INTRODUCTION

The element chromium is widely distributed principally as the ore chromite, FeCr₂O₄. It was first discovered in 1797 in the mineral crocoite, PbCrO₄, 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 Mertz² 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 (3d⁵⁴s¹) 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 species⁵ such as Mo⁵⁺, Mo⁶⁺, Mo⁷+ and $[\text{Mo}_2\text{O}_7]^{n+}$ 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. Gillespie 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 $\pi$-bonding electrons. In the case of terminal oxygen, $M-O_3^-$, valency requirements would be a major contributing factor.

All known compounds of chromium(VI) exist, with the exception of $CrF_6$ which decomposes above -100°C, as oxo species such as $CrO_4^{2-}$, $CrO_3^-$, $CrO_2L^-$, $CrO_2L_2^-$, $CrO_2L_3^-$, $CrO_2L_4^-$ and $CrO(L_2)_2^-$ where $n = 0, 1, 2, ...$ etc. and L is a single atom donor ion or grouping (e.g. 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 $\sigma$- and $\pi$-bonding contributions to the $M-O$ bond strength.

Numerous authors 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 $\pi$-$d\pi$ donation to depend both on the tendency for the oxygen (or ligand) to donate and of the metal
to accept electrons. Consider $\text{CrO}_3L^-$; coordination of ligands (L) which owe their ligational strength primarily to their $\sigma$-electron pair (Lewis base) donating ability will increase the electron density on the chromium d-orbitals and cause a reduction in the amount of $\pi \rightarrow d\pi$ donation from the oxygens. For instance, Kidd\^1 has shown that a linear relationship exists between the $^{17}O$ chemical shifts and the degree of Cr-O $\pi$-bonding in $\text{O}_3\text{CrO}_2\text{CrO}_3^2-$, $\text{CrO}_4^{2-}$, $\frac{0}{3}\text{CrO}_3\text{CrO}_3^2-$ and $\text{CrO}_2\text{Cl}_2$.

The ideal set-up for studying M-O $\pi$-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 $\text{CrO}_2\text{Cl}_2$, $\text{CrO}_3\text{Cl}^-$, $\text{CrO}_4^{2-}$ and $\text{CrO}(\text{O}_2)\text{Cl}^-$, 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), $\text{CrO}_2L_x^{n-}$, 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,\textsuperscript{13,14} \CrO_2F_2, the most corrosive of all, has the greatest thermal stability (up to \(\approx 400^\circ\text{C}\)); \CrO_2Cl_2 decomposes at approximately 180\(^\circ\text{C}\) 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)L), except for the vibrational studies of Stemreich and Sala\textsuperscript{15} and others\textsuperscript{16,17} on the \CrO_3Cl^- and \CrO_3F^- ions and the electronic spectral studies of the same compounds by Helmholtz and Brennam,\textsuperscript{18} there are no vibrational or electronic spectral studies reported on any other stable anionic monosubstituted chromates, \CrO_3L^-\textsuperscript{1-}. The only spectral studies conducted on anionic monosubstituted oxodiperoxochromate(VI) complexes, \CrO(O_2)L^\textsuperscript{1-}, are those of Tuck\textsuperscript{19} and Griffith.\textsuperscript{20}

\textbf{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^-\textsuperscript{1-} and \CrO(O_2)L^\textsuperscript{1-}, 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^-\textsuperscript{1-} or \CrO(O_2)L^\textsuperscript{1-}. 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

\[ \text{CrO}_3L^\text{n-} + L'^\text{n-} \rightleftharpoons \text{CrO}_3L'^\text{n-} + L^\text{n-} \]

and

\[ \text{CrO(O}_2)_2L^\text{n-} + L' \rightleftharpoons \text{CrO(O}_2)_2L' + L \]

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 \( \Delta H \), entropy \( \Delta S \) and free energy \( \Delta G \)), occurring 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 \( (\text{N}^3\text{)} \) and oxide \( (\text{O}^2\text{)} \) ions are isoelectronic, The former has been shown by force constant calculations on \( \text{ReO}_3\text{N}^2\text{)} \) and \( \text{OsO}_3\text{N}^- \) to have the greater \( \pi \)-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(VI) 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(VI) 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 VI B elements (S, Se, etc.), the resemblances 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 and vibrational spectrum 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. It has, however, become abundantly clear that the vibrational spectra of these complexes are complicated. 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-} 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. Except for H_2Cr_2O_7, H_2Cr_3O_10 and M_2Cr_4O_13, 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). The relative simplicity of chromate hydrolysis-polymerization is perhaps due to the greater extent of multiple bonding, Cr=O, for the smaller chromium ion. So that while Cr(VI) appears to be limited to tetrahedral coordination in the oxide structures 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(VI).

The electronic and X-ray structures of the Cr$_2$O$_7^{2-}$ ion have been studied. As is the case with the CrO$_4^{2-}$ ion, the complete assignment of the vibrational spectrum of the Cr$_2$O$_7^{2-}$ ion is not yet established.

\[(a) \text{ Mo(VI) and W(VI)} \]

\[(b) \text{ Substituted Dioxochromium(VI) Complexes} \]

Certain ligands are known 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

<table>
<thead>
<tr>
<th>$V^V$</th>
<th>$Cr^{VI}$</th>
<th>$Mo^{VI}$</th>
<th>$Re^{VII}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VO$_4^{3-}$</td>
<td>CrO$_4^{2-}$</td>
<td>MoO$_4^{2-}$</td>
<td>ReO$_4^{-}$</td>
</tr>
<tr>
<td></td>
<td>CrO$_3X_3$</td>
<td>MoO$_3S^{2-}$, MoO$_3N^{3-}$</td>
<td>ReO$_3X^n$ (for X = S, N,F,Cl, Br)</td>
</tr>
<tr>
<td></td>
<td>CrO$_2X_2$</td>
<td>MoO$_2S^{2-}$</td>
<td>ReO$_4^{-}$</td>
</tr>
<tr>
<td>VOS$_3^{3-}$</td>
<td>CrO(O$_2$)$_2$OH$^-$</td>
<td>MoS$_4^{2-}$</td>
<td>ReO$_4^{-}$</td>
</tr>
</tbody>
</table>

the isoelectronic nitride (N$_3^-$), hydroxide (OH$^-$) and fluoride (F$^-$), and also the "pseudoisoelectronic" peroxide (O$_2^{2-}$) and sulphide (S$_2^{2-}$) ions have formally substituted the oxide ligand.

* The complexes $K_3(CrO_4F)^{29}$ and $2NaOH.Na_2(CrO_4)_3^{30}$ which may contain the CrO$_4$(OH)$_2^{4-}$ ion, have been reported.
Except for CrOF₄, the most heavily substituted chromium(VI) oxo complexes also contain the peroxy 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 dioxygen moiety CrO₂⁺ is coordinated to various donor species. Of these the best known are the dioxygenochromium(VI) compounds, CrO₂Cl₂ and CrO₂F₂. These complexes are prepared by the action of various halogenating agents on CrO₃ or CrO₂⁻. The structure of CrO₂Cl₂ in vapour has been determined by electron diffraction and both CrO₂Cl₂ and CrO₂F₂ have been subjected to infrared, Raman and mass spectral studies. The electronic structure of CrO₂Cl₂ has also been investigated. The mixed halide complex, CrO₂ClF, has been identified as a product in the metathetical reaction of the two pure compounds

\[
\text{CrO}_2\text{Cl}_2 + \text{CrO}_2\text{F}_2 \rightleftharpoons 2\text{CrO}_2\text{ClF}
\]  

[1]

In addition to other synthetic routes, the reaction of CrO₂Cl₂ with silver borate, hydrogen bromide, silver cyanate, silicon thiocyanate (or OP(SCN)₃), dinitrogen pentoxide and peroxodisulphuryldifluoride (S₂O₆F₂) have been reported to yield CrO₂(BO₂)₂, CrO₂Br₂, CrO₂(NCO)₂, CrO₂(NO₃)₂, and CrO₂(SO₃F)₂ respectively. An equally interesting series of compounds have been prepared for reactions with CrO₃. For instance, hydrazoic acid, acetic acid, oxalic acid, acetic anhydride, and various fluorinated anhydrides have been used to prepare CrO₂(N₃)₂, CrO₂(OH)(CH₃COO), CrO₂[p], CrO₂(CH₃COO)₂, and CrO₂[RₕCOO]₂ (for Rₕ = CF₃, C₁F₂C and C₃F₇), respectively. In other studies, Gerlach and Gard reported making new five and six coordinate dioxygenochromium(VI) complexes, KCrO₂(CF₃COO)₃, CrO₂[RₕCOO]₂⁻ (for Rₕ = CF₃ or C₃F₇), and CrO₂[RₕCOO]₃⁻ (for Rₕ = CF₃ or ClCF₃), by reacting the halogenated anhydrides with CrO₃Cl⁻, CrO₂⁻ or...
Substituted Trioxochromium(VI) Complexes

A number of kinetic studies have been published on chromium(VI) species in various aqueous solutions. It is well established that in neutral and basic (pH > 6) solutions the tetrahedral yellow chromate ion, CrO₄²⁻, exists; as the pH is lowered the chromate ion is converted via protonation (HCrO₄⁻) and dimerization to the orange dichromate ion (Cr₂O₇²⁻). Between pH 6 and 2, the ions HCrO₄⁻ and Cr₂O₇²⁻ are in equilibrium.

\[
\begin{align*}
\text{CrO}_4^{2-} + \text{H}^+ & \rightleftharpoons \text{CrO}_3(\text{OH})^- \quad \text{[2]} \\
2\text{CrO}_3(\text{OH})^- & \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \quad \text{[3]}
\end{align*}
\]

The above reactions represent just two of many situations in which the oxide (O²⁻) ion in the chromate (CrO₄²⁻) is replaced by a donor group, in this case hydroxyl (OH⁻) or chromato (CrO₄²⁻) group. The interconversion of HCrO₄⁻ and Cr₂O₇²⁻ (equation 3) has been shown to bring about oxygen exchange between chromium(VI) species and water. Studies of this exchange process in neutral and basic 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 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 $\text{CrO}_2^-$, $\text{HCrO}_4^-$, and $\text{Cr}_2\text{O}_7^{2-}$ ions to the corresponding monosubstituted derivative $\text{CrO}_3\text{L}^{n-}$, where $L = \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{CH}_3\text{CO}_2^-, \text{NO}_3^-, \text{PO}_4^{3-}$, $(\text{HPO}_4^{2-}$ or $\text{H}_2\text{PO}_4^-)$, $\text{PO}_3^{2-}$ ($\text{HPO}_3^2$ or $\text{H}_2\text{PO}_3^-$), $\text{SO}_4^{2-}$ (or $\text{HSO}_4^-$), $\text{SO}_3^{2-}$ (or $\text{HSO}_3^-$) and $\text{IO}_3^-$, respectively. The possible existence of most of these species (as well as others, e.g. $\text{CrO}_3(\text{S}_2\text{O}_3)^2^-$, $\text{CrO}_3(\text{NCS})^{2-}$ .... 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 $\text{KCrO}_3\text{F}$, was first prepared 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 red crystals of potassium chlorochromate, $\text{KCrO}_3\text{Cl}$. Peligot obtained the same salt by treating stoichiometric amounts of potassium chloride with chromic acid (aqueous solution of $\text{CrO}_3$). Crystal structures of $\text{KCrO}_3\text{F}$ and $\text{KCrO}_3\text{Cl}$ have since been reported and the vibrational and electronic spectra established.

The existence of potassium bromochromate, $\text{KCrO}_3\text{Br}$, on the other hand, has been questioned. Original efforts 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 claimed having isolated garnet-red crystals of potassium iodochromate (KCrO$_3$I) 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 on the grounds of their oxidation-reduction potentials.

The preparation of potassium iodochromate, KCrO$_3$I$_2$, by reacting potassium dichromate and iodic acid in nitric acid, originally reported by Berg and Blomstrand, has since been repeated and the product subjected to an X-ray structural study and a nuclear quadrupole resonance analysis. Meyer and Stateczney 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$_2$CrO$_3$(SO$_4$)$_2$, 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 reported the preparation of a series of 1:1 (CrO$_3$.L) and 1:2 (CrO$_3$.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 tribenzylation formed only 1:1
adducts and required lower temperatures to avoid extensive oxidation-reduction reactions. It is believed that the $\text{CrO}_3\cdot 2\text{L}$ 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, $\text{CrO}_3\cdot 2\text{ROH}$, are also known.  

(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, $\text{CrO}_3(\text{SO}_4)_4^{2-}$, along with the condensation copolymers $\text{CrO}_3\cdot \text{SO}_3\cdot 4\text{H}_2\text{CrO}_2\cdot \text{SO}_4\cdot 2$, $\text{H}_2\text{Cr}_4\text{O}_{13}$ and $\text{H}_2\text{Cr}_3\text{SO}_{13}$, was proposed from spectroscopic evidence obtained from studies of various $\text{CrO}_3\cdot \text{H}_2\text{SO}_4\cdot \text{H}_2\text{O}$ systems.

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 have advanced convincing arguments that these oxidations proceed via the formation of esters of chromic acid; e.g. $(\text{CrO}_3\cdot 0\text{R})^{-}$. Similar intermediates $(\text{CrO}_3\cdot \text{L})$ have been proposed for the oxidation of aldehydes.

The mechanisms for the oxidation of non-metallic oxoanions, such as arsenite, sulphite, phosphite and hydrophosphite, 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 has renewed interest in inorganic chromium(VI) oxidations.
For instance, the study of the oxidation of complexes of Ce(IV), Fe(II), Fe(III), As(III), Cr(III), Np(IV), Th(IV) and Co(III) suggests that the reaction occurs via the formation of a complex e.g.

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

The hypothesis is supported by the fact that the solid derivative, [Cr(NH₃)₅Cr₂O₇]Cl, has been isolated, and more recently Coomer and Griffith, reported the vibrational (IR and Raman) spectra of the pentammine and tetrammine cobalt(III) complexes, [Co(NH₃)₅Cr₂O₇]Cl and [Co(NH₃)₄Cr₂O₇]NO₃, 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.

\[ CrO_3Cl^- + H_2O \rightarrow CrO_3(\text{OH})^- + H^+ + Cl^- \]  

Because of this a few studies have been attempted in non-aqueous media. Klang and Symons studied the ultraviolet spectra of dilute solutions of ammonium dichromate, (NH₄)₂Cr₂O₇, 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. From their observations, the authors claimed the identification of monosubstituted esters CrO₃OR⁻, in which R is alkyl, substituted alkyl or acyl, and the substitution reaction was represented by equation [6].

\[ (\text{NH}_4)_2\text{Cr}_2\text{O}_7 + 2\text{ROH} \rightarrow 2(\text{NH}_4)\text{CrO}_3\text{OR} + \text{H}_2\text{O} \]  

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

\[ \text{CrO}_3\text{OR}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCrO}_4^- + \text{ROH} \]
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 $\sigma$-bonding.

### Metal and Ligand Orbital Contributions In Tetrahedral Symmetry

<table>
<thead>
<tr>
<th>Irreducible Representation</th>
<th>Contributions</th>
</tr>
</thead>
<tbody>
<tr>
<td>a$_1$</td>
<td>s</td>
</tr>
<tr>
<td>e</td>
<td>d(z$^2$, x$^2$-y$^2$)</td>
</tr>
<tr>
<td>t$_1$</td>
<td>p(x, y, z), d(xy, xz, yz)</td>
</tr>
<tr>
<td>t$_2$</td>
<td>p$<em>\sigma$, p$</em>\pi$</td>
</tr>
</tbody>
</table>

In the case of CrO$_4^{2-}$ or CrO$_3$L$^-$ 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 $\sigma$ bonds; while the e - orbitals can only participate in $\pi$-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$_2$Cl$_2$ is probably the best studied.

The CrO$_4^{2-}$ and Cr$_2$O$_7^{2-}$ ions have very extensive aqueous (also leading to peroxo complex) chemistry as far as substitution 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$_3$F$^-$ and CrO$_3$Cl are the best known. The general reactions of the complexes are presented in Scheme 1.1 next page.
Where $Y=Z$ and $Y \neq Z$ and $x = n = 0, 1$ or 2

**SCHEME 1.1**

*Reactions of Oxo Complexes of Chromium (VI)*
1.3 Peroxo Complexes of Chromium and Other Transition Metals

The process whereby transition metal compounds interact with an oxygenating agent, oxygen (O₂), ozone (O₃) or hydrogen peroxide (H₂O₂), to form derivatives in which one or more dioxygen groups (O₂⁻, O⁻ or O₂) are coordinated to the metal has been known for over 150 years. The coexistence 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.

**Basic Solution:**

\[
\begin{align*}
2\text{OH}^- & \quad -2.0 \\
\text{OH} + \text{OH}^- & \quad 0.26 \\
\text{HO}_2^- & \quad -0.4 \\
\text{O}_2^- & \quad 0.6 \\
\text{O}_2 & \quad 0.08
\end{align*}
\]  

**Acidic Solution:**

\[
\begin{align*}
2\text{H}_2\text{O} & \quad -2.82 \\
\text{OH} + \text{H}_2\text{O} & \quad -0.72 \\
\text{H}_2\text{O}_2 & \quad -1.5 \\
\text{HO}_2 & \quad +0.13 \\
\text{O}_2 & \quad -0.67
\end{align*}
\]

The schemes above represent the redox potentials in volts for O₂ in basic [8a] and acidic [8b] solutions (at 25°C), respectively.

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-organic-metallic chemistry. 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. 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 to occur between certain dioxygen compounds of Group VIII metals and molecular species such as gaseous non-metallic oxides (CO, SO₂, NO, NO₂, CO₂), CS₂, 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. 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 preceding paragraphs to draw attention to the fact that, depending on the electronic environment of the central metal, the dioxygen species, O₂ⁿ⁻ 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).
Table 1.1. Formal Charge on the Dioxygen Species:

<table>
<thead>
<tr>
<th>Compound</th>
<th>O-O bond length (Å)</th>
<th>Comparable ( O_2^{n-} ) species and their bond lengths (Å)</th>
</tr>
</thead>
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<tr>
<td>( \text{Ir}(O_2)(\text{Cl})(\text{CO})(\text{Ph}_3\text{P})_2 )</td>
<td>1.30 ± 0.03&lt;sup&gt;a&lt;/sup&gt;</td>
<td>( O_2 \ (1.2107 \pm 0.0001) )</td>
</tr>
<tr>
<td>( \text{Ir}(O_2)(\text{I})(\text{CO})(\text{Ph}_3\text{P})_2 )</td>
<td>1.509 ± 0.026&lt;sup&gt;b&lt;/sup&gt;</td>
<td>( O_2^- \ (1.28 \pm 0.02) )</td>
</tr>
<tr>
<td>( [\text{Ir}(O_2)(\text{diphos})_2][\text{PF}_6] )</td>
<td>1.625 ± 0.023&lt;sup&gt;c&lt;/sup&gt;</td>
<td>( O_2^- \ (1.49 \pm 0.01) )</td>
</tr>
</tbody>
</table>


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<sup>116</sup> has shown that each \( O_2 \) group in \( \text{Cr}(O_2)_4^{3-} \) 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 \( \text{Pt}(O_2)(\text{PPh}_3)_2 \).<sup>117</sup> 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 $\text{H}_2\text{O}_2$ and metals of the early transition series. Because the 0-0 bond lengths in these complexes are generally around 1.4 $\pm$ 1.5 Å, 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 aqueous solution. Although a majority of these complexes involve "laterally" coordinated peroxide groups, a few are known in

![diagram]

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 especially when varying amounts of hydrogen peroxide ($\text{H}_2\text{O}_2$ reduces polymerization) are present. The anionic species obtained by treating acidic molybdates or tungstates with $\text{H}_2\text{O}_2$ have variously been given the
formulae such as $\text{M}_2\text{O}_8^{2-}$, $\text{M}_2\text{O}_9^{2-}$, HMoO$_6$ or $\text{M}_2\text{O}_{11}^{2-}$.

(a) Unsubstituted Peroxo Complexes: $\text{M(O}_2\text{)}_4^{n-}$

The NH$_4^+$ and K$^+$ salts containing the unsubstituted peroxo anion $\text{M(O}_2\text{)}_4^{3-}$ are known for $\text{M} = \text{Cr, V, Nb and Ta}^{125}$ The "red" chromium salt, previously formulated $^{126-128}$ as $\text{Cr}_2\text{O}_{12}^{6-}$, $\text{Cr}_2\text{O}_{13}^{6-}$, $\text{Cr}_2\text{O}_{15}^{6-}$, $(\text{Cr}_2\text{O}_{16}^6\cdot\text{H}_2\text{O})^{6-}$ and now known to contain the mononuclear ion $\text{Cr}^V(\text{O}_2)^{3-}$, is prepared by reacting hydrogen peroxide and a dichromate in strongly alkaline solutions, below $0^\circ\text{C}$. 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 Å and the other four at 1.944 Å. The bond length between two oxygen atoms coordinated as peroxides is 1.405 Å, while the shortest distance between oxygens not belonging to the same peroxy ions, are 2.91, 2.57, 2.75 and 2.74 Å. 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^{2+} , Sr^{2+} , Ba^{2+} , Co^{2+} and Zn(NH_3)_4^{2+} were prepared by reacting, under very low temperatures, alkaline solutions of the metallates with excess hydrogen peroxide. The molybdenum(VI) and tungsten(VI) tetraperoxos species are chemically stable while the chromium(VI) derivative is highly explosive.

(b) Oxoperoxo Complexes: M(O_2)_2(0)_y and M(O_2)_x(0)_y L_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 VO(O_2)_3^{3+}+n ), VO(O_2)_2^{2-} [or H_n V(O)_2(O_2)_2^{3+}n and polymers like H_n V(O)_2(O)_2^{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, a triperoxouranium(VI) complex exists, and recently structural studies have established the existence of and a dodecahedral geometry in the triperoxoniobate(V) compounds $K[Nb(O_2)_3\cdot phen] \cdot 3H_2O$ and $K[Nb(O_2)_3\cdot phen] \cdot 3H_2O \cdot H_2O$. The triperoxovanadates are believed to have eight coordination of the metal similar to that observed in the peroxoniobate(V) compounds.

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

$$CrO(O_2)_5\cdot ether \xrightarrow{-10-0^\circ C} K_3[Cr(O_2)_2(CN)_3] \xrightarrow{KCN(aq)+50^\circ C} NH_3(aq) \xrightarrow{NH_3(aq)+50^\circ C} [Cr(O_2)_2(NH_3)_3]$$

The olive-green ethylenediamine derivative $[(C_2H_8N_2)Cr(O_2)_2H_2O] \cdot H_2O$ is also known. Structural investigations on the compounds $Cr(O_2)_2(NH_3)_3$, $[Cr(O_2)_2(H_2O)(C_2H_8N_2)] \cdot H_2O$ and $K_3[Cr(O_2)_2(CN)_3]$ have been reported.

