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5. CHROMIUM

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CONTENTS

INTRODUCTION

The review this year deals mainly with literature on the inorganic and coordination chemistry of chromium which appeared during 1982, but it includes some work published late in 1981. The organometallic chemistry of chromium has not been included.

5.1 CHROMIUM(VI)

The species in the vapours above heated Rb_2CrO_4, Cs_2CrO_4 and In_2CrO_4 have been studied by IR matrix isolation spectroscopy [1]. Together with

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their S, Mo and W analogues, they all show two metal-oxygen stretches in their IR spectra in the ranges 843-853 and 889-894.5cm^{-1}. These two peaks have been interpreted in previous papers as the B_2 and E stretching modes of the tetrahedral anion, with D_{2d} symmetry, arising from the splitting of the $\nu_2(F_2)$ antisymmetric stretch of the free CrO_4^{2-} group. Normal coordinate calculations suggest that the B_2 vibration always occurs at a higher frequency than the E mode and this assignment is supported by ^{18}O isotopic substitution experiments. In addition, the spectral pattern obtained by isotopic substitution is consistent with that expected for bidentate bonding of the CrO_4^{2-} group [1]. The resonance Raman effect of $Ag_2[CrO_4]$ has been investigated and compared with that of the alkali metal chromates [2]. Unlike the latter salts, $Ag_2[CrO_4]$ does not show any overtone progressions involving $\nu_1(a_1)$, although the intensity of the a_1 mode is greatly enhanced. Other differences between alkali metal and silver chromates were discussed in terms of the small but significant distortions from T_d symmetry for the anion in solid $Ag_2[CrO_4]$ and the effect of Ag...O interactions [2].

It is well known that in strong acid solution, dichromate reacts with hydrogen peroxide to yield the blue peroxide $CrO(O_2)_2.2H_2O$

$$2HCrO_4^- + 2H_2O_2 + H^+ \longrightarrow CrO(O_2)_2.2H_2O$$

At pH 4-7 a violet diperoxychromium(VI) species is formed

$$HCrO_4^- + 2H_2O_2 \longrightarrow [CrO(O_2)_2OH]^-$$

and in alkali solution the red brown tetraperoxychromate(V), $[Cr(O_2)_4]^{3-}$, is generated. The kinetics of the formation of the violet Cr(VI) have been studied spectrophotometrically at 540nm using stopped flow techniques [3]. The rate law is of the form

$$-d[HCrO_4^-]/dt = k[HCrO_4^-][H^+][H_2O_2]$$

which is the same as that proposed some years ago [4] for the formation of the blue peroxide. It appears that only the final step in a sequence of reactions is different in the two pH ranges

$$HCrO_4^- + H^+ \rightleftharpoons H_2CrO_4 \qquad \text{fast equilibrium}$$

$$H_2CrO_4 + H_2O_2 \longrightarrow H_2CrO_3(O_2) + H_2O \qquad \text{slow}$$

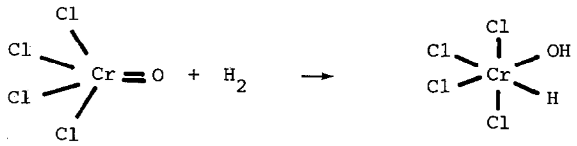
$$H_2CrO_3(O_2) + H_2O_2 \longrightarrow \underset{\text{violet}}{[Cr(O)(O_2)_2OH]^-} + H_2O + H^+ \quad \text{fast}$$

$$\text{or } H_2CrO_3(O_2) + H_2O_2 \longrightarrow \underset{\text{blue}}{CrO(O_2)_2H_2O} + H_2O \quad \text{fast}$$

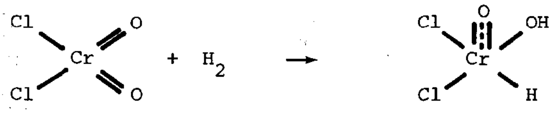
The molecular structure of CrO_2Cl_2 in the gas phase at room temperature has been reinvestigated by electron diffraction techniques [5]. This study confirmed that the O-Cr-O angle is smaller than the Cl-Cr-Cl angle which is against the predictions of the Valence Shell Electron Pair Repulsion theory. The structural parameters for CrO_2Cl_2 are