The most familiar peroxy 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 first isolated a compound which he formulated as \( \text{HCrO}_7 \). Other workers supported the formula. The final formula \( \text{CrO(O}_2)_2 \cdot \text{L} \) was not, however, resolved until the works of Evans, Glasner and Stainberg, and Tuck and Walters. The compound \( \text{CrO(O}_2)_2 \cdot \text{H}_2\text{O} \) 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 \( \text{CrO(O}_2)_2 \cdot \text{H}_2\text{O} \cdot \text{L} \) or, alternatively, one formed by the complete substitution of the water molecule by the donor solvent (L) to give \( \text{CrO(O}_2)_2 \cdot \text{L} \).

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, \( \text{CrO(O}_2)_2 \cdot \text{O(CH}_3)_2 \), which is stable below \(-50^\circ\text{C}\) explodes above \(-30^\circ\text{C}\). \(^{155}\) The three stable adducts \( \text{CrO(O}_2)_2 \cdot \text{L} \) for \( \text{L} = \text{pyridine}, 2,2'\)-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 \( [\text{CrO(O}_2)_2 \cdot \text{py}] \), \(^{156}\) \( [\text{CrO(O}_2)_2 \cdot \text{bipy}] \), \(^{157}\) and \( [\text{CrO(O}_2)_2 \cdot \text{phen}] \), \(^{158}\) have been determined and shown to bear close resemblances to oxodiperoxo adducts of other early transition metals. For instance, the mononuclear oxodiperoxoamminovanadate(V) complex \( \text{NH}_4[\text{VO(O}_2)_2 \cdot \text{NH}_3] \) is shown to have a distorted pentagonal pyramidal geometry analogous to that of the oxodiperoxo pyridinochromium(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 \( [\text{M}_2(\text{O}_2)_4(\text{mu})_4(\text{H}_2\text{O})_2]^2^- \) for \( \text{M} = \text{Mo(VI)} \), \(^{159}\) and \( \text{W(VI)} \), \(^{160}\) showed that the two complexes and \( [\text{Mo}^{\text{IV}}(\text{mu(00H)}_2)\text{Mo}^{\text{IV}}(\text{O}_2)_2(\text{O})]^2^- \) 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 and Griffith and Wickins have studied the peroxo-oxalates \[ \text{[MO(O}_2\text{H}_2\text{O})_2\text{]}^{2-} (M = W, Mo); \] \[ \text{[M(O}_2\text{H}_2\text{O})_2\text{]}^{2-} (M = Mo, W, U), \] \[ \text{[M(O}_2\text{H}_2\text{O})_2\text{]}^{2-} (M = Nb, Ta) \] \[ \text{[M(O}_2\text{H}_2\text{O})_2\text{]}^{2-} (M = Ti, Zr) \] by means of infrared and Raman spectroscopy on the solids and concluded that the oxalato ligands were bidentate. The crystal structure of the compound \[ (\text{NH}_4)_3[\text{Nb(O}_2\text{H}_2\text{O})_2\text{]}\text{H}_2\text{O}, \] originally formulated as \[ (\text{NH}_4)_3[\text{Nb(O}_2\text{H}_2\text{O})_2\text{]} \] supports this conclusion and further shows that, like the \[ \text{Nb(O}_2\text{H}_2\text{O})_2\text{]}^{2-}, \] complex exhibits a dodetahedral 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, \[ (\text{H}_2\text{O})\text{Ti(O}_2\text{H}_2\text{O})\text{[C}_5\text{H}_3\text{N(COO)}_2\text{]} \] and \[ (\text{H}_2\text{O})\text{[V(O}_2\text{H}_2\text{O})_2\text{]} \]
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 that in the non-chelated form these complexes could be assumed to have the composition \([\text{V(O)}(\text{O}_x)\cdot \text{H}_2\text{O})^{+}\) and \([\text{Ti(O}_2)\cdot \text{H}_2\text{O})_2^{2-}\), respectively. The possible existence of such species is further supported by spectroscopic, conductimetric and pH studies of weakly acid solution of vanadium(V) and titanium(IV) 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 who isolated them either by dissolving the exofluorometallates (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:

\([\text{M(O}_2)\text{F}_5]^{n-}\) for \(\text{M(IV)} = \text{Ti} \) and \(\text{Zr}\); \([\text{M(O)}(\text{O}_2)\text{F}_4]^{2-}\) for \(\text{M(VI)} = \text{Mo} \) or \(\text{W}\); and \([\text{Mo(O)(O}_2)\text{F}_2]^{2-}\). The last three complexes \([\text{M(O)(O}_2)\text{F}_2]^{2-}\) and \([\text{Mo(O)(O}_2)\text{F}_2]^{2-}\) have also been made by the action of \(\text{H}_2\text{O}_2\) on the salt carrying the corresponding \([\text{M(O)(O}_2)\text{F}_4]^{2-}\) anion. The X-ray crystal structure of \(\text{K}_2[\text{Mo(O)}(\text{O}_2)\text{F}_4]^{1-}\cdot \text{H}_2\text{O}\) has been published. Griffith and Wickins have also reported the infrared spectra of the oxoperoxotetrachloromolybdate(VI) complex \(\text{Cs}_2[\text{MoO(O}_2)\text{Cl}_4]\) and the peroxodisulphatotitanium(IV) complex \([\text{Ti(O}_2)(\text{SO}_4)_2]^{2-}\). The relatively small number of chloroperoxo and sulphatoperoxo complexes compared to oxalato- or fluoroperoxo complexes probably reflects the relative instability of these ligands to oxidation by hydrogen peroxide.

\(E^0(2X^- = X_2 + 2e^-)\) volts, \(X = \text{Cl}(1.36)\) and \(\text{F}(2.87)\)
The anionic oxodiperoxochromium(VI) complexes $\text{CrO}_2^-$ resemble the neutral adducts $\text{CrO}_2^2$-$\text{L}$ 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\textsuperscript{171} isolated blue-violet salts, which they formulated as $\text{HCrO}_6^-$ from the reaction of the neutral or very slightly acidic solutions of the corresponding dichromates with $\text{H}_2\text{O}_2$. Wiede\textsuperscript{147} obtained relatively purer compounds by reacting perchromic acid ($\text{CrO}_2^2$-$\text{H}_2\text{O}$) solutions with potassium cyanide or hydroxide. Years later, magnetic susceptibility measurements\textsuperscript{172} demonstrated that the potassium salt, originally formulated as $\text{KCrO}_6^-$ or $\text{K}_2\text{Cr}_2\text{O}_7^-$, was very feebly paramagnetic. The molar conductivity of the ammonium salt ($\approx 110$ ohm$^{-1}$ cm$^2$ in $\text{H}_2\text{O}$ or MeOH)\textsuperscript{127} showed conclusively that the compound was a 1:1 electrolyte. More recently, Griffith\textsuperscript{150} showed that the violet perchromate, obtained by treating an anhydrous ethereal solution of $\text{CrO}_2^2$-$\text{H}_2\text{O}$ with a deficiency of ethanolic potassium hydroxide solution at $-10^\circ\text{C}$, contained two peroxo groups per chromium. On the basis of these data, infrared spectra, elemental analysis, and molecular weight measurements, the formula $\text{K[CrO}_2^2\text{(OH)}]$ was suggested for the potassium salt. This formulation was also supported by the observation\textsuperscript{20} that aqueous acid solutions convert the anion into perchromic acid.

$$\text{CrO}_2^2\text{OH}^- + \text{H}^+ \rightarrow \text{CrO}_2^2\text{H}_2\text{O}$$ \[9\]

The only other related anionic chromium(VI) peroxo species has been characterized and reported by Tuck and Faithful.\textsuperscript{19} The royal blue anionic chlorodiperoxochromium(VI) complex $\text{CrO}_2^2\text{Cl}^-$ was prepared by treating the tetraphenylarsonium chlorochromate, $\text{Ph}_4\text{AsCrO}_3\text{Cl}$, 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$_2$)$_2$Cl$^-$ 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$_4$AsCrO(O$_2$)$_2$Cl 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$_2$)$_2$L$^n$-.

Summary

It is obvious from preceding accounts that the preparations and/or decompositions of chromium peroxo complexes are interrelated 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$_2$O, is formed when H$_2$O$_2$ is added to acidified solutions of CrO$^2_4^-$ or Cr$_2$O$_7^{2-}$; while in strongly alkaline solutions the stable peroxo compound is $\text{Cr}(O_2)_4^-$, a derivative of chromium(V). The chromium(V) compound decomposes in alkaline solution to CrO$^2_4^-$ 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$_2$O 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$_2$)$_2$L$_3$. From these accounts it is probable that protonation or ligand basicity plays an important part in the oxidation-reduction relationships amongst these compounds.
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CHAPTER TWO

PREPARATION AND CHARACTERIZATION OF SUBSTITUTED ANIONIC TRIOXO CHROMIUM(VI) COMPLEXES
II.1 INTRODUCTION

The accounts in Chapter 1 show that, except for the much earlier work involving the isolation of the halochromates, \( \text{CrO}_3L^- \) (for \( L^- = \text{F}^- \) or \( \text{Cl}^- \)), sulphatochromate, \( \text{CrO}_3(\text{SO}_4)_{2}^- \), and the iodatochromate, \( \text{CrO}_3\text{IO}_3^- \), 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, \( \text{I}^- \) and \( \text{NCS}^- \) ions have been shown to be readily oxidised by chromium(VI) to iodine \( (\text{I}_2)^1 \) and thiocyanogen \( (\text{SCN})_2^2 \), 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, \( \text{O}_2^- \) 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 \( L^{n^-} = \text{F}^- , \text{Cl}^- , \text{Br}^- , \text{NCO}^- , \text{NCS}^- , \text{NNN}^- , \text{NO}_3^- , \text{CH}_3\text{CO}_2^- , \text{C}_2\text{O}_4^{2-} , \text{NO}_2^- , \) and \( \text{IO}_3^- \), scan a large sector of the inductive drift of bonding electrons by either \( \sigma^- \) or \( \pi^- \)-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 \( \pm 2 \text{ cm}^{-1} \) were obtained.

The Raman spectra of the solids and/or solutions in dimethyl sulphoxide (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. Preproductibilities of \( \pm 1 \text{ cm}^{-1} \) 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 \( \text{CrO}_3\text{I}^n^- \) 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, \( \text{Et}_4\text{NE} \) and \( \text{Et}_4\text{NCl} \), 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% (Et₄NCl requires 11.5% Cl). Analysis of the fluoride, using the Orion Specific Ion Activity Electrodes, gave a low figure - 11.6% F, found (Et₄NF requires 12.8% F).

Reagent grade acids H₂SO₄, HNO₃, HCl, HF and HIO₃ 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 HBr₃ before use.

Reagent grade acetonitrile (CH₃CN or MeCN) was distilled twice from P₂O₅ 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 chromatography 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 SO₂ through the aqueous alkaline solution of the complex. After the reduction was complete the solution was acidified with 2M H₂SO₄ and boiled to expel any excess SO₂; K₂S₂O₈ was then added to the solution and boiled further to oxidise the chromium back to Cr(VI) and standard iodometric titration procedures followed.

(b) Syntheses of Monosubstituted Chromates

(i) Trioxochloro- and Trioxofluorochromate Anions, CrO₃Cl⁻ and CrO₃F⁻.

Potassium and Cesium Salts:

The potassium salts of trioxochloro- and trioxofluorochromates, CrO₃Cl⁻ and CrO₃F⁻, were prepared and preserved in the manner described on page 10. The cesium salt, CsCrO₃Cl, was prepared for spectroscopic purposes.
by treating stoichiometric amounts of CsCl and CrO\textsubscript{3}, dissolved in minimum amounts of water, with 3M HCl; yellow crystals eventually formed.

\[
\text{CsCl} + \text{CrO}_{3} + \text{HCl (3M)} \rightarrow \text{CsCrO}_{3}\text{Cl} \quad [1]
\]

Analysis for Cl in CsCrO\textsubscript{3}Cl gave 13.3% compared to 13.4% (theoretical).

**Tetraphenylarsenium Salts:**

The tetraphenylarsenium chlorochromate was prepared either by the method of Tuck and Faithful\textsuperscript{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\textsubscript{4}AsCrO\textsubscript{3}Cl. On treating a dilute solution of Ph\textsubscript{4}AsCl\textsubscript{x}H\textsubscript{2}O in MeCN with stoichiometric amounts of KCrO\textsubscript{3}Cl, also dissolved in MeCN, a white crystalline precipitate of KCl is formed immediately.

\[
\text{KCrO}_{3}\text{Cl} + \text{Ph}_{4}\text{AsCl} \rightarrow \text{Ph}_{4}\text{AsCrO}_{3}\text{Cl} + \text{KCl} \quad [2]
\]

Crystalline Ph\textsubscript{4}AsCrO\textsubscript{3}Cl can be isolated by adding 1:1 benzene-hexane (or CCl\textsubscript{4}) solution to the filtrate.

To obtain tetraphenylarsenium fluorochromate, an aqueous solution of Ph\textsubscript{4}AsNO\textsubscript{3} was first isolated by reacting the corresponding chloride with silver nitrate.

\[
\text{Ph}_{4}\text{AsCl} + \text{AgNO}_{3} \rightarrow \text{Ph}_{4}\text{AsNO}_{3} + \text{AgCl} \quad [3]
\]

Treating the aqueous nitrate solution with a solution of K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} in 2M HF yields a yellow precipitate.

\[
2\text{Ph}_{4}\text{AsNO}_{3} + \text{K}_{2}\text{Cr}_{2}\text{O}_{7} + 2\text{HF} \rightarrow 2\text{Ph}_{4}\text{AsCrO}_{3}\text{F} + 2\text{KNO}_{3} + \text{H}_{2}\text{O} \quad [4].
\]
The yellow precipitate was filtered, redissolved in a 1:1 chloroform - acetone mixture and reprecipitated with low boiling petroleum ether.

Analysis (%), calculated for \( \text{Ph}_4\text{AsCrO}_3\text{F} \): 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, \( \text{CrO}_3\text{NCO}^- \).

**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.

\[
\text{KCrO}_3\text{Cl} + \text{AgNCO} \rightarrow \text{KCrO}_3(\text{NCO}) + \text{AgCl}
\]

[5]

The precipitate, containing AgCl (found 0.0579 gm Cl compared to 0.0582 gm expected), was filtered off and the KCrO₃(NCO) recrystallized from MeCN solution either by adding dry CCl₄ or 1:1 CH₂Cl₂-petroleum ether, and washing with low boiling petroleum ether.

Analysis (%), calculated for KCrO₃(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, \( \text{Ph}_4\text{AsCrO}_3(\text{NCO}) \), and the cesium salt, \( \text{CsCrO}_3(\text{NCO}) \), 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 CsCrO₃(NCO): Cr, 18.9; C, 4.4; N, 5.1. Found: Cr, 18.7; C, 4.7 and N, 4.9.

(iii) Tetraphenylarsonium trioxoaizidochromate, \( \text{Ph}_4\text{AsCrO}_3\text{N}_3^- \).
Ph₄AsCrO₃Cl (2.498 gm) dissolved in redistilled MeCN was treated with a cold (-10°C) solution of NaN₃ (0.316 gm) also in MeCN. After 1 hr stirring, a white crystalline precipitate formed in the yellow solution.

\[
\text{Ph}_4\text{AsCrO}_3\text{Cl} + \text{NaN}_3 \rightarrow \text{Ph}_4\text{AsCrO}_3\text{N}_3 + \text{NaCl} \quad [6]
\]

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 Ph₄AsCrO₃N₃: 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, CrO₃(NCS)⁻.

Tetraphenylarsonium Salt.

The Ph₄AsCrO₃(NCS) complex was prepared from Ph₄AsCrO₃Cl (0.352 gm) and NH₄NCS (0.052 gm) in a way similar to that of Ph₄AsCrO₃N₃; except that here the reaction is slower (2 hr allowed for reaction time) and the product less stable.

\[
\text{Ph}_4\text{AsCrO}_3\text{Cl} + \text{NH}_4\text{NCS} \rightarrow \text{Ph}_4\text{AsCrO}_3(\text{NCS}) + \text{NH}_4\text{Cl} \quad [7]
\]

The solid NH₄Cl was filtered off in the dry box and in the dark; the Ph₄AsCrO₃(NCS) complex was obtained in the solid state by pumping off the MeCN on a vacuum line.

Analysis (%), calculated for Ph₄AsCrO₃(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) KCrO₃Cl or CsCrO₃Cl solution (in MeCN) with NH₄NCS also in MeCN produces white crystals, NH₄Cl, and a yellow solution containing the CrO₃(NCS)⁻ anion.

\[
\text{CrO}_3\text{Cl}^- + \text{NH}_4\text{NCS} \rightarrow \text{CrO}_3(\text{NCS})^- + \text{NH}_4\text{Cl} \quad [8]
\]

The NH₄Cl is filtered off under N₂ or vacuum and the KCrO₃(NCS) or CsCrO₃(NCS)
can be precipitated by adding ice-cold benzene to the MeCN solution. A flaky yellow powder was formed. Unfortunately, both compounds decompose, sometimes explosively (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 (Z), calculated for KCrO₃(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, KCrO₃(NCS), dissolve in water giving a yellow solution which slowly turns brownish-green. When 2M H₂SO₄ is added to the aqueous solution, it immediately turns completely green — a Cr(III) complex.

(v) Trioxonitratochromate Anion, CrO₃NO₃⁻.

Tetraphenylarsonium Salt.

Ph₄AsCrO₃Cl (0.296 gm) was dissolved in MeCN and treated in the dark with AgNO₃ (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 (Z), calculated for Ph₄AsCrO₃NO₃: 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 KCrO₃Cl (0.826 gm) in MeCN was treated with a solution of tetraethylammonium perchlorate (1.090 gm), a white precipitate of KClO₄
forms in a yellow solution of Et₄NCrO₃Cl. Filtering the white precipitate off and treating the yellow solution with AgNO₃ (0.805 gm) dissolved in MeCN causes AgCl to precipitate out. The Et₄NCrO₃NO solution was then pumped on the vacuum line. This leaves a dark orange light- and moisture-sensitive oil.

\[
\begin{align*}
KCrO₃Cl & + Et₄NCIO₄ \xrightarrow{-10^\circ C} Et₄NCrO₃Cl + KCIO₄ \\
& \downarrow \text{AgNO₃} \xrightarrow{-10^\circ C} Et₄NCrO₃NO₃ + AgCl
\end{align*}
\]

[9]

Analysis (Z), calculated for Et₄NCrO₃NO₃: 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 Et₄NCrO₃NO₃ or Ph₄AsCrO₃NO₃ from the MeCN solution by adding CHCl₃, CH₂Cl₂ or benzene resulted in decomposition.

(vi) Trioxobromochromate Anion, CrO₃Br⁻.

Tetraphenylarsonium Salt.

Ph₄AsCrO₃Br is prepared from KCrO₃NO₃ and Ph₄AsBr.H₂O by the reaction

\[
KCrO₃NO₃ + Ph₄AsBr \xrightarrow{\text{MeCN}, -10^\circ C} Ph₄AsCrO₃Br + KNO₃
\]

[10]

The Ph₄AsBr.H₂O used in the reaction is prepared by passing a solution of Ph₄AsCl.xH₂O (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 Ph₄AsBr.H₂O (melting point 279°C) thus formed, were dried in an oven at 110°C.

Analysis (Z), calculated for Ph₄AsBr.H₂O: C, 60.0; H, 4.6; Br, 16.6. Found: C, 60.7; H, 4.6 and Br, 16.7.
The KCr\(_3\)NO\(_3\) used in the reaction was prepared by reacting KCr\(_3\)Cl (2.190 gm) in MeCN with AgNO\(_3\) (2.120 gm) also in MeCN:

\[
\text{KCr}_3\text{Cl} + \text{AgNO}_3 \xrightarrow{-10^\circ\text{C}} \text{KCr}_3\text{NO}_3 + \text{AgCl} \quad [11]
\]

The AgCl precipitate formed was immediately filtered off and the KCr\(_3\)NO\(_3\) 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 KCr\(_3\)NO\(_3\) from the MeCN by treatment with benzene, ethers, tetrahydrofuran, CH\(_2\)Cl\(_2\), CHCl\(_3\) or CH\(_2\)Cl\(_2\)-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 KCr\(_3\)NO\(_3\), at -10\(^\circ\)C, with Ph\(_4\)AsBr.H\(_2\)O (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\(_4\)AsCrO\(_3\)Br isolated by treating the filtrate with ice-cold 1:1 benzene-hexane mixture.

Analysis (%), calculated for Ph\(_4\)AsCrO\(_3\)Br: 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\(_3\)Br\(^-\) anion.

Cesium Salt.

It was possible to prepare cesium trioxobromochromate by a method similar to that used for CsCrO\(_3\)Cl, 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 CsCrO₃Br 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, Ph₃(n-Bu)PBr gm, was dissolved in CHCl₃, treated with an aqueous solution containing CrO₃ (2.00 gm) and dilute HBr (2M), and allowed to stir for 5 minutes, the yellow product formed by the reaction [12]

\[
\text{Ph}_3(n-\text{Bu})\text{PBr} + \text{CrO}_3 + \text{HBr}(2\text{M}) \rightarrow \text{Ph}_3(n-\text{Bu})\text{PCrO}_3\text{Br} \quad [12]
\]

is extracted into the chloroform layer. The chloroform layer was collected, washed with 20 ml of 2M HBr and the n-BuPh₃PCrO₃Br precipitated from the CHCl₃ solution by adding low boiling petroleum ether. The precipitate was washed with more petroleum ether and pumped dry in 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-BuPh₃PCrO₃Br: 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 CrO₃⁻[^L] (L = acetate, oxalate, selenocyanate, cyanide, nitrite and thiosulphate).

**Potassium Acetatochromate.**

Attempts to prepare K[CrO₃(acetate)] by treating KCrO₃Cl (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[CrO₃(acetate)] that might have formed decomposed (acetic acid was given off) in solution.
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 KCrO₃(CH₃CO₂). There were no absorptions in the infrared spectra assignable to C=H or C=O stretching modes - the only bands observed being: 940 vs, 905 s, 885 s, 790 sh, 570 m-w, sh, 375 m cm⁻¹.

Others:

Attempts were made to prepare potassium oxalatochromate by treating a slurry of silver (or sodium) oxalate in MeCN with KCrO₃Cl 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 CrO₃(NCSe)⁻ by reacting KCrO₃Cl, Ph₄AsCrO₃Cl or CrO(O₂)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 Ph₄AsCrO₃Cl 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 Ph₄AsCrO₃Cl.

Attempts to prepare CrO₃(S₂O₃)²⁻ by reacting MeCN solutions of Ph₄AsCrO₃Cl with a slurry of (NH₄)₂S₂O₃ (or Na₂S₂O₃) also in MeCN gave no evidence of a reaction. It was not possible to prepare (Ph₄As)₂S₂O₃ for
II.3 DISCUSSION OF THE VIBRATIONAL SPECTRA OF CrO₃Lⁿ⁻ COMPLEXES.

(a) Trioxohalogenochromates.

The stereochemistry of the ions CrO₃F⁻ and CrO₃Cl⁻ have been shown by X-ray diffraction ⁵,⁶ to belong to the point group C₃ᵥ. For the CrO₃Cl⁻ ion, the interatomic distances r(Cr-Cl) and r(Cr-O) were found to be 2.16 and 1.58Å, respectively, with all interbond angles approximately those of a regular tetrahedron. Studies of the salts KCrO₃F and CsCrO₃F showed that the structure of the CrO₃F⁻ ion is close to that of a perfect tetrahedron with r(Cr-O) = r(Cr-F) = 1.53Å. With C₃ᵥ symmetry point group for all complexes CrO₃Lⁿ⁻, for L a monatomic ligand (e.g. F⁻, Cl⁻ and Br⁻), the vibrational spectra of the penta-atomic species should give six fundamental modes, 3A₁ + 3E, all active in Raman and in the infrared; with the A₁ modes Raman polarized.

In order to establish the frequencies of some of the fundamentals arising from the CrO₃Lⁿ⁻ ions, it seemed appropriate to compare the spectra of the compounds prepared in the present study with those reported for CrO₃F⁻ and CrO₃Cl⁻. 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), Stammreich et al (IR and R) ⁷ and Carter and Bricker (R). ⁹ The spectra (IR) of CsCrO₃Cl and Ph₄AsCrO₃F were also recorded.

CsCrO₃Cl (IR): 969s, 943vs, 908a, 446s, 399w, 380w, 370w, 358vw, 338vw, 306m-w, 283w, 249w and 228w.

Ph₄AsCrO₃F (IR): 950vs, 923m, 910m, 639m-s and 380w.
**Table II.1** The Raman and Infrared Spectra of KCrO$_3$F, (cm$^{-1}$)

<table>
<thead>
<tr>
<th>Raman (Intensity)</th>
<th>IR (solid)</th>
<th>IR (solid)</th>
<th>IR (solid), this work</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>aqueous soln.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>955(4)</td>
<td>952 vs</td>
<td>946</td>
<td>957 vs</td>
<td>$\nu_4$(E), $\nu$(Cr-O)</td>
</tr>
<tr>
<td>910(10) P</td>
<td>912 s</td>
<td>910</td>
<td>915 s</td>
<td>$\nu_1$(A$_1$), $\nu$(Cr-O)</td>
</tr>
<tr>
<td></td>
<td>888 mw</td>
<td></td>
<td></td>
<td>$\nu_2 + \nu_6 = 890$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>745 w</td>
<td>2($\nu_5$) = 750</td>
</tr>
<tr>
<td></td>
<td>635 s</td>
<td>620</td>
<td>639 s</td>
<td>$\nu_2$(A$_1$), $\nu$(Cr-F)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>487 w</td>
<td>?</td>
</tr>
<tr>
<td>370(7)</td>
<td>370 m</td>
<td></td>
<td>375 w, br</td>
<td>$\nu_3$(E), $\delta$(O-Cr-O)</td>
</tr>
<tr>
<td></td>
<td>338 ms</td>
<td>340</td>
<td>343 m</td>
<td>$\nu_3$(A$_1$), $\delta$(O-Cr-F)</td>
</tr>
<tr>
<td>261(6)</td>
<td>257 m</td>
<td>260</td>
<td>250 w</td>
<td>$\nu_6$(E), $\nu$(O-Cr-C)</td>
</tr>
</tbody>
</table>


**Table II.2** The Infrared and Raman Spectra of KCrO$_3$Cl, (cm$^{-1}$)

<table>
<thead>
<tr>
<th>Raman (Intensity)</th>
<th>IR$_4$(solid)</th>
<th>IR (solid), this work</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>solution</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>954(4)</td>
<td>963 $\nu$s</td>
<td>964 $\nu$s</td>
<td>$\nu_4$(E), $\nu$(Cr-O)</td>
</tr>
<tr>
<td>907(10) P</td>
<td>915 s</td>
<td>914 s</td>
<td>$\nu_1$(A$_1$), $\nu$(Cr-O)</td>
</tr>
<tr>
<td></td>
<td>735 vW</td>
<td></td>
<td>$\nu_2 + \nu_3 = 733$</td>
</tr>
<tr>
<td></td>
<td>726 vW</td>
<td></td>
<td>2$\nu_5$</td>
</tr>
<tr>
<td>438(2) P</td>
<td>438 s</td>
<td>445 ms</td>
<td>$\nu_2$(A$_1$), $\nu$(Cr-Cl)</td>
</tr>
<tr>
<td>365(7)</td>
<td>378 $\nu$ w</td>
<td>397 m</td>
<td>$\nu_5$(E), $\delta$(O-Cr-O)</td>
</tr>
<tr>
<td>295(0.5)</td>
<td></td>
<td>300 w</td>
<td>$\nu_3$(A$_1$), $\delta$(O-Cr-Cl)</td>
</tr>
<tr>
<td>209(10)</td>
<td></td>
<td>281 w</td>
<td>$\nu_6$(E), $\delta$(O-Cr-Cl)</td>
</tr>
</tbody>
</table>

* Solutions in CH$_3$COCH$_3$, CH$_3$COC.C.H$_5$ or C$_2$H$_5$COC.H$_5$. a. H. Stammreich Spectrochimica Acta, 27, 226 (1961).
Tables II.1 and II.2 give the frequencies of the normal modes of vibration of the \( \text{CrO}_3 \) and \( \text{CrO}_3 \text{Cl}^- \) ions with the descriptions of the approximate intramolecular motions involved.

The \( A_1 \) modes are particularly interesting. The totally symmetric stretching vibration of the \( \text{CrO}_3 \) group, \( \nu_1 \), 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, \( \nu_{\text{sym}} \) \( \text{CrO}_3 \), may be dependent in part on the formal covalent bond orders, the symmetric \( \text{CrO}_3 \) stretching frequencies of the different substituted \( \text{CrO}_3 \text{L}^n^- \) 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, \( \text{ReO}_3 \text{X}^n^- \) for \( X^n^- = \text{F}^-, \text{O}^{2-}, \text{Cl}^-, \text{Br}^-, \text{S}^{2-} \) and \( \text{N}_3^2^- \), support this approach.

Stammreich and coworkers\(^7 \) have shown, by normal coordinate analysis, that the \( \nu_2 \) and \( \nu_3 \) modes of \( \text{CrO}_8 \text{Cl}^- \) 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 \( \nu_2 \) the motion of the same atoms are in opposite directions along this axis. Thus the observed \( \nu_2 \) frequency cannot be regarded as truly characteristic of the Cr-Cl bond stretching frequency. Further-
more, Miller and coworkers\textsuperscript{12} have suggested that in \( \text{CrO}_2\text{Cl}_2 \) the 'true' frequencies of the two unperturbed \( A_1 \)-modes, \( \nu_2 \) and \( \nu_3 \), \( \nu(\text{Cr-Cl}) \) and \( \delta(\text{O-Cr-O}) \), should fall close to 400 cm\(^{-1}\) but are probably spread apart by resonance interaction. In the case of the \( \text{CrO}_3\text{F}^- \) ion, however, the \( \nu_2^- \) and \( \nu_3^- \)-modes would be less mixed\textsuperscript{7} since \( \nu_2(\text{Cr-F}) \) occurs at 637 cm\(^{-1}\).

For \( \text{CrO}_3\text{Br}^- \), the six frequencies ascribed to the fundamental modes of vibration of the \( \text{CrO}_3L \) group were observed and assignments made, in a straightforward manner, by comparison with those reported for the \( \text{CrO}_3\text{Cl}^- \) and \( \text{CrO}_3\text{F}^- \) ions (See Tables II.3a and 3b). The positions of the \( \text{CrO}_3^+ \) stretching and deformation bands would not be expected to change greatly between \( \text{CrO}_3\text{Cl}^- \) and \( \text{CrO}_3\text{Br}^- \). The band occurring rather consistently at \( \approx 380 \) cm\(^{-1}\) was assigned to \( \nu_2(A_1)^\prime \) and, by analogy with the \( \text{CrO}_3\text{Cl}^- \) spectrum, the absorption at \( \approx 360 \) cm\(^{-1}\) is assigned to \( \nu_5(E) \). The doubly degenerate mode, \( \nu_5 \), essentially a deformation of the \( \text{O-Cr-O} \) angles, has sometimes been hard to observe for the \( \text{Ph}_4\text{AsCrO}_3\text{L} \) compounds reported in this study because the \( \text{Ph}_4\text{As}^+ \) cation has a strong absorption in the same region. But the frequencies of such vibrations in \( \text{CrO}_2\text{Cl}_2 \), \( \text{CrO}_4^2- \), \( \text{Cr}_2\text{O}_7^2- \), \( \text{CrO}_3\text{Cl}^- \) and \( \text{CrO}_3\text{F}^- \) 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, \( \text{CsCrO}_3\text{Br} \), 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 \( \text{Cs}^+ \) and \( \text{Ph}_4\text{As}^+ \) salts suggest that the \( \text{CrO}_3\text{Br}^- \) ion experiences cation-dependent lattice and polarizing effects.
### Table II.3(a), The Vibrational Spectra of the CrO$_3$Br$^-$ Anion, (cm$^{-1}$)

<table>
<thead>
<tr>
<th>Infrared (solid)</th>
<th>Raman (solid)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph$_4$AsCrO$_3$Br</td>
<td>Ph$_4$AsCrO$_3$Br</td>
<td>Ph$_4$AsCrO$_3$Br</td>
</tr>
<tr>
<td>950s</td>
<td>951s</td>
<td>$\nu_4(E)$, $\nu(Cr-O)$</td>
</tr>
<tr>
<td>920m</td>
<td>929w, br</td>
<td></td>
</tr>
<tr>
<td>905m</td>
<td>903vs</td>
<td>$\nu_1(A_1)$, $\nu(Cr-O)$</td>
</tr>
<tr>
<td>380s</td>
<td>379m</td>
<td>$\nu_2(A_1)$, $\nu(Cr-Br)$</td>
</tr>
<tr>
<td>360m, sh</td>
<td>361s</td>
<td>$\nu_5(E)$, $\delta(O-Cr-O)$</td>
</tr>
<tr>
<td></td>
<td>272w</td>
<td>$\nu_3(A_1)$, $\delta(O-Cr-Br)$</td>
</tr>
<tr>
<td></td>
<td>234m</td>
<td>$\nu_6(E)$, $\delta(O-Cr-Br)$</td>
</tr>
<tr>
<td></td>
<td>180m-s</td>
<td></td>
</tr>
</tbody>
</table>

### Table II.3(b), IR Spectra and Possible Assignments for CsCrO$_3$Br, (cm$^{-1}$)

<table>
<thead>
<tr>
<th></th>
<th>959s</th>
<th>908s</th>
<th>670vw</th>
<th>665vw</th>
<th>393s</th>
<th>379w</th>
<th>363w</th>
<th>315w</th>
<th>307w</th>
<th>282w</th>
<th>247w</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\nu_4$</td>
<td>$\nu_1$</td>
<td>$?\quad\nu_3a$</td>
<td>$\nu_5a$</td>
<td>$\nu_5b$</td>
<td>$\nu_5a$</td>
<td>$\nu_5b$</td>
<td>$\nu_3a$</td>
<td>$\nu_3b$</td>
<td>$\nu_3c$</td>
<td>$\nu_6$</td>
</tr>
</tbody>
</table>
(b) Trioxonitratochromate Anion.

The free NO\textsubscript{3}\textsuperscript{−} 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 modes of coordination\textsuperscript{16}, the most common of which are the symmetrical bidentate and unidentate nitrato groups.

Table II.4 Correlation Table for ZXY\textsubscript{2} Molecule in D\textsubscript{3h}, C\textsubscript{2v} and C\textsubscript{s} Symmetries.

<table>
<thead>
<tr>
<th>Point Group</th>
<th>(\nu_1(\nu_{XZ}))</th>
<th>(\nu_2(\pi ZXY))</th>
<th>(\nu_3(\nu_{asy}(XY)))</th>
<th>(\nu_4(\delta(ZXY)))</th>
</tr>
</thead>
<tbody>
<tr>
<td>D\textsubscript{3h} (free ion)</td>
<td>A'\textsubscript{1}(R)</td>
<td>A'\textsubscript{2}(ir)</td>
<td>E'(ir,R)</td>
<td>E'(ir,R)</td>
</tr>
<tr>
<td>C\textsubscript{2v} (unidentate)</td>
<td>A\textsubscript{1}(ir,R)</td>
<td>B\textsubscript{1}(ir,R)</td>
<td>A\textsubscript{1}(ir,R) + B\textsubscript{2}(ir,R)</td>
<td>A\textsubscript{1}(ir,R) + B\textsubscript{2}(ir,R)</td>
</tr>
<tr>
<td>C\textsubscript{s} (unidentate)</td>
<td>A'\textsubscript{1}(ir,R)</td>
<td>A''(ir,R)</td>
<td>A'(ir,R) + A''(ir,R)</td>
<td>A'(ir,R) + A''(ir,R)</td>
</tr>
</tbody>
</table>

The free NO\textsubscript{3}\textsuperscript{−} ion has bands at ca. 1390 (R,IR), 1050 (R), 830 (IR) and 720 (R, IR) cm\textsuperscript{-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\textsuperscript{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\textsubscript{1} (Raman polarized) and B\textsubscript{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\(^{-1}\))

<table>
<thead>
<tr>
<th>Ph(_4)AsCrO(_3)NO(_3) (KBr)</th>
<th>Tentative Assignments</th>
<th>C(_2)H(_5)(_4)CrO(_3)NO(_3) (Smear, CsI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1580 (w-m)</td>
<td>(v_3 (\nu\text{NO}))</td>
<td>1585 m</td>
</tr>
<tr>
<td>1550 (s)</td>
<td></td>
<td>1550 s</td>
</tr>
<tr>
<td>1380 (vs, br)</td>
<td></td>
<td>1370 (m, sh)</td>
</tr>
<tr>
<td>1340 (s, sh)</td>
<td></td>
<td>1340 (s, br)</td>
</tr>
<tr>
<td>1315 (m, sh)</td>
<td></td>
<td>1310 (s, sh)</td>
</tr>
<tr>
<td>1287 (s, sharp)</td>
<td></td>
<td>1280 (vs, br)</td>
</tr>
<tr>
<td>1210 (w, sh)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>975 (m, sh)</td>
<td>(v_1 \text{ in NO}_3^-)</td>
<td>1095 (s, br)</td>
</tr>
<tr>
<td>945 (vs)</td>
<td>(v_{\text{asy}} (\text{CrO}_3))</td>
<td>1050 (m, sh)</td>
</tr>
<tr>
<td>905 (s, sharp)</td>
<td>(v_{\text{sym}} (\text{CrO}_3))</td>
<td>975 (s)</td>
</tr>
<tr>
<td>835 (m, sharp)</td>
<td>(\pi(\text{NO}_3^-) [v_2 (A'' \text{ in free NO}_3^-)])</td>
<td>945 (vs)</td>
</tr>
<tr>
<td>780 (m-s)</td>
<td>(\delta(\text{ONO}) [v_4 (E' \text{ in free NO}_3^-)])</td>
<td>850 (vs)</td>
</tr>
<tr>
<td>540 (w-m, br)</td>
<td>(v_{\text{asy}} (\text{CrON}) \text{ or } v_{\text{asy}} (\text{CrO}_3\text{N}))</td>
<td>780 (vs, br)</td>
</tr>
<tr>
<td>435 (w)</td>
<td>(v_{\text{sym}} (\text{CrON}) \text{ or } v_{\text{sym}} (\text{CrO}_3\text{N}))</td>
<td>685 (m)</td>
</tr>
<tr>
<td>380 (m)</td>
<td></td>
<td>620 (m)</td>
</tr>
<tr>
<td>(350)?</td>
<td>(\delta(O-Cr-O))</td>
<td>435 (w)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>420 (w)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>390 (w)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>350 (m, sh)</td>
</tr>
</tbody>
</table>

† There is the possibility of NO\(_3^-\) ion impurities from exchange with the windows.
Ph₄AsCrO₃NO₃ and (C₂H₅)₄NCrO₃NO₃ are readily decomposed by the Ne/He exciting laser and other criteria have not proved adequate.

The spectra and assignments for the complex ion CrO₃NO₃⁻ in Ph₄AsCrO₃NO₃ and (C₂H₅)₄NCrO₃NO₃ are given in Table II. 5.

By comparison with the spectra of CrO₃L⁻ for L = F⁻, Cl⁻, and Br⁻, the absorptions between 900 and 1000 cm⁻¹ have been assigned to ν(CrO₃). Although one of these bands could also arise from the symmetric stretching mode, ν₁, of the coordinated nitrate - cf. Me₃Sb(NO₃)₂ (945 cm⁻¹), SbF₃(NO₃)₂ (940 cm⁻¹), SnP₃NO₃ (965 cm⁻¹) and [As(NO₃)₄]⁺[AsF₆]⁻ (915 cm⁻¹).

A definite assignment of the ligand deformation modes ν₂ and ν₄ 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 ν₄(6(ONO)) and ν₂(πONO₂) respectively, have been identified. Comparing the values observed for ν₄ with those of the hexanitratocomplexes, [M⁴⁺(NO₃)₆]²⁻ for M = Zr, Hf and Sn, and for SnP₃NO₃ and SbF₃(NO₃)₂ suggests that the second ν₄ 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.

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 the distinction between symmetrically bidentate and unidentate nitrate 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 have suggested that occurrence 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 \(\text{CrO}_3\text{NO}_3^-\) complex is such that no definite conclusions can be drawn regarding the type of nitrate coordination. The \(\text{CrO}_3\text{NO}_3^-\) absorptions at 1585, 1550, 1380, 1340, 1315, 1287, and 1210 cm\(^{-1}\) are similar to those reported for anhydrous rare-earth metal nitrates. Although the list 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 \(\text{Cr}-\text{O(NO}_2^-\) bond in the \(\text{CrO}_3\text{NO}_3^-\) ion. The nitrate coordination in \(\text{CrO}_2(\text{NO}_3)_2\), which also contains chromium(VI), has not yet been established.
(c) Trioxopseudohalogenochromate(VI) Complexes:

(i) Electronic and Geometrical Structures of Pseudohalides.

In discussing the vibrational spectra of the complexes \( \text{CrO}_3 \text{Ps}^- \), where \( \text{Ps}^- \) stands for a pseudohalide grouping, \( \text{NYZ}^- \), where \( YZ = \text{NN}, \text{CO} \) or \( \text{CS} \), 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 resonance 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 \( \pi \)-bond Orders for \( \text{NYZ}^- \) (Wagner \( ^{30} \)).

<table>
<thead>
<tr>
<th>Atom</th>
<th>( \pi )-electron charges</th>
<th>( \pi )-bond orders</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>-0.48</td>
<td>+0.19</td>
</tr>
<tr>
<td></td>
<td>1.82</td>
<td>( S ) 0.71</td>
</tr>
<tr>
<td>C</td>
<td>+0.61</td>
<td>1.39</td>
</tr>
<tr>
<td></td>
<td>-0.04</td>
<td>( N ) 1.39</td>
</tr>
<tr>
<td>N</td>
<td>-0.77</td>
<td>-0.04</td>
</tr>
<tr>
<td></td>
<td>1.55</td>
<td>( C ) 1.26</td>
</tr>
</tbody>
</table>

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

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

<table>
<thead>
<tr>
<th>Ion</th>
<th>$\nu_{NYZ(\text{asy})}$ (cm$^{-1}$)</th>
<th>$\delta(NYZ)$ cm$^{-1}$</th>
<th>$\nu_{NYZ(\text{sym})}$ (cm$^{-1}$)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>NNN$^-$</td>
<td>2041</td>
<td>645</td>
<td>1344</td>
<td>a</td>
</tr>
<tr>
<td>NCO$^-$</td>
<td>2165</td>
<td>637</td>
<td>1254$^{b1}$</td>
<td>b</td>
</tr>
<tr>
<td>NCS$^-$</td>
<td>2053</td>
<td>486</td>
<td>746</td>
<td>c</td>
</tr>
</tbody>
</table>

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

The pseudo-symmetric vibration, $\nu_{sym}(\text{NCO})$, expected at 1254 cm$^{-1}$, in the same region as the first overtone $2\delta(\text{NCO})$, 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 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", M"$_{M}$ZYN-M") and the acceptor character of the central metal. The hard-soft acid-base concepts of Pearson have failed, however, in predicting the preferred bonding modes in a large number of complexes. For instance, Pd(II), a soft acid (class "b"), forms the S-bonded complex Pd(SCN)$_4$$^-$ but in the presence of π-bonding ligands.
isomers of the type \( \text{cts} \cdot \text{P} \rightleftharpoons (\text{Ncs})(\text{SCN})(\text{P} \rightleftharpoons \text{P}(\text{CH} \rightleftharpoons \text{PP} \rightleftharpoons \text{P})\rightleftharpoons \text{P})_2 \) 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.

<table>
<thead>
<tr>
<th>( \sigma )-Donor (or hard) ligand</th>
<th>( \pi )-acceptor (or soft) ligand</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class &quot;a&quot; acceptor</td>
<td>-NCS</td>
</tr>
<tr>
<td>Class &quot;b&quot; acceptor</td>
<td>-SCN</td>
</tr>
<tr>
<td></td>
<td>-NCS</td>
</tr>
</tbody>
</table>

Thus it appears likely that in the trioxochromium(VI) complex, \( \text{Cr}_3(\text{NCS})^- \), and the oxodiperoxo analog, \( \text{CrO}(\text{O}_2)_2(\text{NCS})^- \), 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—S—C—N.