Cr = O	1.581(2) Å	O-Cr-O	108.5(4)°
Cr - Cl	2.126(2) Å	Cl-Cr-Cl	113.3(3)°
O....O	2.564(8) Å	O-Cr-Cl	108.7(1)°
O....Cl	3.026(4) Å		
Cl...Cl	3.546(7) Å		

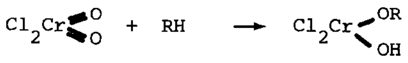
In an interesting theoretical study based on *ab initio* calculations the differences in the behavior of CrO_2Cl_2 and $CrOCl_4$ in the oxidation of alkanes, alcohols and alkenes was investigated [6]. It appears that the second oxygen in CrO_2Cl_2 (the so called 'spectator atom') has a dramatic effect on the reaction even though it is not directly involved. In CrO_2Cl_2 the double bonds to oxygen are just that - simple double bonds, but in $CrOCl_4$ the Cr - O linkage has triple bond character because there are two chromium *d* orbitals to interact with two 2*p* orbitals on the oxygen. Thus when $CrOCl_4$ reacts with H_2 the resulting hydrido-hydroxo complex is unstable (ΔG = +71 Kcalmole^{-1})



but with CrO_2Cl_2 the resultant species is much more stable (ΔG = -7Kcalmole^{-1})

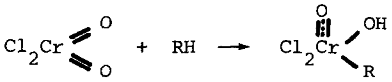


because the spectator atom drives the reaction by forming a partial triple bond. It is often assumed that addition of RH to CrO_2Cl_2 gives



$$Cl_2CrO_2 + RH \longrightarrow Cl_2Cr(OR)(OH)$$

but these workers [6] show by calculation that only one Cr - O bond reacts and the other is used to stabilize the intermediate



Similar intermediates are proposed in the oxidation of alcohols.

The chromic acid esters $ROCrO_3^-$ (R = Me, Et, Pr) catalyze the photoreduction of $[Fe(bipy)_3]^{3+}$ and $[Fe(phen)_3]^{3+}$ [7]. The quantum yields for the reductions are directly proportional to the amount of light absorbed by the chromic acid ester at metal concentrations $>10^{-4}$M for irradiation wavelengths >350nm. There is a linear correlation between quantum yield and the square root of the concentration of metal complex. A radical mechanism was suggested for the reduction process.

A study has been made [8] of the solvent extraction of Cr(VI), Mo(VI) and W(VI) from HCl solution using di-*n*-octylsulphoxide (DOSO) and diphenylsulphoxide (DPSO). Chromium is extracted as $HCrO_3Cl.2DOSO$ or $HCrO_3Cl.2DPSO$ while Mo(VI) and W(VI) are extracted as $HMO_2Cl_3.2DOSO$ or $HMO_2Cl_3.2DPSO$. Quantitative separation of chromium from molybdenum and tungsten was achieved in 3.5M HCl solution using 0.02M DPSO in CCl_4.

5.2 CHROMIUM(V)

At 0°C the reaction between CrO_3 and ClF yields CrO_2F_2, but at higher temperatures the amount of CrO_2F_2 formed decreases until at 100°C a brick red solid is isolated instead [9]. Composition of the product was found to vary between $CrOF_3.0.1ClF$ and $CrOF_3.0.2ClF$. Heating the solid does not give $CrOF_3$, but it was found that reaction with F_2 at 120°C does result in the formation of purple $CrOF_3$. The solid is only mildly hygroscopic and in water it gives a yellowish green solution due to disproportionation

$$3Cr(V) \longrightarrow 2Cr(VI) + Cr(III)$$

The magnetic moment of $CrOF_3$ was found to be 1.82BM and the Cr=O stretch occurs at $1000cm^{-1}$ and it was suggested that $CrOF_3$ has a polymeric structure involving fluorine bridging. On heating to 500°C it gives CrF_3 and oxygen while reaction with F_2 at 150°C gives CrF_5 and oxygen. It reacts with KF in anhydrous HF to give $K[CrOF_4]$ which has its Cr=O stretch at $1020cm^{-1}$.

Excitation at 313nm of $[CrN_3(sal_2en)H_2O]$ gives the chromium(V) nitrido complex $[CrN(sal_2en)H_2O]$ and nitrogen [10]. The complex was characterized analytically and by EPR and IR studies.

Two communications have appeared [11,12] which present EPR evidence that relatively stable chromium(V) species are rapidly produced when chromate or dichromate react with ribonucleotides, but not deoxyribonucleotides. It seems likely that the *cis* diol grouping of the ribonucleotide is necessary for the formation of the chromium(V) species. It is possible that this intermediate is involved in the known carcinogenicity of chromium.