The cyanate ion has received less attention. Norbury and Sinha\(^{29}\) studied complexes of the type \( \text{ML}_2(\text{NCO})_2 \), where \( M = \text{Pd(II)} \) or \( \text{Pt(II)} \), and used various ligands (\( L \)) with a wide range of ligand \( \sigma \)- and \( \pi \)-bonding properties, but failed to change the bonding mode, as has been done with NCS and NCS\(^-\) ions. More recently Norbury et al\(^{29a}\) claimed the isolation of the first examples, \( \text{Rh}(\text{PPh}_3)_3\text{NCO} \) and \( \text{Rh}(\text{PPh}_3)_3\text{OCN} \), of solid cyanate linkage isomers.
(ii) Discussion of Vibration Spectra of Trioxopseudohalogenochromates

Because there is no structural information on the complexes, CrO₃Ps⁻ for Ps = NCO, NNN and NCS, we will apply some of the arguments used on the germyl pseudohalide GeH₃Ps, for Ps = N₃, NCO, and NCS. Where the complex has a linear skeleton, i.e., the angle Cr-X-Y in CrO₃(XYZ)⁻ is 180°, it will belong to C₃ᵥ point group; for other angles, the maximum possible symmetry is Cₛ. Table II.8 gives the vibrational modes expected for the pseudohalide complex, CrO₃(XYZ)⁻, for the alternative assumptions of C₃ᵥ or Cₛ symmetry.

Table II.8 Vibrational Modes and Symmetry Classes for Structures of CrO₃(XYZ)⁻

<table>
<thead>
<tr>
<th>Vibrations</th>
<th>Point Group</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C₃ᵥ</td>
</tr>
<tr>
<td></td>
<td>Class A₁</td>
</tr>
<tr>
<td>XYZ str. (asy)</td>
<td>v₁</td>
</tr>
<tr>
<td>XYZ str. (sym)</td>
<td>v₂</td>
</tr>
<tr>
<td>CrO₃ str. (asy)</td>
<td>v₃</td>
</tr>
<tr>
<td>CrO₃ str. (sym)</td>
<td>v₄</td>
</tr>
<tr>
<td>XYZ bend (π(XYZ) and δ(XYZ))</td>
<td>v₅</td>
</tr>
<tr>
<td>Cr-X(YZ) str.</td>
<td>v₆</td>
</tr>
<tr>
<td>CrO₃ def. (asy)</td>
<td>v₇</td>
</tr>
<tr>
<td>CrO₃ def. (sym)</td>
<td>v₈</td>
</tr>
<tr>
<td>CrO₃ rock</td>
<td>v₉</td>
</tr>
<tr>
<td>CrXY bend and CrO₃ torsion</td>
<td>v₁₀</td>
</tr>
</tbody>
</table>
For $C_{3v}$ 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 $\text{CrO}_3\text{Ps}^-$ 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.

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

Both steric effect and the hybridization on the bonding atom X (or Z) may vary the angle MXY (or MZY) from $109^0$ to $180^0$, thus affect the degeneracy of certain vibrations. The structure and bonding in $\text{CrO}_3\text{Ps}^-$ complexes are discussed on pages 71-72.
Tetraphenylarsonium Trioxothiocyanatochromate.

While the Ph₄As⁺ 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 CrO₃(NCS)⁻ ion was hindered both by the superposition of the Ph₄As⁺ vibrations over those of the anion (Table II.9) and by the decomposition of the complex. The analysis of the vibrational spectra of Ph₄AsCrO₃(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 Ph₄AsCrO₃(NCS) complex is assigned to v(CN). The small increase from the free ion value of 2053 cm⁻¹ suggests Cr-NCS coordination, according to an analysis by Tramer. 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 or lattice effects may be responsible for the splitting of v(CN). The larger increase in the v(CN) mode in the K⁺ or Cs⁺ salts is probably a result of the greater polarizing effects of these cations relative to Ph₄As⁺.

The pseudosymmetric stretch, vCS⁻, is somewhat harder to assign. The position and intensity of this mode in a variety of thio- cyanate complexes is known to be very dependent on the environment of
Table II.9 The Vibrational Spectra of the CrO₃(NCS)⁻ Anion in Ph₄AsCrO₃(NCS)

<table>
<thead>
<tr>
<th>Raman (cm⁻¹)</th>
<th>Infrared (cm⁻¹)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2060s, sh</td>
<td>ν₃(NCS)</td>
</tr>
<tr>
<td>969w</td>
<td>1260(w)(?)</td>
<td>ν₃(NCS)</td>
</tr>
<tr>
<td>960w</td>
<td>950s (sharp)</td>
<td>ν₃(CrO₃)</td>
</tr>
<tr>
<td>914s</td>
<td>912m-s (sharp)</td>
<td>ν₃(NCS)</td>
</tr>
<tr>
<td>884w</td>
<td>885w</td>
<td>ν₃(CrO₃)</td>
</tr>
<tr>
<td>495s (broad)</td>
<td>415 (m-s)</td>
<td>δ(NCS)</td>
</tr>
</tbody>
</table>

Table II.10 Spectra of the CrO₃(NCS)⁻ Ion at Different States of Decomposition

<table>
<thead>
<tr>
<th>CsCrO₃(NCS)</th>
<th>CsCrO₃(NCS)</th>
<th>CsCrO₃(NCS)</th>
<th>KCrO₃(NCS)</th>
<th>KCrO₃(NCS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nujol, fresh</td>
<td>KBr, 24 hrs, later</td>
<td>In MeCN, 1 hr, later</td>
<td>Nujol, partly decomposed</td>
<td>KBr, partly decomposed</td>
</tr>
<tr>
<td>3100w, br</td>
<td>3180m, v-br</td>
<td>3100s, v-br</td>
<td>2320vw</td>
<td>2340w, sh</td>
</tr>
<tr>
<td>2060s, sh</td>
<td>2060vs, br</td>
<td>2085vs</td>
<td>2098vs</td>
<td>2080vs, br</td>
</tr>
<tr>
<td>2020vs, br</td>
<td>1600w</td>
<td>1610w</td>
<td>1400w</td>
<td>1400vs, br</td>
</tr>
<tr>
<td>1150w, br</td>
<td>1130w</td>
<td>1150w, br</td>
<td>1080w</td>
<td>1080m, br</td>
</tr>
<tr>
<td>940vs</td>
<td>940vs</td>
<td>955s, sh</td>
<td>940vs, br</td>
<td>930vs</td>
</tr>
<tr>
<td>920s, sh</td>
<td>920s, sh</td>
<td>927m, sh</td>
<td>900m</td>
<td>970-700 v-br</td>
</tr>
<tr>
<td>890m, sh</td>
<td>890m, sh</td>
<td>889m, sh</td>
<td>770s, br</td>
<td>780vs</td>
</tr>
<tr>
<td></td>
<td>780m, br</td>
<td>810m, br</td>
<td>660w</td>
<td>660w</td>
</tr>
<tr>
<td></td>
<td>480w</td>
<td>485w</td>
<td>485w, 445m</td>
<td></td>
</tr>
<tr>
<td></td>
<td>420m</td>
<td>420w</td>
<td>430s, 370s</td>
<td>350-330sh</td>
</tr>
</tbody>
</table>
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\(_3\) NCS 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\(_4\)AS\(^{+}\) salt.\(^{45}\) This assignment favours a N-bonded thiocyanate for which, according to Tramer, \(v_{CS}\) would occur between 780 and 860 cm\(^{-1}\) compared to 690 and 720 cm\(^{-1}\) for S-bonded thiocyanates.

The bending modes, \(v_4\) and \(v_6\), would be expected in the far-infrared region and therefore outside the range of the spectrophotometer used.

The ligand bending vibration, \(v_5\), 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\(_3\)NCS\(^{-}\) 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 $\nu_{\text{Cr-N}}$ in $\text{CrO}_3\text{N}_2$ and $\text{CrO}_3\text{NCO}^-$ and $\text{CrO}_3\text{CIN}_3$ are consistently observed at $\approx 495 \text{ cm}^{-1}$, and it is generally argued that the metal-ligand vibration becomes less pure M-N as the pseudohalide becomes heavier in the series $\text{NCO}$, $\text{NCS}$ and $\text{NCSe}$, so that the Cr-N vibration for Cr-NCS could well be lower than 495 cm$^{-1}$. For instance in the $\text{Ph}_4\text{AsCrO}_3(\text{NCS})$ 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 $\delta(\text{NCS})$ deformation. The position and intensity of this mode in other transition metal isothiocyanates support the assignment.

In general, the vibrational spectrum of the $\text{Ph}_4\text{AsCrO}_3(\text{NCS})$ complex is compatible with a $\text{CrO}_3(\text{NCS})^-$ 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, larger increases have generally been observed for isocyanates by Forster and Goodgame, and Bailey and Kozak. In Table II.11, the frequency of the band at 2206 cm\(^{-1}\) in \(\text{Ph}_4\text{AsCrO}_3(\text{NCO})\) and 2276 cm\(^{-1}\) in \(\text{KCrO}_3(\text{NCO})\) clearly shows the presence of a coordinated NCO group; in the case of \(\text{KCrO}_3\text{NCO}\) the evidence for N-bonding is strong.

The other interesting mode involves the pseudosymmetric stretching of the NCO unit. It has been shown that the \(\nu_{\text{CO}}\) for isocyanates are generally of weak-to-medium intensity, higher in frequency than those of the cyanates, 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 \(\text{CrO}_3(\text{NCO})\). Because the \(\nu_{\text{sym}}(\text{NCO})\) 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 \(\text{CrO}_3(\text{NCO})\) ion.

The weak bands at 630 and 616 (or 638 and 605) cm\(^{-1}\) have been assigned to the bending modes \(\delta(\text{NCO})\) and \(\delta(\mu\text{NCO})\), by analogy with the 570 - 640 cm\(^{-1}\) absorption bands in the spectra of isocyanato complexes of other electropositive metals.
Table II.11 The Vibrational Spectra of the CrO₂(NCO)⁻ Anion.

<table>
<thead>
<tr>
<th>Raman(solid)</th>
<th>(Infrared Solid)</th>
<th>Tentative Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCrO₃NCO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2276vs,br</td>
<td>2204vs,sh</td>
<td>ν&lt;sub&gt;asy&lt;/sub&gt; (NCO)</td>
</tr>
<tr>
<td>2206vs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1392w</td>
<td>1387w,br</td>
<td>ν&lt;sub&gt;sym&lt;/sub&gt; (NCO)</td>
</tr>
<tr>
<td>970w</td>
<td>965vs,sh</td>
<td>ν&lt;sub&gt;asy&lt;/sub&gt; (CrO₃)</td>
</tr>
<tr>
<td>954w</td>
<td>951vs</td>
<td>ν&lt;sub&gt;sym&lt;/sub&gt; (CrO₃)</td>
</tr>
<tr>
<td>940w</td>
<td>925w,sh</td>
<td></td>
</tr>
<tr>
<td>915vs</td>
<td>910s</td>
<td></td>
</tr>
<tr>
<td>887w-m</td>
<td>638w-m</td>
<td>δ (NCO)</td>
</tr>
<tr>
<td>605m</td>
<td>616w</td>
<td></td>
</tr>
<tr>
<td>573w</td>
<td>570vw</td>
<td>δ (π-NCO)</td>
</tr>
<tr>
<td>516w</td>
<td>512s</td>
<td>ν&lt;sub&gt;Cr-N&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>500s,sh</td>
<td></td>
</tr>
<tr>
<td></td>
<td>485m,sh</td>
<td></td>
</tr>
<tr>
<td></td>
<td>420</td>
<td>420w</td>
</tr>
<tr>
<td></td>
<td>397</td>
<td>390w</td>
</tr>
<tr>
<td></td>
<td>386</td>
<td></td>
</tr>
<tr>
<td>379s</td>
<td>376</td>
<td></td>
</tr>
<tr>
<td>371m</td>
<td>353</td>
<td></td>
</tr>
<tr>
<td>362w</td>
<td>326 very</td>
<td>330w</td>
</tr>
<tr>
<td></td>
<td>316 weak</td>
<td>307m</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td></td>
</tr>
<tr>
<td></td>
<td>280</td>
<td>283m</td>
</tr>
<tr>
<td></td>
<td>266</td>
<td>268w</td>
</tr>
<tr>
<td></td>
<td>245</td>
<td>243w</td>
</tr>
<tr>
<td></td>
<td>250-240m,br</td>
<td>226</td>
</tr>
<tr>
<td></td>
<td></td>
<td>229w</td>
</tr>
</tbody>
</table>
The strong 512 cm\(^{-1}\) band in KCr\(_3\)NCO (485 cm\(^{-1}\) in Ph\(_4\)AsCr\(_3\)NCO) 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 Cr\(_3\)N\(^-\), Cr\(_2\)CIN\(_3\)\(^{52}\) and Ge(NCO)\(_4\)\(^{59}\) but higher than the Fe-N stretching fundamental at 410 cm\(^{-1}\) in (Ph\(_4\)As)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 \(\delta(CrO_3)\), \(\delta(OCN)\) 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, i.e. monodentate or bridging, cannot generally be established solely by consideration of infrared data.\(^{61}\) Consider, for instance, the complexes \([Cu_2(diphos)\(_3\)N\(_3\)]\(^{62}\) \([(CO)_3Mn(N_3)_3Mn(CO)_3]\)\(^{63}\) and \([Cu(PPh_3)_2(N_3)]_2\)\(^{64}\) which represent, respectively, the three bonding modes known for azido.
complexes. The solid state spectra (IR and Raman) of the CrO$_3$N$^-$ anion (Table 11.12) has absorptions.

Table II.12 The Vibrational Spectra of the CrO$_3$N$^-$ Ion in Ph$_4$AsCrO$_3$N$^-$.

<table>
<thead>
<tr>
<th>Raman (solid)</th>
<th>Infrared (KBr)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>2380vw</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2160vw</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2073vs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1280m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>956w</td>
<td>953vs</td>
<td></td>
</tr>
<tr>
<td>936w</td>
<td>929s,sh</td>
<td></td>
</tr>
<tr>
<td>899s</td>
<td>898s</td>
<td></td>
</tr>
<tr>
<td>674w</td>
<td>670m,sh</td>
<td></td>
</tr>
<tr>
<td>580w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>490s,br</td>
<td>492s</td>
<td></td>
</tr>
<tr>
<td>313w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>235m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>220</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

at 953, 929 and 898 cm$^{-1}$ which are assignable to the CrO$_3$ stretching vibrations. The frequencies of the pseudosymmetric (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 has demonstrated that there is in fact a linear relationship between the degree of the asymmetry and the energy of \( \nu_{\text{asy}}(N_3) \) (or \( \nu_{\text{sym}}(N_3) \)) by plotting \( \nu_{\text{asy}}(N_3) \) against the \( \Delta d \) for a series of related or similar complexes. We can, therefore, compare the vibrational spectra of the complex ion \( \text{CrO}_3\text{N}_3^- \) with that of the neutral solid complex \( \text{CrO}_2\text{ClN}_3 \). In the latter complex \( \nu_{\text{asy}}(N_3) \) occurs at 2145 cm\(^{-1}\) while \( \nu_{\text{sym}}(N_3) \) drops down to 1223 cm\(^{-1}\).

In addition to the stretching modes, the spectrum of the \( \text{CrO}_3\text{N}_3^- \) ion also has absorptions at 580 and 670 cm\(^{-1}\) (674 cm\(^{-1}\) in Raman) assignable to the \( \delta(\pi\text{NNN}) \) and \( \delta(\text{NNN}) \) modes. Although these have no diagnostic value, they compare well with the 702 and 622 cm\(^{-1}\) bands observed for \( \text{GeH}_3\text{N}_3 \), the 637 cm\(^{-1}\) band observed in \( \text{CrO}_2\text{ClN}_3 \) and those of other azido complexes.

The M-N stretching vibrations are observed at 466 cm\(^{-1}\) in \( \text{GeH}_3\text{N}_3 \), at 492 cm\(^{-1}\) in \( \text{CrO}_3\text{N}_3^- \), and 495 cm\(^{-1}\) in \( \text{CrO}_2\text{ClN}_3 \). In the \( \text{CrO}_3\text{NCO}^- \), which is isoelectronic with and possibly isostructural with \( \text{CrO}_3\text{N}_3^- \), the Cr-N stretching frequency is at 512 cm\(^{-1}\). This increase is comparable to that from \( \text{GeH}_3\text{N}_3 \) (466 cm\(^{-1}\)) to \( \text{GeH}_3\text{NCO} \) (493 cm\(^{-1}\)). Assignments of the lower frequency deformation modes are less certain.

(iii) The Structure of \( \text{CrO}_3\text{Ps}^- \) Complexes and the Nature of the Cr-Ps Bond

Except for the spectroscopic evidence suggesting Cr-N bonds in all \( \text{CrO}_3\text{Ps}^- \) 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.

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

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

In the ground state, the effects of substituents are reflected in the gradual shift of the \( \nu_{\text{sym}} \) (Cr=O) as the substituent is changed from \( L^- = F^- \) to \( L^- = N_3^- \). It has been established that the value of the M=O stretching frequencies in metal oxocations \( M^{n+}_{xy} \), is dependent on the other ligands attached to the cation. McGlynn and co-workers used the frequencies of the symmetric and asymmetric U-O stretching vibrations in the complexes \( K_{\frac{x}{2}} UO_{\frac{y}{2}}(NO_3)_\frac{3}{2} \) and established a

* 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 $\nu_{\text{sym}}(\text{Cr} = \text{O})$ as a function of the anionic ligand $L$ in $\text{CrO}_3L^\text{n}^-$. The Raman technique was used because $\nu_{\text{sym}}(\text{Cr} = \text{O})$ has a particularly strong band in the Raman, and accuracies of $\pm 1 \text{ cm}^{-1}$ 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 $\text{Ph}_4\text{AsCrO}_3L$ compounds were measured in DMSO ($\varepsilon$=46.6) and $\text{CH}_2\text{Cl}_2$ ($\varepsilon$=8.9). Other solvents ($\text{MeCN}$, acetone, $\text{MeNO}_2$) were unsuitable on the basis of solubility, stability or interfering solvent bands in the 800 – 950 cm$^{-1}$ region.

Table II.13 The $\nu_{\text{sym}}(\text{Cr} = \text{O})$ Frequencies (Raman) of $\text{CrO}_3L^\text{n}^-$ Compounds

<table>
<thead>
<tr>
<th>Substituent $(L)$</th>
<th>DMSO $\nu_{\text{Raman}}$</th>
<th>$\text{CH}_2\text{Cl}<em>2$ $\nu</em>{\text{Raman}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F$</td>
<td>910</td>
<td>low solubility.</td>
</tr>
<tr>
<td>$\text{Cl}$</td>
<td>904</td>
<td>905</td>
</tr>
<tr>
<td>$\text{NCO}$</td>
<td>903</td>
<td>904</td>
</tr>
<tr>
<td>$\text{Br}$</td>
<td>902</td>
<td>903</td>
</tr>
<tr>
<td>$\text{NO}_3$</td>
<td>898? (decomposes)</td>
<td>decomposes</td>
</tr>
<tr>
<td>$\text{N}_3$</td>
<td>897</td>
<td>898</td>
</tr>
<tr>
<td>$\text{NCS}$</td>
<td>884?</td>
<td>decomposes</td>
</tr>
</tbody>
</table>


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,\textsuperscript{70,71} that the effect of the substituent (L) on \(\nu_{\text{Cr}=\text{O}}\) 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 negligible even with lighter atoms, since the Cr-L vibrational frequencies (\(\nu_{\text{Cr}=\text{F}}=637 \text{ cm}^{-1}\)) are lower than \(\nu_{\text{Cr}=\text{O}}\). In agreement with this, the shift in \(\nu_{\nu_{\text{O}}} (995 \text{ cm}^{-1} \text{ to } 964 \text{ cm}^{-1})\) is much larger than would be expected (989 \text{ cm}^{-1}) from mass effects alone\textsuperscript{70}. So that for a series of ligands attached to the CrO\(_3\) moiety, the order of the ligands based on the position of \(\nu_{\text{Cr}=\text{O}}\) 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 \(\nu_{\text{Cr}=\text{O}}\) is taken to be a reflection of the difference in the electronegativities of O and CrO\(_2\)L. The results are shown in Figure II.2. A shift of the \(\nu_{\text{sym}}(\text{CrO}_3)\) to lower frequency is interpreted to mean a weakening of the Cr=O bond (c.f. the \(\nu_{\text{sym}}\text{Cr}=\text{O}\) for the isoelectronic \(\text{CrO}_3\text{NCO}^- (903 \text{ cm}^{-1})\) and \(\text{CrO}_3\text{N}_3^- (897 \text{ cm}^{-1})\), and the small shift from \(\text{CrO}_3\text{Cl}^- (904 \text{ cm}^{-1})\) to \(\text{CrO}_3\text{Br}^- (903 \text{ cm}^{-1})\) despite the large mass difference.)
Fig. II.2 Effect of Substituent (L), in CrO$_3$L, on $\nu_{\text{sym}}$ Cr=0.

Electronegativities ( Mulliken$^{256}$)

- 4.0
- 3.5
- 3.0
- 2.5

895  900  905  910

$\nu_{\text{sym}}$ Cr=0 (Raman) cm$^{-1}$
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 $\sigma_1$ constants (the inductive substituent constant for aliphatic compounds). Figure II.3 shows that a plot of $\nu_{sym} (CrO_3)$ against $\sigma_1$ for F(0.52), Cl(0.47), and Br (0.45) gives a straight line. From this plot it is established that $\sigma_1$ 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, who derived their value indirectly from the $\sigma_{meta}$ and $\sigma_{para}$ constants.

The most important conclusion to be drawn from the present results is that $\nu_{sym} (Cr-O)$ in CrO$_3$L$^-$ 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 $\sigma_I$ Versus $\nu_{sym}(\text{CrO}_3)$ observed for CrO$_3$L$^-$ 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$_2$O$_7^{2-}$ 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 $\text{O}_3\text{Cr}-\text{L}$. The evidence for equilibria or reaction intermediate(s) is generally obtained directly from changes in the HCrO$_4^-$ absorption spectrum. In some cases the change is very small and in others competing hydrolytic reactions e.g.

$$\text{CrO}_3\text{L} + \text{H}_2\text{O} \rightarrow \text{HCrO}_4^- + \text{HL} \quad [14]$$

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 ($g+u$ in O$_h$ symmetry), transition occurring from non-bonding orbitals on the oxygens (or a $\pi$-bonding MO consisting of oxygen atomic orbitals) to the Cr $\pi^*$-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 Helmholtz and coworkers 82 on the CrO$_4^{2-}$ and MnO$_4^{2-}$ 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

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

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 $1A_1 - 1T_2$ 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 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 $1A_1 - 1T_2$ transitions, there are at least four orbitally forbidden transitions concealed, plus singlet → triplet transitions. The latter scheme was supported by other molecular orbital calculations and the single crystal electron spin resonance spectra of certain $d^1$ and $d^2$ ions. More recent and extensive MO calculations (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 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 of the dichroism of the KCrO$_3$Cl complex has, however, established that the electronic ground state
Figure II. 4 MO Energy Level Diagram for MnO₄⁻
Reproduced from Ref. 89.

Figure II. 5 Effect of Tₐ→C₃ᵥ Symmetry Reduction on the Assignment of the First Excitation.
of the CrO$_3$Cl$^-$ 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$_3$L$^n$-(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 mu, 360 mu and 270 mu.

(a) The Absorption Band Centered at 450mu.

The lowest energy band (= 450 mu) is relatively weak ($\epsilon = 100 - 300$), 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 $\sim 700$ 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 CrO₃(NCS) (25°C) in the 450 μm Region.
suggested that this weak transition is a $^1A_1 \rightarrow ^1T_1$, corresponding to $(t_{1g}^5e_e^1)_{92,95,96}$, which is electric-dipole forbidden in the $T_d$ point group.

In the $C_{3v}$ (LiClO$_4$·3H$_2$O/LiMnO$_4$·3H$_2$O$^{96}$ and K$_3$Na(SO$_4$)$_2$/Na$_2$CrO$_4$$^{95}$) and the $C_3$ (Ba(ClO$_4$)$_2$·3H$_2$O/Ba(MnO$_4$)$_2$·3H$_2$O$^{96}$ and LiKSO$_4$K$_2$CrO$_4$$^{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$_4^{2-}$, CrO$_3$F$,^{94}$ CrO$_3$Cl$^{-}$, CrO$_3$OR$^{-}$ and CrO$_3$L$^{n-}$ (for $L^{n-}$ = Br$^{-}$, NCO$^{-}$, NCS$^{-}$, N$_3$, acetate and NO$_3$), it becomes attractive to think of the substituted ions, CrO$_3$L$^{n-}$, 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 360 μm.

The intense band in the 360 μm region (400 μm to 320 μm)
Table II.14. Electronic Spectra and Vibrational Structure in the 360 μm
(and the 270μm) Absorption Band of CrO₃L⁻. **

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The maximum absorption

** All numbers are averages of four determinations.

Acetonitrile solution of Ph₄AsCl has electronic absorption bands at 271, 264, 258 and 253 µm.

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 µm in all cases, and that the overlap of this with the second band does not extend above 450 µm.

The uv-visible spectra were also recorded in CH₂Cl₂ at -10°C to try to improve spectral resolution and possibly locate the O=O bands, but without success.

Attempts to locate the O=O bands (in MeCN or CH₂Cl₂ 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$_3$L$^-$ 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$_3$Cl and calculations 92 on KCrO$_3$F and KCrO$_3$Cl indicate that the transition in CrO$_3$L$^-$ 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 μm band is ascribed to the coupling of the electronic transition with the $\nu_{\text{sym}}$ CrO$_3$ since all Cr-L vibrations are below 650 cm$^{-1}$ and the $\nu_{\text{sym}}$(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$_3$L$^-$ 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$_3$L$^-$ 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$_2$L$^-$ in the 360 mu Region (MeCN) 22$^\circ$C.

1. KCrO$_3$Cl
2. 'KCrO$_3$NCO
3. Ph$_4$AsCrO$_3$ (NCS)
4. Ph$_4$AsCrO$_3$ NO$_3$
Fig. II.8 Absorption Spectra of $\text{CrO}_3^-$, in the 360 $\mu$m Region (MeCN), 22°C.

- $\text{Ph}_4\text{AsCrO}_3\text{F}$
- $\text{Ph}_4\text{AsCrO}_3\text{Br}$
- $\text{Ph}_4\text{AsCrO}_3\text{N}_3$
- $\text{Ph}_4\text{AsCrO}_3$(acetate)
CrO$_4^{2-}$ ion is reported$^{100}$ to show a comparable decrease, with a change from the ground state $\nu_{\text{sym}}$(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$^\circ$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 $\rightarrow$ 0 bands.

While the position ($\nu_{\text{max}}$, or $\lambda_{\text{max}}$) 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 350$\mu\mu$ in CrO$_3$OH$^-$, CrO$_3$PO$_4^{2-}$, and CrO$_3$SO$_4^{2-}$ (all of which have Cr-O bonds) is shifted to 360$\mu\mu$ in CrO$_3$Cl$^-$ (with a Cr-Cl bond), 380$\mu\mu$ in CrO$_3$(NCS)$^-$ (with either a Cr-N or Cr-S bond) and to 390$\mu\mu$ in CrO$_3$S$_2$O$_3^{2-}$ (assumed to have a Cr-S bond). In the case of CrO$_3L^{n-}$, for L = NCS$^-$, NO$_3^-$, N$_3^-$ and S$_2$O$_3^{2-}$, 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 $\lambda_{\text{max}}$ with Hammett $\sigma$ constant (inductive substituent constant for aliphatics) - Fig.11.9 gives a straight line.
Figure II.9  Plot of Hammett Inductive Substituent Constant $\sigma_1$

Versus $\lambda_{\text{max}}$ observed for CrO$_3$L$^- \text{ Derivatives}$
Thus one effect of the substituent L, in CrO$_3$L$^-$ may be to decrease the chromium-oxygen dπ-π 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 O-electron pair donation. This could explain why the shifts in the present spectra are larger than those reported for the complexes CrO$_3$.OR$^+$ for R = alkoxide, PO$_3$, SO$_3$, NO$_2$, CrO$_3$ etc., 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), iso-NCO(3.0), iso-NCS(2.6) and N$_3$(2.7), and the absorption maxima ($\lambda_{max}$ or $\nu_{max}$). This supports the proposal by Jørgensen 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, 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, so that for the substrates whose oxidation products and redox potentials are known, the relationship given in Fig. II.11, can be drawn.

$$2L^- = L_2 + 2e^- \quad \text{(for L = F, Cl, Br and NCS)} \quad [15]$$
Fig. II.10 The relationship between the $\lambda_{\text{max}}$ and the electronegativity of the substituent (L) in $\text{CrO}_3\text{L}^-$.
Fig. III. II Dependence of Absorption maxima ($\lambda_{\text{max}}$) on the Oxidation Potentials of the substituents ($2X^{-} = X_{2} + 2e^{-}$)
The Absorption Band Centered at 270\(\mu\).  

The third set of bands (the 270\(\mu\) region) are weakly structured, very intense and appear in the UV end of the spectrum (36,000 - 41,000 cm\(^{-1}\)) where they are generally overlaid by cation and intraligand absorptions (especially where \(L^{n-} = NO_{3}^{-108}, NCS^{-109}, S_{2}O_{3}^{2-109}\) 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 \(CrO_{3}L^{n-}\) complexes. By comparison with studies on the MnO\(^4\) and CrO\(^2\), 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 240\(\mu\) region. The corresponding band in the spectrum of CrO\(^2\) 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

Methodological procedures were used to synthesize a series of new anionic monosubstituted trioxochromium(VI) complexes, \(CrO_{3}L^{n-}\). 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(VI) COMPLEXES
III.1 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 $\text{H}_3\text{Cr}^\text{V}(\text{O}_2)_4$, $\text{Cr}^{\text{IV}}(\text{O}_2)_2\text{L}_3$ and $\text{Cr}^{\text{VI}}\text{O}(\text{O}_2)_2\text{L}$ 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 preceding 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$_2$)$_2^-$, donor, appears to follow the sequence.

$$\text{H}_2\text{O} < \text{ether} < \text{py, bipy, phen, OH}^-, \text{Cl}^-.$$  

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$_2$)$_2\text{L}$ for $\text{L} = \text{NCO}^-$, 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 preceding chapter, reagent grade pyridine used was first dried with KOH, redistilled and stored over molecular sieves. Nitromethane was spectro-quality. Ph₄AsN0₃ was prepared by either precipitating out the chloride in Ph₄AsCl, as AgCl, with AgNO₃ dissolved in dilute HNO₃ and then evaporating the solution, or by acidifying the PhAsOH solution with 1M HNO₃ and evaporating. OPPh₃ 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, OPCl₃ and OPPhCl₂ 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 Ph₄AsCrO(O₂)₂Cl, it is appropriate to describe a new and convenient method used in the preparation of the Ph₄AsCrO(O₂)₂Cl. The new method uses CrO(O₂)₂py, instead of Ph₄AsCrO₃Cl⁴⁻, as the starting material.

(i) Oxodiperoxopyridinoochromium(VI) Complex, CrO(O₂)₂py,

The solid CrO(O₂)₂py was prepared by established methods. The blue needle-like crystals of CrO(O₂)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(O₂)₂py precipitate was extracted with CHCl₃ 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(O₂)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.
The Ph₄AsCrO(O₂)₂Cl can be conveniently prepared at room temperature by adding a stoichiometric amount of reagent grade Ph₄AsCl, dissolved in chloroform, to the chloroform solution of freshly prepared CrO(O₂)₂py.

\[
\text{CrO(O₂)₂py + Ph₄AsCl} \rightarrow \text{Ph₄AsCrO(O₂)₂Cl + pyridine}
\]  

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 Ph₄AsCrO(O₂)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 (χₘ = 4.20 \times 10^{-4} \text{ cm}^3 \text{ mole}^{-1}) to other Cr(VI) compounds. 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.

Ph₄AsCrO(O₂)ₐNCO

Ph₄AsCrO(O₂)₂Cl (1.902 gm) dissolved in 10 ml acetonitrile reacts with a slurry of AgNCO (0.272 gm), also in 10 ml acetonitrile, to form

\[
\text{Ph₄AsCrO(O₂)₂Cl + AgNCO} \rightarrow \text{Ph₄AsCrO(O₂)₂NCO + AgCl}
\]  

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 Ph₄AsCrO(O₂)₂NCO. The AgCl was filtered off and the Ph₄AsCrO(O₂)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 $\text{Ph}_4\text{AsCrO(O}_2\text{)}_2\text{NCO}$: 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 Oxodiperoxoxoazidochromium(VI) Complex, $\text{Ph}_4\text{AsCrO(O}_2\text{)}_2\text{N}_3$.

$\text{Ph}_4\text{AsCrO(O}_2\text{)}_2\text{Cl}$ (0.750 gm) dissolved in 10 ml of MeCN was treated, at $-10^\circ\text{C}$, with an acetonitrile solution of sodium azide (0.124 gm, finely ground).

$$\text{Ph}_4\text{AsCrO(O}_2\text{)}_2\text{Cl} + \text{NaN}_3 \rightarrow \text{Ph}_4\text{AsCrO(O}_2\text{)}_2\text{N}_3 + \text{NaCl} \quad [3]$$

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 $\text{Ph}_4\text{AsCrO(O}_2\text{)}_2\text{N}_3$.

Analysis (%), calculated for $\text{Ph}_4\text{AsCrO(O}_2\text{)}_2\text{N}_3$: 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, $\text{Ph}_4\text{AsCrO(O}_2\text{)}_2\text{NCS}$.

When a solution of $\text{Ph}_4\text{AsCrO(O}_2\text{)}_2\text{Cl}$ (0.6061 gm) in 10 ml of acetonitrile was stirred, at $-10^\circ\text{C}$, with NH$_4$NCS (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.
and the \( \text{Ph}_4\text{AsCrO}(O_2)_2\text{NCS} \) 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 \( \text{Ph}_4\text{AsCrO}(O_2)_2\text{NCS} \): 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 \( \text{Ph}_4\text{AsCrO}(O_2)_2\text{NCS} \) 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 \( \text{Ph}_4\text{AsH(NCS)}_2 \) with \( \text{CrO}(O_2)_2\text{py} \), or \( \text{AgNCS} \) with \( \text{Ph}_4\text{AsCrO}(O_2)_2\text{Cl} \), failed to produce \( \text{Ph}_4\text{AsCrO}(O_2)_2\text{NCS} \), and no precipitate of \( \text{AgCl} \) was detected.

(vi) Tetraphenylarsonium Oxodiperoxonitratochromium(VI) Complex.

\[ \text{Ph}_4\text{AsCrO}(O_2)_2\text{Cl} + \text{NH}_4\text{NCS} \rightarrow \text{Ph}_4\text{AsCrO}(O_2)_2\text{NCS} + \text{NH}_4\text{Cl} \] [4]

Numerous analyses of the \( \text{Cl} \) content of \( \text{Ph}_4\text{AsCrO}(O_2)_2\text{Cl} \) have been conducted by reacting with solutions of \( \text{AgNO}_3 \) in MeCN. 0.0643 gm of \( \text{Cl} \), as \( \text{AgCl} \), was obtained from 1gm of \( \text{Ph}_4\text{AsCrO}(O_2)_2\text{Cl} \) - 0.0644 gm was expected. The \( \text{Ph}_4\text{AsCrO}(O_2)_2\text{NO}_3 \) solution in MeCN is stable for up to 24 hr without much apparent decomposition, when kept in the dark at \(-10^\circ\text{C}\). The metathetical reaction is given below.

\[ \text{Ph}_4\text{AsCrO}(O_2)_2\text{Cl} + \text{AgNO}_3 \rightarrow \text{Ph}_4\text{AsCrO}(O_2)_2\text{NO}_3 + \text{AgCl} \] [5]

When the silver chloride precipitation was carried out at room temperature, the solution of \( \text{Ph}_4\text{AsCrO}(O_2)_2\text{NO}_3 \) gradually turned yellow. Attempts to precipitate the \( \text{Ph}_4\text{AsCrO}(O_2)_2\text{NO}_3 \) by adding \( \text{CCl}_4 \), petroleum ether and mixed solvents have also failed. But when the freshly prepared \( \text{Ph}_4\text{AsCrO}(O_2)_2\text{NO}_3 \)
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$_2$)$_2$.NO$_3$. CrO(O$_2$)$_2$.OMe$_2$ is known and reported 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

\[
\text{Ph}_4\text{AsCrO(O}_2\text{)}_2\text{NO}_3 + \text{solvent} \rightarrow \text{Ph}_4\text{AsCrO(O}_2\text{)}_2\text{NO}_3 \leftarrow \text{solvent.} \quad [6]
\]

\[
\text{Ph}_4\text{AsCrO(O}_2\text{)}_2\text{NO}_3 \leftarrow \text{solvent} \rightarrow \text{Ph}_4\text{AsCrO}_3\text{NO}_3 + (\text{solvent} + \text{O}_2) \quad [7]
\]

occurring (where solvent = MeCN or OEt$_2$) in solution instead of

\[
\text{Ph}_4\text{AsCrO(O}_2\text{)}_2\text{NO}_3 + \text{solvent} \rightarrow \text{Ph}_4\text{AsNO}_3 + \text{CrO(O}_2\text{)}_2\text{solvent.} \quad [8]
\]

The freshly prepared solid gave C, 51.3; N, 3.6; N, 2.0; compared to C, 50.0; H, 3.46; N, 2.4 expected for Ph$_4$AsCrO(O$_2$)$_2$NO$_3$.

Other attempts at preparing the CrO(O$_2$)$_2$NO$_3^-$ anion involved treating CHCl$_3$ solutions of the pyridine adduct, CrO(O$_2$)$_2$.py, with Ph$_4$AsNO$_3$; but this was inconclusive.

Analysis (%), calculated for Ph$_4$AsCrO(O$_2$)$_2$NO$_3$: 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$_2$)$_2$NO$_3^-$ anion in either product was unobtainable because of decomposition.

Treating a MeCN solution of CrO(O$_2$)$_2$.py with AgNO$_3$, also in MeCN, produced red-brown precipitate found to contain Ag$_2$CrO$_4$. 
(vii) *Oxodiperoxo(triphenylphosphine oxide)chromium(VI) Adduct,*

\[ \text{CrO(O}_2\text{)}_2\cdot \text{OP(C}_6\text{H}_5\text{)}_3.\]

The initial interest in preparing the oxodiperoxochromium(VI)-phosphine oxide adducts, \( \text{CrO(O}_2\text{)}_2\cdot \text{OP}_3 \), was to study the effects of coordination on the phosphorus-oxygen stretching frequency and on the \(^{31}\text{P}\) nuclear magnetic resonance frequency.

100 ml of ether was added to 100 ml of aqueous \( \text{CrO}_3 \) (5.0 gm). When the mixture had acquired the temperature of the salt-ice bath, 25 ml of 5% \( \text{H}_2\text{O}_2 \) solution was added dropwise with stirring. The blue colour of \( \text{CrO(O}_2\text{)}_2\cdot \text{OEt}_2 \) 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 \( \text{OPPh}_3 \) solution in 1:2 chloroform-ethyl ether mixture was added with stirring to the ether solution. The use of less than stoichiometric amount of \( \text{OPPh}_3 \) safeguards against excess ligand. The mixture was allowed to react in the cold (\( \approx 0^\circ\text{C} \)) for about three minutes.

\[
\text{CrO(O}_2\text{)}_2\cdot \text{OEt}_2 + \text{OPPh}_3 \rightarrow \text{CrO(O}_2\text{)}_2\cdot \text{OPPh}_3 + \text{Et}_2\text{O} \quad [9]
\]

The solid \( \text{CrO(O}_2\text{)}_2\cdot \text{OPPh}_3 \) 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 \(-20^\circ\text{C}\).

**Analysis (%)**, calculated for \( \text{CrO(O}_2\text{)}_2\cdot \text{OPPh}_3 \): Cr, 12.7; C, 52.7; H, 3.7.

**Found**: Cr, 12.7; C, 52.5 and H, 3.7.

Attempts to prepare \( \text{CrO(O}_2\text{)}_2\cdot \text{OPPh}_3 \) by reacting \( \text{CrO(O}_2\text{)}_2\text{py} \) in chloroform with \( \text{OPPh}_3 \) also dissolved in chloroform failed, probably, because the pyridine is more strongly coordinated than the \( \text{OPPh}_3 \) would be. The \( ^{31}\text{P} \) 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) Tetraphenylarsionium Oxodiper oxy fluoro chromium(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 OPCl₃ and CrO(O₂)₂·OEt₂, producing an olive green ether-insoluble oil. The same reaction and colour were observed when OPPhCl₂ 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 OPPhCl₂.

Trifluoro β-diketones

Attempts to prepare CrO(O₂)₂L₁ for L = TAA, TTA, BTA, and NTA, failed. When ethereal solutions of CrO(O₂)₂·OEt₂ or CrO(O₂)₂py were treated with solutions of the ligand (L) in ether, the mixtures underwent gradual decomposition.

Monosubstituted Pyridines (NC₅H₄X, for X = F, Cl, Br and NH₂)

Using the procedure for the preparation of CrO(O₂)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(O₂)₂·OEt₂, the blue solution was stable for about 1 hr but the ¹⁹F NMR spectra of the mixture was identical to that of fresh 2-fluoropyridine. Similar decomposition reaction occurred when attempts were made to prepare the CrO(O₂)₂·L adducts with 2- and 3- monosubstituted pyridines, NC₅H₄X for X = Cl, Br or NH₂, using the methods above.
Bromide, CrO(O₂)₂Br⁻.

Treating a chloroform solution of CrO(O₂)₂py with Ph₄AsBr or reagent grade n-Bu₃PBr failed to produce CrO(O₂)₂Br⁻ because of competing decomposition reactions. But the visible spectra of Ph₄AsCrO(O₂)₂NCS in MeCN is similar to that of a solution containing 1:1 Ph₄AsCrO(O₂)₂NCS and Et₄NBr, indicating that the CrO(O₂)₂Br⁻ anion probably exists. The pale blue color of Ph₄AsCrO(O₂)₂NCS went noticeably darker, although the shift in the visible spectrum was only from 569 to 563 μm.

Acetate, CrO(O₂)₂(OAc)⁻

When an acetonitrile solution of Ph₄AsCrO(O₂)₂Cl was treated with a slurry of silver acetate, in MeCN at 22°C, a quantitative yield of AgCl was obtained. But the Ph₄AsCrO(O₂)₂(OAc) solution gradually turned grayish blue and finally yellow.

\[
\text{Ag(OAc)} + \text{Ph₄AsCrO(O₂)₂Cl} \rightarrow \text{AgCl} + \text{Ph₄AsCrO(O₂)₂(OAc)}
\]

[9] (decomposes)

Attempts to precipitate out the freshly prepared complex Ph₄AsCrO(O₂)₂(OAc) failed.
III.3 INFRARED SPECTRA OF SUBSTITUTED OXODIPEROXOCHROMIUM(VI) COMPLEXES

\[ \text{CrO(O}_2\text{)}_2L \]

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\(_2\))\(_2\)py (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 \(\approx1580\) 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\(_2\))\(_2\)py 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, 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 occurring at \(\approx 1580\) 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 and coworkers observed a +41 cm\(^{-1}\) shift for tetrahedral Co(py)\(_2\)Cl\(_2\) (monomeric) and a +30 cm\(^{-1}\) for octahedral Co(py)\(_2\)Cl\(_2\) (polymeric) and a +58 cm\(^{-1}\) shift for monomeric cis-Pt(py)\(_2\)Br\(_2\). The out-of-plane ring deformation occurring 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\(_2\)\(_2\))py**

<table>
<thead>
<tr>
<th>&quot;O=O Stretch&quot; (cm(^{-1}))</th>
<th>Cr=O Stretch (cm(^{-1}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>875m</td>
<td>937s</td>
<td>122</td>
</tr>
<tr>
<td>880m</td>
<td>910 - 960vs</td>
<td>121</td>
</tr>
<tr>
<td>---(? )</td>
<td>934s, 942w, 950w</td>
<td>123</td>
</tr>
<tr>
<td>881w</td>
<td>946vs, (914w, sh, 970m, sh)</td>
<td>This work</td>
</tr>
</tbody>
</table>

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 oxodiperoxo chromium(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 OPPh₃ occurs at 1195 cm⁻¹ (in nujol) compared to the higher (1200 - 1400 cm⁻¹) absorptions in phosphoryl halides. IR studies of numerous OPPh₃ 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 OPPh₃ and that of CrO(O₂)₂OPPh₃ 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. Fig. III(a) and (b).

(c) Tetraphenylarsonium Oxodiperoxochlorochromate

The IR, the Ph₄AsCrO(O₂)₂Cl complex shows the following absorptions in addition to the bands assignable to the Ph₄As⁺ cation.

Table III.2. The Vibrational (IR) Spectrum of Ph₄AsCrO(O₂)₂Cl

<table>
<thead>
<tr>
<th>Frequency(cm⁻¹)</th>
<th>Tentative Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>950 vs</td>
<td>νCr=O</td>
</tr>
<tr>
<td>935 vs</td>
<td></td>
</tr>
<tr>
<td>907 m</td>
<td>νO=O</td>
</tr>
<tr>
<td>900 w, sh</td>
<td>νCr=O₂</td>
</tr>
<tr>
<td>615 m, br</td>
<td>νCr=Cl</td>
</tr>
<tr>
<td>435 m</td>
<td></td>
</tr>
</tbody>
</table>
**Fig. III.3a** \ OPPH\text{\textsubscript{3}}, IR (KBr)

849\text{w}, 858\text{w}, 864\text{w}, 939\text{w}, 974\text{vw}, 983\text{w},
998\text{m-s}, 1031\text{l\textsubscript{w}}, 1070\text{m}, 1094\text{m}, 1121\text{vs},
1157\text{s,sh}, 1187\text{vs,br}.

**Fig. III.3b** \ CrO(O\textsubscript{2})\textsubscript{2}OPPH\text{\textsubscript{3}}, IR (KBr)

851\text{l\textsubscript{w}}, 946\text{s \nu(Cr=O)}, 994\text{s}, 1028\text{m}, 1068\text{s},
1075\text{s}, 1124\text{s (\nu_{O-p})}, 1165\text{w}, 1185\text{w}.
The spectrum is relatively simple and consistent with that previously reported and will not be discussed further.

(d) Tetraphenylarsonium Oxodiperoxoazidochromate

The spectrum of the azido complex, CrO(O₂)₂N₃⁻, 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(O₂)₂N₃⁻ 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 ν₆s(N₃). Splittings have also been observed in the IR spectra of SnCl₃(N₃), TiCl₃(N₃), CrO₂Cl(N₃), MoCl₄(N₃)₂, VCl₄(N₃), and GeH₄(N₃)₄-n,¹³¹ the pseudosymmetric mode is comparable to that of GeH₄(N₃)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 ν₀-₀ and the ν(Cr=O) (for CrO₃Lⁿ⁻ 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\(^{-1}\) and at 683 and 614 cm\(^{-1}\), for the complex \(\text{MoCl}_4(N_3)_2\), some of the bands (at 615, 595, 560 and 525 cm\(^{-1}\)) observed in the spectrum of the \(\text{Ph}_4\text{AsCrO(O}_2)_2N_3\) complex could be assigned to the bending modes of the azido group, except that these same bands occur rather consistently through the oxodiperoxopseudohalogeno-

chromium(VI) complexes \(\text{CrO(O}_2)_2\text{Ps}^-\) for \(\text{Ps}^- = \text{N}_3^-, \text{NCO}^-\) and \(\text{NCS}^-\). Because of this and the fact that Griffith's \(\text{MoCl}_4(N_3)_2\) peroxo complexes exhibit absorptions in the same region, it is very likely that these are vibrations of the \(\text{M-O}_2\) group.

e) Tetraphenylarsonium Oxodiperoxocyanatochromate

On the basis of the arguments used for \(\text{KCrO}_3\text{(NCO)}\), the following features are recognizable, Table III.3. The sharp unsplit 2195 cm\(^{-1}\) absorption, assigned to \(\nu_{\text{CN}}\), 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 \(\nu_{\text{CN}}\) 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, \(\nu_{\text{CO}}\) 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 (\(\approx 1300 \text{ cm}^{-1}\)) \(^56\) from the free ligand value of 1254 cm\(^{-1}\). Such increases have been observed in the vibrational spectra of isocyanato complexes: \(\text{Si(NCO)}_4\) (1482 cm\(^{-1}\)), \(\text{Ge(NCO)}_4\) (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\textsubscript{2})\textsubscript{2}(NYZ\textsuperscript{−}) Anions in Ph\textsubscript{4}AsCrO(O\textsubscript{2})\textsubscript{2}(NYZ\textsuperscript{−}), (cm\textsuperscript{-1}).

<table>
<thead>
<tr>
<th>CrO(O\textsubscript{2})\textsubscript{2}N\textsubscript{3}\textsuperscript{−}</th>
<th>CrO(O\textsubscript{2})\textsubscript{2}(NCO\textsuperscript{−})</th>
<th>CrO(O\textsubscript{2})\textsubscript{2}(NCS\textsuperscript{−})</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2070m</td>
<td>2195s</td>
<td>2080vs, broad base</td>
<td>$\nu_{\text{asy}}$(NYZ)</td>
</tr>
<tr>
<td>2030vs, broad base</td>
<td></td>
<td></td>
<td>$\nu_{\text{sym}}$(N\textsubscript{3})</td>
</tr>
<tr>
<td>1275m, br</td>
<td></td>
<td></td>
<td>$\nu_{\text{(Cr=O)}}$</td>
</tr>
<tr>
<td>950s</td>
<td>948s</td>
<td>985m, shr</td>
<td>$\nu_{\text{(Cr=O)}}$</td>
</tr>
<tr>
<td>935vs</td>
<td>942s, shr</td>
<td>940s, shr</td>
<td>$\nu_{\text{(Cr=O)}}$</td>
</tr>
<tr>
<td>905m</td>
<td>906w</td>
<td>910m, sh</td>
<td>$\nu_{\text{0-0 or CS}}$</td>
</tr>
<tr>
<td>898vw, sh</td>
<td>906w</td>
<td>910m, sh</td>
<td>$\nu_{\text{CS}}$</td>
</tr>
<tr>
<td>615m</td>
<td>620m</td>
<td>625m, br</td>
<td>$\nu_{\text{(M-O\textsubscript{2}) or δ(NYZ)}}$</td>
</tr>
<tr>
<td>595w</td>
<td>590m</td>
<td>610m</td>
<td>$\nu_{\text{(M-O\textsubscript{2}) or δ(NYZ)}}$</td>
</tr>
<tr>
<td>560vw</td>
<td>555vw</td>
<td>610m</td>
<td>$\nu_{\text{(M-O\textsubscript{2}) or δ(NYZ)}}$</td>
</tr>
<tr>
<td>525w</td>
<td>525vw</td>
<td>530m</td>
<td>$\nu_{\text{Cr=N}}$</td>
</tr>
<tr>
<td>490m, sh</td>
<td></td>
<td></td>
<td>$\nu_{\text{Cr=N}}$</td>
</tr>
<tr>
<td>410w</td>
<td>415w</td>
<td>415w</td>
<td>$\nu_{\text{Cr=N}}$</td>
</tr>
</tbody>
</table>
The presence of a band in the 610 cm\(^{-1}\) region through the series of complexes \(\text{CrO(O}_2\text{)}_2\text{Ps}\) for \(\text{Ps} = \text{N}_3, \text{NCO}^-\) and \(\text{NCS}^-\) 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 \(\approx 495\) cm\(^{-1}\) in \(\text{KCrO}_3\text{NCO}\) and \(\text{CrO}_2\text{Cl(N}_3)\), 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 \(\text{CrO(O}_2\text{)}_2\text{NCO}^-\) compared to \(\text{CrO}_3\text{NCO}^-\). What appears to be the \(\nu_{\text{Cr-N}}\) in \(\text{CrO(O}_2\text{)}_2\text{NCO}^-\) is observed as a weak band at 415 cm\(^{-1}\) as compared to the strong \(\nu_{\text{Cr-Cl}}\) stretch in \(\text{CrO(O}_2\text{)}_2\text{Cl}^-\) which occurs at 437 cm\(^{-1}\). It is generally argued that the M-NCO stretch occurs above the \(\nu_{\text{M-Cl}}\) of the analogous complex. The assignment of the 415 cm\(^{-1}\) band to \(\nu_{\text{Cr-N}}\) is favoured because it compares with the assignment of the isoelectronic species \(\text{CrO(O}_2\text{)}_2\text{N}_3^-\) and with metal-isocyanate vibrations of other complexes in which the metal is highly electropositive.\(^{31}\) For instance, \(\text{Ph}_4\text{As[Fe(NCO)}_4\text{]}\) is reported\(^{56}\) to have the Fe-N stretch at 410 and the other ligand vibrations at 2208, 2171 (\(\nu_{\text{as}}\text{(NC0)}\)), 1307, 626 and 619 cm\(^{-1}\).

(f) Tetraphenylarsonium Oxodiperoxothiocyanatochromate

The spectrum of the anionic complex, \(\text{CrO(O}_2\text{)}_2\text{(NCS)}^-\) (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 955\(^m\), 940\(^vs\), 920\(^s\), 910\(^m\), 880\(^w\), 625\(^m\), 610\(^m\), 530\(^m\) and 415\(^m\) 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, \(\nu\(_{CN}\)\), 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.\(^4\)\(^8\)

According to Sabatini and Bertini\(^4\)\(^9\) and Lewis and coworkers,\(^1\)\(^3\)\(^8\) the ligand pseudosymmetric stretch, \(\nu\(_{CS}\)\), 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 \(\approx700\) cm\(^-1\) for S-bonded thiocyanates. Unfortunately, this band could not be identified in Ph\(_4\)AsCrO\((O_2)_2(NCS)\) as a result of masking absorptions arising from the Ph\(_4\)As\(^+\) cation. But there are two strong absorptions, one at 985 cm\(^-1\) and the other at \(\approx740\) cm\(^-1\) (shoulder), the origins of which are doubtful, though either could very well be the ligand C-S stretch. Knox and Brown\(^1\)\(^3\)\(^9\) have reported a series of hexaisocyanato complexes, Nb(NCS)\(^n-\) for \(n = 1\) or 2, and Ta(NCS)\(^-\) 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\(_2\)HGe(NCS) and MeGe(NCS)\(_3\), gave the values of \(\nu\(_{CS}\)\) 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 \(\nu\(_{CS}\)\) 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, 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 and Griffith and Wickins have reported the infrared (and some Raman) spectra of a large number of such complexes, but have positively identified only the ν_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 ν_2(A_1) or ν_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 \(\text{H}_2\text{O}_2\) and the 870 - 900 cm\(^{-1}\) band in organic peroxides,\(^{139}\) have been assigned to the 0-0 stretching vibrations of the coordinated peroxo groups with, maybe, some contribution from the O-M-O deformation vibration.

In addition to the "\(\nu_{0-0}\)" band in these complexes, weak high frequency absorptions also occur between ~950 and 975 cm\(^{-1}\). Other peroxo complexes, including the \(\text{Cr}(\text{O}_2)_3\)\(^{3-}\), 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>
<thead>
<tr>
<th>Complex</th>
<th>(\nu_{0-0})</th>
<th>(\nu_{\text{Cr=O}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{K[CrO(O}_2)_2\text{OH]})</td>
<td>876s</td>
<td>984m, 924s</td>
</tr>
<tr>
<td>(\text{Tl[CrO(O}_2)_2\text{OH]})</td>
<td>870s</td>
<td>970w, 920s</td>
</tr>
<tr>
<td>(\text{NH}_4[\text{CrO(O}_2)_2\text{OH]})</td>
<td>932s</td>
<td>980s</td>
</tr>
<tr>
<td>(\text{CrO(O}_2)_2\text{(in ethyl acetate)})</td>
<td>864s</td>
<td>940s</td>
</tr>
<tr>
<td>(\text{CrO(O}_2)_2\text{py})</td>
<td>875m</td>
<td>937s</td>
</tr>
<tr>
<td>(\text{CrO(O}_2)_2\text{bpy})</td>
<td>890m</td>
<td>922s</td>
</tr>
</tbody>
</table>

Because opposing factors\(^{142-144}\) result in minimal shifts in the "\(\nu_{0-0}\)" band even when the character of the coordinating metal or substituents\(^{145}\) is changed drastically, no positive correlation can be made between the \(\nu_{0-0}\) frequency and the 0-0 bond length or the donor (\(\sigma\) or \(\pi\)) properties of the substituent. Furthermore, vibrational coupling with
M=O modes in the case of oxoperooxo complexes, are probably inevitable. This would tend to raise the frequency of $\nu_{0-0}$. 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 $\nu_{0-0}$.

The use of the large cation Ph$_4$As$^+$ to stabilize the anionic complexes CrO(O$_2$)$_2$L$^-$ has also meant that certain important vibrations $\nu$(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$^1$ of the absorption spectra of CrO(O$_2$)$_2$OE$_2$, CrO(O$_2$)$_2$py, CrO(O$_2$)$_2$CH$_3$OH 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 $\approx 360$ m$\mu$ ($\varepsilon \approx 10^3 - 10^6$) and a doublet with the maxima at $\approx 580$ ( $\varepsilon=700$) and 750 m$\mu$ ( $\varepsilon=400$). 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 m$\mu$ ( $\varepsilon=441$) for methanolic and aqueous solutions of the NH$_4$[CrO(O$_2$)$_2$OH] 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 ($\approx 10^3$).$^{30,146}$ 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 correla-
ation 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(O₂)₂L⁻, for L = Cl⁻, NCO⁻, Br⁻, N₃⁻, NCS⁻ and NO₃⁻, were investigated, Figure III.4. A solution of CrO(O₂)₂OPPh₃ in most non-donor solvents (CHCl₃, 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(O₂)₂OH⁻. The intense band occurring at = 360 μ 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(O₂)₂L⁻, for L = N₃⁻, 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 N₃⁻, 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⁻                     | μ | cm⁻¹ | ε (x 10⁻³) | Ref |
| OH⁻                             | 531 | 18,800 | 0.44 | 141 |
| N₃⁻                             | 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 \( \text{Cr} \text{O}_2 \text{L} \text{Cl} \) in the 580m\( \mu \) Region (MeCN, 22°C).

- \( \text{Ph}_4 \text{AsCrO}_2 \text{Cl} \)
- \( \text{Ph}_4 \text{AsCrO}_2 \text{NCO} \)
- \( \text{Ph}_4 \text{AsCrO}_2 \text{NCS} \)
- \( \text{Ph}_4 \text{AsCrO}_2 \text{NO}_2 \text{(-10°C)} \)
- \( \text{Ph}_4 \text{AsCrO}_2 \text{Br} \text{(?)} \)
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 coordination sphere) than necessarily that of the coordinated substituent. This is reflected in the solvent studies on CrO(O₂)₂Cl⁻, (Fig. III.5).

The absorption spectrum of Ph₄AsCrO(O₂)₂NO₃ (at -10°C), which, because of decomposition could not be obtained at room temperature, has the maximum absorption occurring at 587 μ (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(O₂)₂CH₃OH was temperature-dependent. Because of the large variations in the temperatures and the media necessary to ensure the stability of the oxodiperoxo-chromium(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(O₂)₂L⁻, for L = N₃, 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 μ (≈ 18,000 cm⁻¹) region can be readily compared with the absorption energies in the corresponding CrO₃Lⁿ⁻ anions, using the results from Chapter II.
A Trend in the Effect of the Ligand (L) Upon the Absorption Spectra of CrO(0₂)₂L⁻ and CrO₃L⁻ Complexes

<table>
<thead>
<tr>
<th>Ligands</th>
<th>CrO(0₂)₂L⁻ (± 100) cm⁻¹</th>
<th>CrO₃L⁻ (± 50) cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₃⁻</td>
<td>18,100</td>
<td>26,670</td>
</tr>
<tr>
<td>Br⁻</td>
<td>17,800</td>
<td>27,400</td>
</tr>
<tr>
<td>NCO⁻</td>
<td>17,700</td>
<td>27,330</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>17,600</td>
<td>27,550</td>
</tr>
<tr>
<td>NCS⁻*</td>
<td>17,500</td>
<td>27,320</td>
</tr>
</tbody>
</table>

* 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(0₂)₂L⁻ and 880 cm⁻¹ (± 50) in CrO₃L⁻ with the estimated accuracy in the measurement of the energy given.

The results for L = N₃⁻, 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(0₂)₂L where L = py, and phen, 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 OXODIPEROXOCROMIUM(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(0₂)₂L. Of the oxodiperoxo chromium(VI) complexes with established structures, probably CrO(0₂)₂py most closely resembles the new monosubstituted complexes. The pyridine complex is described as a pentagonal pyramid with the peroxy groups and the pyridine nitrogen forming the basal plane, 147.

\[
\begin{array}{c}
\text{Cr} \quad \bullet \\
C \quad \bigcirc \\
N \quad \bigcirc \\
O \quad \bigcirc \\
\end{array}
\]

and the chromium being displaced some 0.51Å from the plane in the direction of the apical oxygen atom. One of the factors that might influence the geometry of the complex CrO(0₂)₂L, for L = OH⁻, Cl⁻, Br⁻, NCO⁻, NCS⁻, N₃⁻, NO₃⁻ and OPPh₃ is the extent of mutual repulsions between the oxygens (0₂⁻ or 0²⁻) and substituent group, resulting in C₂ᵥ (not very likely), C₈ or no symmetry.

\[
\text{C}_2\nu \\
\begin{array}{c}
\bigcirc \\
\text{L} \\
\end{array} \\
\text{C}_8 \\
\begin{array}{c}
\text{Cr} \\
\bigcirc \\
\text{L} \\
\end{array}
\]
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(02)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 O2, O2-, and O23-. The electronic configuration of molecular oxygen, O2, as described by MO theory[148,149] is either

\[(\sigma_1)^2(\sigma_2^*)^2(\sigma_3^*)^2(\pi_1^*^*)^2\] or \[(\sigma_1)^2(\sigma_2^*)^2(\pi_1^*)^4(\sigma_3^*)^2(\pi_2^*)^2\]

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 (\(\pi_2^*\)) orbital on O2 leads to the superoxide O2-. And, as expected, the removal of this electron from the \(\pi^*\) 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\(^a\)

<table>
<thead>
<tr>
<th>Species</th>
<th>Example Compound</th>
<th>No. Unpaired Electrons</th>
<th>O-O Bond Length (Å)</th>
<th>Bond Order</th>
<th>Bond Energy (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2</td>
<td>O2 (gas)</td>
<td>2</td>
<td>1.2107 ± 0.0001</td>
<td>2</td>
<td>118(^b)</td>
</tr>
<tr>
<td>O2-</td>
<td>K2O2 (solid)</td>
<td>1</td>
<td>1.28 ± 0.02</td>
<td>1.5</td>
<td>69(^c)</td>
</tr>
<tr>
<td>O2-</td>
<td>K2O2 (solid)</td>
<td>0</td>
<td>1.49 ± 0.01</td>
<td>1</td>
<td>(-125)</td>
</tr>
</tbody>
</table>

\(^a\) 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 (\(\pi^*\)) 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 \(\text{Ir}(O_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2\), \(\text{Cr}(O_2)_2\text{L}_3\) and \(\text{Cr}(O_2)_4^{3-}\). 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 0-0 bond length and the \(\mu\text{0-M-0}\) in \(\text{CrO}(O_2)_2\text{L}\), for \(\text{L} = \text{py, bipy or phen}, \text{average}\ 1.40\text{\AA}\) and 45\(^\circ\), respectively.

Fergusson,\textsuperscript{123} Duffey\textsuperscript{151} and Cartmell and Fowles\textsuperscript{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 \(d^4\text{sp}^3\) or \(d^3\text{sp}^3\) hybrid orbitals. This explanation presupposes that each of the oxygen atoms of an \(O_2^{2-}\) ligand donates a pair of \(\sigma\)-bonding electrons and, for the 0-Cr-0 angles to be small, the hybrid orbitals must subtend small angles. Griffith\textsuperscript{135} supported the above \(\sigma\)-bonding scheme and went on and postulated a "bent bond" hypothesis, similar to that used for cyclopropane\textsuperscript{154} and ethylene oxide,\textsuperscript{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, who suggest a donation of peroxide \( \pi \) electrons to the empty d-orbitals on the metal atom in a manner analogous to that suggested for the olefin and ethylene complexes of transition metals. 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 two alternate \( \pi \)-bonding interactions in association with the \( \sigma \)-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 \( \pi^* \) to the \( \pi \) orbitals on \( O_2^2- \), as a result of \( \sigma \)-donation, such that backbonding to \( \pi^* \) 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 \( \pi \)- or \( \pi^* \) orbitals of the peroxo-group. Force constant calculations 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 \( \pi \)(2p) electron density from the \( O_2^2- \), erroneous interpretation of this bonding mode has led others 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 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(O₂)₂L complexes, or Cr(O₂)₃⁻, where the O-O bond length average 1.40(± 0.02) and 1.405 ± 0.03Å¹,¹²¹ 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(O₂)₂L 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(O₂)₃⁻ the O-O π-bonding orbitals (in the CrO₂ plane) make the largest contributions to the Cr-O σ-bonds. Another large part comes from the overlap of the Cr π-orbitals (3dₓ², 3dₓz and 4pₓ) with O²⁻ π* molecular orbitals (in the plane of CrO₂). The electrons in the O-O π bonding orbitals above the CrO₂ plane were also shown to be partially delocalized toward the chromium by way of the Cr(4pₓ) and Cr(3dₓz) 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 O²⁻ π-orbitals, which are of the same symmetry. Furthermore, these same σ-orbitals also make small contributions to the Cr-O σ-
π-bonding. Finally, these authors postulated "bent bonds", i.e. the overlap density of the Cr π(3d_2, d_xz, and d_yz) orbitals with O_2^2- π*(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)_3^3-, 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^- 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, Ph_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; \( \text{Ph}_4\text{AsCrO}(O_2)_2\text{Cl} \) has been kept at room temperature for over 9 months without decomposition, while \( \text{Ph}_4\text{AsCr}(O_2)_2\text{NCO} \) was stable for about 3 months under similar conditions.
CHAPTER FOUR

SUBSTITUTION REACTIONS IN CHROMIUM(VI) TRIOXO

AND OXODIPEROXO COMPLEXES
IV.1 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 HCrO₄⁻ and Cr₂O₇²⁻ 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 HCrO₄⁻ with the inorganic anions

\[ \text{HPO}_4^{2-}, \text{H}_2\text{PO}_4^{-}, \text{S}_2\text{O}_3^{2-}, \text{SO}_4^{2-}, \text{NCS}^-, \text{C}_2\text{O}_4^{2-}, \text{etc.} 162 \]

proceed by a mechanism similar to the dimerization reaction. The observed hydrogen ion dependent forward rate constants \( k_f^H \approx 5 \times 10^5 \text{ M}^{-2} \text{ sec}^{-1} \) 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 HOCrO₃⁻, to form the departing water molecule. Unfortunately, however, the observed rates, for instance, in the dimerization reaction [1]

\[ 2\text{HCrO}_4^- \leftrightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \]  \[ [1] \]

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, CrO₂ClF, in the solvent-free mixture of the parent chromyl halides, CrO₂F₂ and CrO₂Cl₂. There have, however, been no reports...
of substitution studies of trioxo- and oxodiperoxochromium(VI) species in non-aqueous media. Holley and Baldwin, 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 ($k_1 = k_1/H_2O = 7 \times 10^{-7} \text{sec}^{-1}$) and pH independent, suggesting that the main process was probably:

$$^{*}\text{OCrO}_3^{2-} + H_2O \rightleftharpoons \text{CrO}_4^{2-} + H_2O^* \quad [2]$$

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

$$\text{HCrO}_4^- + \text{CrO}_4^{2-} \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{OH}^- \quad [3]$$

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

$$2\text{HCrO}_4^- \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + H_2O \quad [4]$$

These authors also noted an alternative path, involving a symmetrical transition state and reported $k_F = 70 \text{ mol}^{-1} \text{ sec}^{-1}$ 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 $\text{CrO}_3F^-$ are isoelectronic with $\text{OH}^-$ and $\text{CrO}_3\text{OH}^-$ ions, respectively. The study of the exchange processes was also extended to include pseudo-isoelectronic systems $\text{CrO}_3L^{n-}/L^{n-}$ and $\text{CrO}(O_2)_2L^{n-}/L^{n-}$ 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 quantitative 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.,
\[ \text{CrO}_3\text{F}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCrO}_4^- + \text{HF} \] [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 \text{CrO}_3\text{F}^-/\text{F}^- and \text{CrO}_3\text{F}^-/\text{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 \( \lambda_{\text{max}} \) and changes in the \( \varepsilon_{\text{max}} \) of these
complexes, for the series of processes, except for
\[ \text{CrO}_3\text{L}^{n-} + \text{F}^- \rightleftharpoons \text{CrO}_3\text{F}^- + \text{L}^{n-} \] [7]
were not large enough to allow the use of UV-visible technique in the
study of the exchange reactions in \( \text{CrO}_3\text{L}^{n-}/\text{L}'^{n-} \) or \( \text{CrO(O}_2\text{)}_2\text{L}^{n-}/\text{L}'^{n-} \).
This limited the investigation of the kinetics of the substitution
processes to those in which \( ^{19}\text{F} \) and \( ^1\text{H} \) can be used as probes.
IV.2 EXPERIMENTAL

The preparation 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 $^{19}\text{F}$ 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 $^{19}\text{F}$, defined as

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

were measured relative to CFCI$_3$ as an external standard. The $^1\text{H}$ 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$_4$Cl in the reactions;

$$\begin{align*}
\text{Cr}^{\text{VI}}\text{Cl} + \text{AgNCO} &\rightarrow \text{Cr}^{\text{VI}}(\text{NCO}) + \text{AgCl} \quad [8] \\
\text{Cr}^{\text{VI}}\text{Cl} + \text{NaN}_3 &\rightarrow \text{Cr}^{\text{VI}}\text{N}_3 + \text{NaCl} \quad [9] \\
\text{Cr}^{\text{VI}}\text{Cl} + \text{NH}_4\text{NCS} &\rightarrow \text{Cr}^{\text{VI}}(\text{NCS}) + \text{NH}_4\text{Cl} \quad [10] \\
\text{Cr}^{\text{VI}}\text{Cl} + \text{AgNO}_3 &\rightarrow \text{Cr}^{\text{VI}}(\text{NO}_3) + \text{AgCl} \quad [11] \\
\text{Cr}^{\text{VI}}\text{Cl} + \text{Ag(CH}_3\text{CO}_2) &\rightarrow \text{Cr}^{\text{VI}}(\text{CH}_3\text{CO}_2) + \text{AgCl} \quad [12]
\end{align*}$$

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).

\[
\begin{align*}
KCrO_3X + AgNO_3 &\rightarrow KCrO_3NO_3 + AgX \quad (\text{for } X = Br \text{ or } Cl) \quad [13] \\
KCrO_3Cl + NH_4NO_3 &\rightarrow NH_4CrO_3Cl + KNO_3 \quad [14] \\
KCrO_3Cl + Ph_4AsNO_3 &\rightarrow Ph_4AsCrO_3Cl + KNO_3 \quad [15] \\
KCrO_3Cl + Et_4NClO_4 &\rightarrow Et_4NCrO_3Cl + KClO_4 \quad [16] \\
KCrO_3NO_3 + Ph_4AsBr &\rightarrow Ph_4AsCrO_3Br + KNO_3 \quad [17]
\end{align*}
\]

which occur in acetonitrile.

The stability of certain Cr-ligand bonds have sometimes been inferred from chemical reactions. For instance, the trioxochlorochromate anion reacts with ice cold 30% \( H_2O_2 \) to form \( CrO(0_2)_2Cl^- \), and undergoes the reduction reaction

\[
CrO_3Cl^- \rightarrow Cr(H_2O)_5Cl^{++} \quad [18]
\]

in which the oxidation state of chromium is changed from VI to III. 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, \( (NH_4)_2Cr_2O_7 \), \( 123 \) from aqueous \( NH_4Cl \), \( (NH_4)_2Cr_2O_7 \), acetic acid and 30% \( H_2O_2 \) at \(-10^\circC \) probably proceeds by a different mechanism.

(b) Substitution Reactions of \( CrO(0_2)_2py \)

The present study investigated the proton NMR spectrum of \( CrO(0_2)_2py \) in the hope of using the \( ^1H \) resonance in following the substitution reaction \( CrO(0_2)_2py/L \), for \( L = \) pyridine (d5), F\textsuperscript{−}, Cl\textsuperscript{−}, Br\textsuperscript{−}, NCO\textsuperscript{−}, NCS\textsuperscript{−}, N\textsuperscript{−}_3
Figure IV.1 shows that the room temperature $^1$H 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 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. 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$_2$)$_2$py/py (and py-d$_5$) exchange studies – see next two pages).

Attempts were made to follow the substitution reaction

$$\text{CrO}(O_2)_{2}\text{pyridine/pyridine (and pyridine} \quad \text{d}_5) \text{ in acetonitrile and in chloroform (both deuterated). The acetonitrile solution of CrO(O$_2$)$_2$py 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$_2$)$_2$py 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.

$$\text{CrO(O}_2\text{N}_5\text{H}_5 + \text{NC}_5\text{D}_5 \rightarrow \text{CrO(O}_2\text{N}_5\text{D}_5 + \text{NC}_5\text{H}_5}$$

[19]

In the CrO(O$_2$)$_2$NC$_5$H$_5$/NC$_5$D$_5$ 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. VI.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).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridine</td>
<td>8.60, 7.50, 7.15</td>
</tr>
<tr>
<td>CrO(O_2)_2py</td>
<td>9.00, 8.30, 7.80</td>
</tr>
</tbody>
</table>

Assignment

- A: a, b, c
- B: a, b, c

Diagram:

- A: spectrum with peaks at 8.60, 7.50, 7.15 ppm
- B: spectrum with peaks at 9.00, 8.30, 7.80 ppm

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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)_{2}py, reacts with Ph₄AsCl in chloroform to form blue, air stable crystals of the chloro derivative, Ph₄AsCrO(O_2)_{2}Cl. The visible spectrum of a MeCN solution containing stoichiometric amounts of CrO(O_2)_{2}py and Ph₄AsCl or Ph₄AsCrO(O_2)_{2}Cl and pyridine were found to be identical to that of Ph₄AsCrO(O_2)_{2}Cl (λ_{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 Et₄NBr and CrO(O_2)_{2}py at -10°C has maximum absorption at 573 mp (the absorption, λ_{max} for CrO(O_2)_{2}py is 575 mp) ¹⁴¹; that for "Ph₄AsCrO(O_2)_{2}Br" is at 563 mp (see page 106), suggesting that Br⁻ does not displace pyridine. Unfortunately, this mixture, like mixtures of CrO(O_2)py and Et₄NX (X=F or I), Ph₄AsH(NCS)_2, Ph₄AsNO₃, AgNCO, NaN₃ or AgNO₃, evolves molecular oxygen and decomposes within minutes.

All together, the ease of substitution, CrO(O_2)_{2}L/L', observed in the non-precipitating reactions seem to follow the order:

H₂O > ethers, acetates > OPPh₃ > pyridine > Cl⁻

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

(i) **The Fluorochromate(VI) - Chloride System**

The absorption spectrum of a millimolar solution of Ph₄AsCrO₃F in MeCN was unaffected over a time span of three days by the addition of an equimolar quantity of Ph₄AsCl. 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 $\text{Ph}_4\text{AsCrO}_3\text{F}$ solution in dry DMSO (50°C) is at $\delta = 163.0 \pm 0.5$ ppm from (external), CFCl$_3$. The resonance in recrystallized Et$_4$NF dissolved in DMSO occurs at $\delta = 142.7$ ppm, but because the latter signal was very broad, the substitution reactions $\text{CrO}_3\text{L}^-/\text{F}^-$ were studied by following the development or disappearance of the more easily detectable $^{19}$F resonance in $\text{CrO}_3\text{F}^-$. The addition of 0.25M solution of either $\text{Ph}_4\text{AsCl}$ or Et$_4$NCl in DMSO to equimolar quantities of $\text{Ph}_4\text{AsCrO}_3\text{F}$ also in DMSO had no effect on either the frequency or the intensity of the $^{19}$F resonance. When the solutions were 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]

$$\text{CrO}_3\text{F}^- + \text{Cl}^- \rightleftharpoons \frac{k_f}{k_r} \text{CrO}_3\text{Cl}^- + \text{F}^- \quad [20]$$

can be obtained from these results, I estimate that the minimum change which could have escaped detection in the UV-visible spectroscopic measurements is $\sim 5\%$. From the stoichiometry of the exchange reaction [20] and if we let $[\text{CrO}_3\text{F}^-]_0$ and $[\text{Cl}^-]_0$ represent the initial concentrations and $[\text{CrO}_3\text{F}^-]_t$ and $[\text{Cl}^-]_t$ denote the concentrations at time $t$, then the rate of the reaction is expressed by equation [21]
The initial concentrations are $[\text{CrO}_3\text{F}^-]_0 = [\text{Cl}^-]_0 = 0.0005$ molar, and because they are equimolar the rate expression becomes

$$\frac{d}{dt} \left( [\text{CrO}_3\text{F}^-]_0 - [\text{CrO}_3\text{F}^-]_t \right) = k_f [\text{CrO}_3\text{F}^-]_t [\text{Cl}^-]_t$$

and the integrated expression

$$\frac{1}{[\text{CrO}_3\text{F}^-]_t} = k_f t + C$$

From this equation, the constant, $C$, was evaluated by setting $[\text{CrO}_3\text{F}^-]_0 - [\text{CrO}_3\text{F}^-]_t = 0$ at $t = 0$. Therefore, the new rate expression becomes

$$k_f = \frac{1}{t} \cdot \frac{[\text{CrO}_3\text{F}^-]_0 - [\text{CrO}_3\text{F}^-]_t}{[\text{CrO}_3\text{F}^-]_0 [\text{CrO}_3\text{F}^-]_t}$$

Since the reaction is estimated to be no more than 5% complete in 3 days, the upper limit for $k_f$ in acetonitrile is $2 \times 10^{-4}$ mol$^{-1}$ sec$^{-1}$.

Similarly, analysis of the NMR results shows that the decrease in CrO$_3$F$^-$ concentration over 1 hour could not have exceeded 5%. The rate constant in DMSO is then less than $5 \times 10^{-5}$ mol$^{-1}$ sec$^{-1}$.

(11) The Fluorochromate - Fluoride System

When equal volumes of 0.25M solutions of Ph$_4$AsCrO$_3$F and Et$_4$NF in DMSO were mixed at 50°C, no appreciable change in the 19F peak intensity or width was observed. The CrO$_3$F$^-$/19F resonance, which was recorded over 2 hours, indicated the absence of significant fluorine exchange in the CrO$_3$F$^-$/F$^-$ system at this temperature. In order for the two separate peaks to be observed at the frequencies -9.17 Kc and -8.05 Kc, the lifetimes of each of the species CrO$_3$F$^-$ and F$^-$ must be
greater than \(1/(u_{F} - u_{CrO_{3}F^{-}})\) \(10^{-3}\) seconds, corresponding to a gross upper limit for the rate constant in dry DMSO for the fluorine exchange of \(10^{3}\) \(1\) mol\(^{-1}\) sec\(^{-1}\).

\[
\text{CrO}_{3}F^{-} + F^{-} \rightleftharpoons \text{CrO}_{3}F^{-} + F^{-}
\]  
\[\text{[25]}\]

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 \(\text{CrO}_{3}F^{-}\) anion collapsed at a readily measurable rate. For instance, using reagent grade \(\text{Et}_{4}\text{NF}\) (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 \(\ln(\text{intensity})\) versus time and \(1/(\text{intensity})\) 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 \[\text{[25]}\], the equilibria

\[
\text{CrO}_{3}F^{-} + \text{H}_{2}\text{O} \rightleftharpoons \text{CrO}_{3}(\text{OH})^{-} + \text{HF}
\]  
\[\text{[26]}\]

\[
\text{HF} + F^{-} \rightleftharpoons \text{HF}_{2}
\]  
\[\text{[27]}\]

In addition, the formation of the \(\text{Cr(III)}\) complexes \([\text{Cr(H}_{2}\text{O})_{5}\text{Cl}]^{2+}\) (broad absorptions at \(24,700\) and \(16,250\) cm\(^{-1}\)) and \([\text{Cr(H}_{2}\text{O})_{5}\text{F}]^{2+}\) (absorption at \(25,300\) cm\(^{-1}\)) \(167\) was detected spectroscopically, in solutions of \(\text{CrO}_{3}\text{Cl}^{-}\) and \(\text{CrO}_{3}F^{-}\) left for longer periods - up to 24 hours.

For that reason no attempt was made to follow the hydrolysis process.

(iii) Systems Involving \(\text{CrO}_{3}L^{n-}/F^{-}\) and \(\text{CrO(O}_{2}^{n-})_{2}L^{n-}/F^{-}\)

When 0.5M solutions of \(\text{CrO}_{3}L^{-}\), for \(L = \text{NCO}^{-}, \text{NCS}^{-}, \text{N}_{3}^{-}, \text{Br}^{-}\)
and NO₃⁻, are mixed with equal volumes of equimolar Et₄NF, in DMSO,

\[
\text{CrO}_3\text{L}^{\text{n}^-} + \text{F}^- \rightleftharpoons \text{CrO}_3\text{F}^- + \text{L}^{\text{n}^-} \quad [7]
\]

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
\( ^{19}\text{F} \) chemical shift, \( \delta = 160 \text{ ppm} \), and the UV-visible spectrum were
consistent with that of the CrO₃F⁻ anion. Attempts to slow down the
process by cooling failed because DMSO freezes at 18°C.

Treating solutions of Ph₄AsCrO(O₂)₂L, for L = Cl⁻, NO₂⁻, NCS⁻,
NO₃⁻ and N₃⁻ in MeCN at room temperature, with stoichiometric amounts of
Et₄NF, also dissolved in MeCN, caused the blue peroxo complexes to
decompose with effervescence. CrO(O₂)₃py reacts similarly with Et₄NF.
The yellow solution produced, after the decomposition has stopped, has
an absorption maximum at \( \sim 353 \text{ nm} \) and a \( ^{19}\text{F} \) resonance at \( \delta = 162 \text{ ppm} \)
characteristic of the CrO₃F⁻ 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 Ph₄AsCrO(O₂)₂Cl or
Ph₄AsCrO(O₂)₂NO₃ was treated with equimolar Et₄NF 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 \( \delta = 127.5 \text{ ppm} \) for the Ph₄AsCrO(O₂)₂Cl - Et₄NF system.
and \( \delta = 127.0 \text{ ppm} \) for the Ph₄AsCrO(O₂)₂NO₃ - Et₄NF 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 \( \delta = 128.0 \text{ ppm} \) and \( \delta = 147.5 \text{ ppm (broad)} \), respectively. The \( ^{19}\text{F} \) resonance for Et₄NF in dry MeCN
is at \( \delta = 115 \text{ ppm} \). (Also see Chapter III Experimental Section).
The blue-brown intermediate in the decomposition is

\[ \text{CrO(O}_2\text{)}F^- \rightarrow ? \rightarrow \text{CrO}_3\text{F}^- \]  \[28\]

probably a monoperoxochromium species.

IV.4 POSSIBLE MECHANISMS FOR SUBSTITUTION REACTIONS IN NON-AQUEOUS
\(\text{CrO}_x\text{L}^{n-}\) SYSTEMS

The mechanisms of substitution reactions of tetrahedral
metal complexes in non-aqueous solvents have been little studied. Both
\(S_N^1\) and \(S_N^2\) type reactions occur in the prototype organic carbon com-
ounds. 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 \(S_N^1\) or \(S_N^2\). The kinetics of
the chromium VI oxidations of \(\Gamma^-\), NCS \(\text{CN}^2\), \(\text{HSO}_3^-\), and \(\text{HSO}_3^2\) 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 \(\text{CrO}_3\text{L}^{n-}\text{L'}^{n-}\) or \(\text{CrO(O}_2\text{)}_2\text{L}^{n-}\text{L'}^{n-}\). A dissociative mechanism
involving the formation of \(\text{CrO}_3\) or \(\text{CrO(O}_2\text{)}_2\) species would probably require
too high an energy to be consistent with the generally high rates observed
for $\text{CrO}_3L^n/F^-$ (except for $L^m = F^-$ and $\text{Cl}^-$) and $\text{CrO}_2(\text{O}_2)\text{L}^m/F^-$.

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 ($C = 46.6$) and MeCN ($C = 36.2$) will favour singly charged anions.

Without necessarily involving solvent or steric effects in the exchange process, the faster substitution reactions in $\text{CrO}_3L^m/F^-$ where $L = \text{Br}^-$, NCO$, NCS$, N$_3^-$ compared to when $L = F^-$ or $\text{Cl}^-$ also suggests electronic factors. The mechanisms mentioned above emphasize the significance of bond breaking, or formation of the leaving group, in the activation process. 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) center would be expected to increase in going from $F^-$ to $\text{H}_2\text{O}$ (through the series $F^-$, $\text{OH}^-$, $\text{NO}_3^-$, $\text{Cl}^-$, NCO$, \text{Br}^-$, NCS$, N_3^-$, $\text{H}_2\text{O}$ where the $\lambda_{\text{max}}$ are at 352, $\approx 350$, 360, 363, 363, 365, 366, 365 and 372 m$\mu$, 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. $\text{CrO}_3N_3^-/F^-$ to $\text{CrO}_2F^-/F^-$ and $\text{O}_3\text{CrO}_2^2-/O^2^-$. In the case of aqueous substitution reactions $\text{O}_3\text{CrOH}^+/L^m$, the available evidence points to $\text{H}_2\text{O}$ (a $\sigma$-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

*OH$^-$, like the $O^2-$ and $F^-$, is considered to be a strong electron donor not only through the $\sigma$-bond but also through HO-$M\pi$-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$_3$L$^{n-}$ are pseudotetrahedral and therefore have relatively high molecular symmetry. It seems probable that the symmetrical $\sigma$- and $\pi$-bonding system would resist rearrangement to five, six or seven coordinate configuration. Consequently, where there is extensive Cr-O $\pi$-bonding, e.g. CrO$_3$F$^-$, this means higher resistance and decreased availability of Cr d-orbitals with which to form a chromium-substrate bond. Decreased $\pi$-bonding would relax the resistance 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$_2$)$_2$L/L' and CrO$_3$L$^{n-}$/F$^-$ where L=F$^-$, OH$^-$, NO$_3^-$, Cl$^-$, NCO$^-$, Br$^-$, NCS$^-$, N$_3^-$ and H$_2$O. These effects had not been demonstrated by studies in aqueous solutions.
CHAPTER FIVE

FURTHER ASPECTS: COMPOUNDS CONTAINING CHROMIUM-NITROGEN MULTIPLE BONDS
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 \( \text{CrO}(O_2)_2\text{py}, \text{CrO}(O_2)_2\text{bipy}, \text{CrO}(O_2)_2\text{phen}, \text{CrO}_2\text{ClN}_3, \text{CrO}_2N_3^- \) and most probably in \( \text{CrO}_3\text{NCO}^- \) and \( \text{CrO}_3\text{NCS}^- \) 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 \( \text{Zr}, \text{Hf}, \text{Mn}, \text{Tc}, \text{Rh}, \text{Pd} \) and \( \text{Pt} \). 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 \( \pi \)-donor capability of the \( N^3- \) ion, a factor which favours heavier elements in higher oxidation states. The greater \( \pi \)-bonding ability of the \( N^3- \) ion was demonstrated by force constant calculations on \( \text{MO}_3\text{N}^3- \) and \( \text{MO}_4\text{N}^3- \) for \( \text{M}=\text{Re} \) VIII 11 and \( \text{Os} \) VIII 175.

The remarkable general chemical property is the stability of the metal-nitrogen bond to both addition and substitution. For instance, when the \( \text{OsO}_3\text{N}^3- \) 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 \([\text{Os}^\text{VI} \cdot \text{NХ}_{5}]^n\) and \([\text{Os}^\text{VI} \cdot \text{N(H}_2\text{O)X}_{4}]^n\) have also been isolated. With stronger reducing agents (e.g. SnCl\(_2\)) the nitrido group is reduced to an amino group.\(^{176}\) The \(\text{M}_2\text{N}\) groups in \([\text{M}_2\text{N} \cdot \text{X}_8\text{(H}_2\text{O)2}]^3\), for \(\text{X} = \text{Cl, Br and I}\); and \(\text{M} = \text{Os and Ru}\) display the same stability.\(^{313}\) Even in the iridium complexes, e.g. \([\text{Ir}_3\text{N(SO}_4)_6 \cdot \text{(H}_2\text{O)3}]^4\), containing the coplanar \(\text{Ir}_3\text{N}\) 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:

K\(\text{ReO}_4\) or complexes of rhenium(V) halides containing tertiary phosphines, e.g. \(\text{ReOCl}_3\cdot\text{(PR}_3)_2\) are reported to form the five- and six- coordinate nitrido complexes \(\text{ReN}_2\cdot\text{(PR}_3)_n\), for \(\text{X} = \text{Cl, Br, I, R} = \text{alkyl or acyl and n} = 2\) or 3, from reactions with a hydrazine salt (\(\text{N}_2\text{H}_4\cdot\text{Cl}_2\) or \(\text{N}_2\text{H}_4\cdot\text{SO}_4\)) and the tertiary phosphine in ethanol.\(^{178}\) Substitution and addition reactions yielding \(\text{ReCl}_4^-, \text{ReCl}_5^{2-}\) \(^{176}\), \(\text{K}_3\text{Re(N(CN))}_5\) \(^{179}\), and \((\text{PET}_2\text{Ph})_3\text{X}_2\text{Re} \equiv \text{N} \rightarrow \text{L}\) (for \(\text{X} = \text{Cl or Br and L} = \text{BBr}_3, \text{BCl}_3, \text{PtCl(PET}_3\text{) etc})\(^{180}\) have also been reported.

Unfortunately, the deprotonation of hydrazine to yield nitrido complexes has so far only worked for \(\text{Re}(\text{V})\); products containing the NR\(^2-\) and N\(^2-\) \(\text{R}^\text{R}\) groups as ligand have been observed in platinum chemistry.\(^{176}\) Chromium(\text{VI}) is readily reduced by hydrazine to chromium(\text{III}).\(^{181}\) For instance \(\text{Cr(\text{VI}) in HClO}_4\) reacts with \(\text{N}_2\text{H}_5^+\) in the presence of a wide variety of ligands (\text{NO}_3^-, \text{Cl}^-, \text{HBrO}_3, \text{HSO}_4^-).
HSeO₄⁻, HN₃, SCN⁻, H₃PO₂, H₃PO₃, H₃PO₄, H₄P₂O₇, H₃AsO₄, H₃CCO₂H, Cl₂CCO₂H and H₂C₂O₄ producing coordinated Cr(III) species.

(b) \textbf{Reactions in Liquid Ammonia:}

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

\[ 2\text{NH}_3 \leftrightharpoons \text{NH}_4^+ + \text{NH}_2^- \quad [1] \]

and the generally slow reduction reaction

\[ \text{M} + \text{NH}_3 \rightarrow \text{MNH}_2^- + \frac{1}{2}\text{H}_2 \quad [2] \]

Furthermore, with ammonia, the analogues of the oxo and hydroxo compounds in hydrolysis reactions are the compounds containing the groups, amide (-NH₂), imide (=NH), and nitride (≡N). The hydrolysis reactions of CrO₃, CrO₃L and Cr₂O₇²⁻ are well established. Chapter 1, Section 1.2 also showed depolymerization-substitution reactions of CrO₃ producing the adducts CrO₃L and CrO₃.2L, 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, MO₃N³⁻ (for M = Mo and W)¹⁸² and ReO₃N²⁻; these products are probably results of the deprotonation of the adducts MO₃·NH₃ or MO₃·NH₂⁻. MO₄·NH₃, for \( M = Os \) and Ru¹⁸³ have been shown to contain the MO₃N⁻ anion. While the ruthenium analog explodes above -20°C, the OsO₃N⁻ 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 CrO₃, KCrO₃Cl or \((\text{NH}_4)_2\text{Cr}_2\text{O}_7\) (with or without KNH₂) at -33°C indicate that some of the Cr(VI) is reduced to Cr(III)¹⁸⁴.
light of the fact that both NH₃ and NH₂ have the ability to act (although slowly) as reducing agents and it has not been possible to prevent or control reduction reactions occurring in the analytical steps (c.f. the reaction of KCrO₃(NCS) with dilute H₂SO₄ 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. For instance, the complex Re³⁺(PPhMe₂)₃Cl₃ reacts very readily with sodium azide to give Re(V)PPhMe₂NCl₂ and N₂, although the intermediate azido complex could not be isolated. Attempts to obtain nitrido complexes by decomposition of Os(₃)₂(PMe₂Ph)₄ and OsCl₂(N₃)(PPhR₂)₃ (for R = Me, Et, n-Pr and n-Bu) have been unsuccessful.

Applying the thermal decomposition technique to azido complexes of metals of the early transition series, e.g. MCl₅N₃ (for Mo and W) resulted in the formation of (MCl₃N)₄(Cl₃VNCI)₂, TiNCI and VON, respectively. The addition compounds, MNCI₂⁻, MNCI₃(PPh₃) and MNCI₃·3py for M = Mo and W, have also been reported. RuO₄ reacts with HX (X = Cl or Br) and azide producing RuNX₄⁻ and RuNX₅²⁻.

Dehnicke and Strahle found, however, that when CrO₂ClN₃ is heated above 150ºC, the whole molecule, not just the azido group, decomposed liberating nitrogen and oxygen. The new complexes, CrO₂(N₃)₂ and CrO₃N₃⁻ [CrO₂(N₃)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.

\[
(NH_4)_2OsCl_6 + 400^\circC \xrightarrow{Cl_2} Os_NCl_5^2^- \quad [3]
\]

\[
K_2RuO_4 + NH_4OH, OH^- \rightarrow Ru_N(OH)_5.nH_2O \quad [4]
\]

Numerous derivatives containing the M\(_2\)N unit have been reported. Unfortunately, however, these reductive decomposition reactions would not work for chromium(VI). The product of a CrO\(_4^{2-}\) - NH\(_4\)OH - OH\(^-\) reaction is (NH\(_4\))\(_2\)CrO\(_4\). Upon heating, (NH\(_4\))\(_2\)Cr\(_2\)O\(_7\) decomposes according to the equation

\[
(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + N_2 + 4H_2O. \quad [5]
\]

(e) Miscellaneous Nitriding Reactions

Reduction reaction between \(K_2Ru(NO)X_5\) (\(X = Cl\) or \(Br\)) complexes and formaldehyde or stannous chloride have been reported \(^{190}\) to yield the polynuclear complex Ru\(_2\)NX\(_8\)(H\(_2\)O)\(_2\)\(^{3-}\). It is also reported that ruthenium trichloride and sulphamide react to produce RuN(OH)\(_5\).nH\(_2\)O\(^{190}\). These methods were discarded on the grounds that Cr(VI) compounds are highly oxidising and these reactants are strongly reducing.

The ability of trifluoroacetanitrile 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\(_3\)CN and WCl\(_6\).CCl\(_3\)CN, containing tungsten(VI). Analogous reactions with molybdenum(VI) and niobium(IV) yield mixed products consisting largely of MoCl\(_5\).2CCl\(_3\)CN and NbCl\(_5\).CCl\(_3\)CN, 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 \( \text{WCl}_6\text{CCl}_3\text{CN} \) and \( \text{WCl}_6\text{2CCl}_3\text{CN} \). 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 \( \text{Cr}_2\text{Cl}_2 \)) or by complexation of the trifluoroacetonitrile with \( \text{Cr}_2\text{Cl}_2 \) and \( \text{CrO}_3 \), 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 occurring. 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.

\[
\text{Na} + \text{NH}_3 (\text{H}_2\text{O}) → \text{NaOH} + \text{NaNH}_2 \quad [6]
\]

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, \( \text{Ag(NH}_3\text{)}_2\text{NO}_3 \) was obtained by dissolving silver nitrate in liquid ammonia - analysis (%) calculated for \( \text{Ag(NH}_3\text{)}_2\text{NO}_3 \): Ag, 50.5; found: Ag, 51.5. The silver (or chloride) was analysed as AgCl. The chloride in Cl\(_3\)CCN reactions was determined as in ref.194.
The nitrogen content was determined by the method of Akimoto et al., 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 investigated the reactions of \( \text{CrO}_3 \), \( \text{KCrO}_3 \text{Cl} \) and \( (\text{NH}_4)_2 \text{Cr}_2\text{O}_7 \) with liquid ammonia (with or without \( \text{KNH}_2 \)) at \(-33^\circ\text{C} \). 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 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, \( \text{KCrO}_3 \text{Cl} \).

Potassium chlorochromate, \( \text{KCrO}_3 \text{Cl} \), reacts with dry liquid ammonia in an enclosed system releasing gas (which has been identified as nitrogen) and changing its colour from orange to light brown-yellow. The experiment was set up such that the \( \text{KCrO}_3 \text{Cl} \), 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 NH₄Cl) is washed down from the KCrO₃Cl-NH₃ reaction. The chromium and chlorine analyses of the product gave

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<tr>
<td>%Cr</td>
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<td>*</td>
<td>25.7</td>
<td>26.2</td>
<td>27.3</td>
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and showed clearly that not all the chloride was removed as NH₄Cl. KCrO₃Cl 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 Cr-Cl band, normally occurring at 435 cm⁻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 NH₄⁺ (3200 and 1400 cm⁻¹) cation and possibly K(NH₄)₂CrO₃N being formed.

Attempts to prepare the tripotassium salt K₃CrO₃N by treating potassium trioxochlorochromate and KCl in liquid ammonia did not work because KCl is insoluble.

This result and the absence of the Cr-Cl band suggested that KCl is possibly formed in the KCrO₃Cl - NH₃ reaction, and is analysed with the brown product. One remedial approach would be to use ammonium salts in the reaction, since NH₄Cl is soluble in liquid ammonia.

* Not analysed.
(ii) With Ammonium Trioxochlorochromate \( \text{NH}_4\text{CrO}_3\text{Cl} \).

In other attempts to prepare the triammonium salt, \((\text{NH}_4)_3\text{CrO}_3\text{N}\), \(\text{NH}_4\text{CrO}_3\text{Cl}\) was used. The brownish-yellow product gave Cl, 0.2 and 0.3%; and Cr, 35.1 and 38.9% respectively. \((\text{NH}_4)_3\text{CrO}_3\text{N}\) requires 31.0% Cr, \((\text{NH}_4)_2\text{HCrO}_3\text{N}\) requires 34.4% Cr, and \((\text{NH}_4)_2\text{H}_2\text{CrO}_3\text{N}\) requires 38.8% Cr.

The infrared spectrum (KBr) is given in Table V.1. There was no Cr-Cl stretching vibration; and because the \(\text{NH}_4\text{CrO}_3\text{Cl}\) used was the following absorptions

<table>
<thead>
<tr>
<th>3100 vs (br)</th>
<th>1600 vw(br)</th>
<th>1395 vs</th>
<th>955 s, sh</th>
<th>940 vs</th>
</tr>
</thead>
<tbody>
<tr>
<td>905s</td>
<td>880 w-m 770 m</td>
<td>438 s</td>
<td>385 vw and 364 vw</td>
<td></td>
</tr>
</tbody>
</table>

it can be established that the 3100, 1395, 955-905 and 438 cm\(^{-1}\) bands are due to N-H, \(\text{NH}_4^+\), 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 \((\text{NH}_2\text{O}, \text{NO}_2, \text{NH}_3\text{O})\) in the complex.

(iii) With Ammonium Dichromate, \((\text{NH}_4)_2\text{Cr}_2\text{O}_7\).

When finely powdered ammonium dichromate was treated with liquid ammonia, it produced light yellow ammonia-insoluble powder: The analysis gave 33.3% Cr and 19.3% N; \((\text{NH}_4)_2\text{Cr}_2\text{O}_7\) requires 41.3% Cr and 11.1% N; \((\text{NH}_4)_2\text{CrO}_4\) requires 34.2% Cr and 18.4% N; \((\text{NH}_4)_2\text{H}_2\text{CrO}_3\text{N}\) requires 38.8% Cr and 20.9% N, and \((\text{NH}_4)_2\text{HCrO}_3\text{N}\) requires 34.4% Cr and 27.8% N. It is also possible that the product is a mixture of \((\text{NH}_4)_2\text{CrO}_4\) and a compound containing a \(\text{CrO}_3\text{NH}_n\) species, because the \(\text{CrO}_2^2-\) ion, which could be formed in the depolymerization of \(\text{Cr}_2\text{O}_7^{2-}\), is very unreactive toward \(\text{NH}_3\).

The infrared data (KBr), given in Table V.1, shows that the product is definitely different from the starting material \((\text{NH}_4)_2\text{Cr}_2\text{O}_7\), which has the following absorptions; 3100vs, 1380vs, 900vs, 720vs, 550vs, 550m, sh and 350m
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 3400 cm\(^{-1}\) 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\(_2\)SO\(_4\) giving an orange solution and in NH\(_4\)OH giving a yellow solution, suggesting it is probably K\(_2\)CrO\(_4\).

(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. \((\text{NH}_4\)\)_\text{3}CrO\(_3\)N requires 31.0% Cr and \((\text{NH}_4\)\)\(_2\)HCrO\(_3\)N (\(\cong\) CrO\(_3\).3NH\(_3\)) requires 34.4% Cr. In the Sisler and Jirik\(^{196}\) CrO\(_3\)-NH\(_3\) reactions, an average of \(\cong\)26.0% of the chromium content was reportedly reduced to Cr(III). And when NH\(_4\)NO\(_3\) 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

\[
\text{CrO}_3 + 4\text{NH}_3 \rightarrow (\text{NH}_4)_3\text{CrO}_3 \text{N} \quad \text{Ag}_3\text{CrO}_3 \text{N}
\]

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\(_3\))\(_2\)NO\(_3\) 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\(_3\)CrO\(_3\)N requires 73.7% Ag and 11.8% Cr, Ag\(_2\)(NH\(_4\))CrO\(_3\)N requires 62.0% Ag and 14.9% Cr, and Ag(NH\(_4\))\(_2\)CrO\(_3\)N 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 1400 cm\(^{-1}\) 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

<table>
<thead>
<tr>
<th></th>
<th>KCrO$_3$Cl-NH$_3$ (KBr)</th>
<th>NH$_4$CrO$_3$Cl-NH$_3$ (KBr)</th>
<th>((\text{NH}_4\text{)}_2\text{Cr}_2\text{O}_7\text{-NH}_3) (KBr)</th>
<th>CrO$_3$-NH$_3$ (KBr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3200 vs, br</td>
<td></td>
<td></td>
<td>3160 vs</td>
<td>3300 s (vbr)</td>
</tr>
<tr>
<td>3000 vs (br)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1610 s (br)</td>
<td>1600 m (br)</td>
<td>1610 m</td>
<td></td>
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<tr>
<td>1400 vs</td>
<td>1400 s</td>
<td>1400 s</td>
<td></td>
<td>1360 vs</td>
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<tr>
<td>1290 m-s</td>
<td></td>
<td></td>
<td></td>
<td>1270 w</td>
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<td>1260 s</td>
<td>1260 m-s (br)</td>
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<tr>
<td>1230</td>
<td></td>
<td>1105 w-m</td>
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<td>1080 m (br)</td>
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<tr>
<td>1000 m (shoulder)</td>
<td>995 m</td>
<td>1000 w (shoulder)</td>
<td>1010 m-s</td>
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<tr>
<td>980 s</td>
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<tr>
<td>-950-700 vs (br)</td>
<td>950-700 vs (br)</td>
<td>900 s</td>
<td>870 vs (br)</td>
<td>800 m (br)</td>
</tr>
<tr>
<td>540 m (vbr)</td>
<td>530 w (br)</td>
<td>770 vs (br)</td>
<td>530 w (br)</td>
<td>380 v vw</td>
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<tr>
<td>380 m</td>
<td>380 w (br)</td>
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<tr>
<td>340 v w</td>
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<tr>
<td></td>
<td>KCrO₃Cl-KNH₂-NH₃ (Nujol)</td>
<td>KCrO₃Cl-NaNH₂-NH₃ (KBr)</td>
<td>CrO₃-KNH₂-NH₃ (Nujol)</td>
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<tr>
<td>3200s (br)</td>
<td></td>
<td></td>
<td>3250s (br)</td>
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<tr>
<td>1580w (br)</td>
<td></td>
<td>1600m (b)</td>
<td>1600m</td>
<td></td>
</tr>
<tr>
<td>1300w</td>
<td></td>
<td>1430s (br)</td>
<td>1290m</td>
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<td>1240m</td>
<td></td>
<td></td>
<td>1240m</td>
<td></td>
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<tr>
<td>1110w</td>
<td></td>
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<tr>
<td>1000-700vs (br)</td>
<td></td>
<td>1010m (shoulder)</td>
<td>1000-700vs (br)</td>
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<tr>
<td>890 (max); 780 (max)</td>
<td></td>
<td>960-800s (br)</td>
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<tr>
<td>570w</td>
<td></td>
<td>530w (br)</td>
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<tr>
<td>435w</td>
<td></td>
<td>400 (shoulder)</td>
<td></td>
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</tr>
<tr>
<td>390m</td>
<td></td>
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<tr>
<td>380m</td>
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<td>380m</td>
<td>380s</td>
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<td>350w</td>
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<td></td>
<td></td>
<td></td>
<td>340w</td>
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</tbody>
</table>
CrO₃ - NH₃ 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 CrO₃N³⁻, CrO₃NH²⁻ and/or CrO₃NH₂⁻ species.

(b) Reactions of KNH₂ (or NaNH₂) with KCrO₃Cl and CrO₃ 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 KNH₂. The elemental analyses gave 18.9, 17.8 and 17.7% Cr; 2.0% N and 11.4 and 10.1% Cl, K₃CrO₃N requires 22.5% Cr. Apparently not all the chloride 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 coworkers¹⁹⁷ investigated the same reaction and observed that the amount of Cr(III) which was formed varied with the mole ratio of KNH₂ 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 CrO₃ was attempted. The product was found to have 29.9% Cr, 2.2% N; K₃CrO₃N requires 22.5% Cr and 6.0% N; K₂HCrO₃N requires 27.0% Cr and 7.2% N; KH₂CrO₃N requires 33.8% Cr and 9.1% N. K₃Cr₂O₆ (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 CrO₃-KNH₂-NH₃ system; the presence of KNH₂ had little effect on the reactions of K₂CrO₇ and K₂Cr₄ in liquid ammonia.
(e) **Reactions of Trichloroacetonitrile**

In the present investigation, the reactions of chromium(VI) compounds, \( \text{CrO}_3 \), \( \text{CrO}_2\text{Cl}_2 \), and \( \text{KCrO}_3\text{Cl} \) with neat trichloroacetonitrile were studied in an all-glass vacuum line under air and moisture-free conditions.

(i) **With \( \text{CrO}_3 \)**

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; \( \text{CrO}_3\text{NCCl}_3 \) 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, \( \text{KCrO}_3\text{Cl} \) and \( \text{Ph}_4\text{AsCrO}_3\text{Cl} \)**

When trichloroacetonitrile was left in contact with \( \text{Ph}_4\text{AsCrO}_3\text{Cl} \) for 3 days, there was no color change or apparent reaction. \( \text{Ph}_4\text{AsCrO}_3\text{Cl} \) 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 \( \text{KCrO}_3\text{Cl} \) (3.335 gm) and trichloroacetonitrile (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. \( \text{KCrO}_3\text{Cl.NCCl}_3 \) 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\(\equiv\)N stretch. The only bands not present in the spectrum of the free ligand occurred at 1880\(\text{w}\), 1850\(\text{m}\), 1380\(\text{m}\), 910\(\text{vs}\)(\(\nu\)(CrO\(_3\))), 435\(\text{s}\)(\(\nu\)(CrCl)) and 350\(\text{m}\)(\(\delta\)(O-Cr-O)) cm\(^{-1}\).

(iii) With Chromyl Chloride

Leaving chromyl chloride in the dark in contact with trichloroacetoni- nitrile for 24 hours, produced no observable reaction. But when the two reactants were mixed in dichloromethane and kept at -10\(^\circ\)C for 24 hours, white crystals formed and the red solution turned green. The white solid melts at 144\(^\circ\)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\(_3\)CCOH\(_2\)) requires C, 14.8; H, 1.2 and N, 8.6). This reaction suggest that although Cl\(_3\)CCN may be strongly oxidizing in the presence of CrO\(_2\)Cl\(_2\) and CH\(_2\)Cl\(_2\) the Cl\(_3\)CCN is oxidized and the CrO\(_2\)Cl\(_2\) reduced. Dichloromethane was used in the tungsten(V and VI) chloride - Cl\(_3\)CCN reactions but no hydrogen abstraction was reported.

(iv) With Cesium Pentachloro-oxo-chromium(V), Cs\(_2\)CrOCl\(_5\)

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\(_2\)CrOCl\(_5\) 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\(_2\)CrOCl\(_5\). But when the Cs\(_2\)CrOCl\(_5\) was left in contact with trichloroacetonitrile at 65\(^\circ\)C for two days, there was no observable reaction; Analysis (%): Cl, 34.0 Cs\(_2\)CrOCl\(_5\) requires 34.8\% Cl.
(d) Thermal Decomposition of Ph₄AsCrO₃N₃

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(O₃)₂N₃⁻ and CrO₃N₃⁻.

Heating Ph₄AsCrO₃N₃ resulted in spontaneous decomposition to a green solid.

When Ph₄AsCrO₃N₃ was heated under vacuum, for about 2 hours at 210°C, it melted and turned dark brown. The dark brown product gave the analysis(%) C, 51.2; H, 3.6 and N, 3.0. Ph₄AsCrO₃N₃ 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 ν_{asy}(N₃) and ν_{sym}(N₃) bands which occur at 2073 and 1280 cm⁻¹ in Ph₄AsCrO₃N₃ 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 495 cm⁻¹ in Ph₄AsCrO₃N₃ 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 decomposition of the azido group to a nitride might have occurred. But for a nitrogen cleavage (equation [8]) to occur, this preparative method would require more cation to balance off the charges.

\[
\text{Ph}_4\text{AsCrO}_3\text{N}_3 \xrightarrow{\text{heat}} \left[\text{Ph}_4\text{AsCrO}_3\text{N}_3\right]^2+ + \text{N}_2 \quad [8]
\]

Other reactions might also have occurred. Attempts to prepare KCrO₃N₃ from KCrO₃Cl and NaN₃ (solutions in MeCN) for alternative reactions involving heating KCrO₃N₃ and K, failed.
Analysis of the Vibrational Spectra

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

The vibrational spectra of many nitrido complexes have been studied. The $M \equiv N$ stretching mode in $(\text{Me}_4N)_2\text{MoNCl}_5$, $(\text{Me}_4N)_2\text{WNCI}_5$, $^{189}\text{MoNCl}_3\cdot4$ and $^{130}\text{WNCI}_3$ are assigned to the bands at 1023, 1035, 1045 and 1068 cm$^{-1}$, respectively. Generally, the $M \equiv N$ stretching mode falls in the comparatively narrow range of 1020-1150 cm$^{-1}$.

From the infrared spectra of amine complexes, the bands in the regions 3040-3400, 1570-1710, 1235-1400 and 590-890 cm$^{-1}$ can be assigned to the stretching and deformation modes $\nu(N-H)$, $\delta_{\text{asy}}(\text{NH}_3)$, $\delta_{\text{sym}}(\text{NH}_3)$ and $\text{NH}_3$ rocking (i.e. $\delta(M-N-H)$, $\rho(\text{NH}_3)$ respectively. Vibrational modes of coordinated nitro groups have also been observed in these same regions ($\nu_{\text{asy}}(\text{NO}_2)$, (1363-1497) cm$^{-1}$); $\nu_{\text{sym}}(\text{NO}_2)$, 1300-1373 cm$^{-1}$ $\delta(\text{NO}_2)$, (798-849 cm$^{-1}$) and $\text{NO}_2$ wag (585-650)$^{198}$. The infrared spectrum of $\text{Cr(NH}_3)_5\text{ONOCl}_2$ containing complexed nitrito group$^{198}$ $\text{Cr-ONO}$, has bands at 1460 ($\nu_{\text{asy}}(\text{NO}_2)$), 1048 ($\nu_{\text{sym}}(\text{NO}_2)$) and 839 ($\delta(\text{NO}_2)$). It is therefore not possible to make unequivical assignments of the bands observed at 1250 and 1025 (or 1010) cm$^{-1}$ to either $\nu_{\text{Cr-N}}$ $\delta(\text{NH}_2)^{199}$, $\nu_{\text{Cr=N}}$ or $\nu_{\text{sym}}(\text{ONO})$ vibrations. Drago and Sisler assigned the bands at 1005 and 982 cm$^{-1}$ to the skeletal vibrations of the chromium(III) chromate polymers produced in the $\text{CrO}_3$-$\text{NH}_3$ 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, K₂CrO₄ to react with NH₃. It is therefore less likely that chromium(VI) would form the MO₂N⁻ anion formed by Os VIII, Re VII, Mo VI and W VI. It may be possible to prepare chromium nitrido complexes by reacting CrOF₄ with either kNH₂, NH₃ or Cl₃CCN.
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