5.3 CHROMIUM(IV)

Heating $Cr(NO_3)_3.9H_2O$ is said to give CrO_2 as a black intractable solid [13]. It is amorphous to X-rays and the characterization was based on the weight losses in the reaction

$$2Cr(NO_3)_3.9H_2O \longrightarrow 2CrO_2 + 18H_2O + 6NO_2 + O_2$$

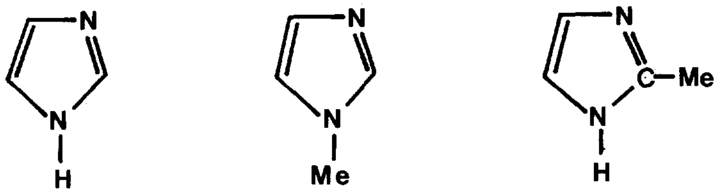
There have been two reports on the oxidation of porphyrinato complexes of chromium(III) to give oxoporphyrinatochromium(V) species [14,15]. The complexes Cr(OH)TTP and Cr(OH)OEP (TTP^{2-} = *meso*-tetra-*p*-tolylporphyrinato and OEP^{2-} = octaethylporphyrinato dianions) were oxidized using hypochlorite to give CrO(TTP) and CrO(OEP). These chromium(IV) complexes oxidize alcohols, perhaps in a manner similar to the action of peroxidases [14]. In the second report the oxidation of CrCl(TPP) with iodosylbenzene or hypochlorite to give CrO(TPP) was described [15] (TPP^{2-} = 5,10,15,20-tetraphenylporphyrinato dianion). Several similar complexes of substituted phenylporphyrins (including TTP) were also reported [15]. These red complexes are diamagnetic and CrO(TPP) shows a Cr=O stretch at $1025cm^{-1}$ which is shifted to $981cm^{-1}$ on ^{18}O substitution [15]. The crystal structure of CrO(TTP) has been determined by X-ray methods; the stereochemistry of the chromium atom is square pyramidal with the apical position occupied by oxygen (Cr=O 1.572(6)Å) with the average Cr-N distance being 2.032(7)Å. The chromium atom is 0.469Å above the plane of the four pyrrole nitrogens towards the oxygen [15]. CrO(TPP) in CH_2Cl_2 reacts with PPh_3 to give PPh_3O and a chromium(II) complex which then reacts with the solvent to generate CrCl(TPP). The same reaction in benzene gives a complex identified as $[Cr(TPP)]_2O$ [15].

5.4 CHROMIUM(III)

This largest section of the review is arranged according to the identities of the donor atoms in the order Group IV, Group V etc.

5.4.1 Complexes of simple ligands

The preparation of chromium(III) derivatives of imidazole and some substituted imidazoles *(1)* have been reported [16].



imidazole (imidH)   N-methylimidazole (imidMe)   2-Me imidazole (Me-imidH)

(1)

These were $[Cr(imidH)_6]Cl$, $[Cr(imidH)_5X]X$ (X = Cl,Br), *cis* and *trans*-$[Cr(imidH)_4Cl_2]Cl$, *trans*-$[Cr(imidMe)_4Cl_2]Cl$ and *trans*-$[Cr(Me\text{-}imidH)_4Cl_2]Cl$. The band in the visible spectrum associated with the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition for the *trans*-$[CrL_4Cl_2]^+$ complexes is split suggesting the species have D_{4h} symmetry. The visible spectrum of *cis*-$[Cr(imidH)_4Cl_2]Cl$ suggests that isomerization to *trans* occurs in solution. The EPR spectra of the complexes have been observed in frozen glasses. $[Cr(imidH)_6]^{3+}$ gives a singlet as expected, but the signals due to the *trans*-$[CrL_4Cl_2]^+$ cations are multiplets due to zero field splittings. The EPR spectrum of *cis*-$[Cr(imidH)_4Cl_2]^+$ confirms that isomerization occurs in solution.

In order to further elucidate the mechanisms of photoaquation of chromium(III) complexes a study was made of the effect on the rate of aquation of varying viscosity in water/glycerol mixtures [17]. The complexes studied were $[Cr(CN)_6]^{3-}$, $[Cr(NCS)_6]^{3-}$, $[Cr(NH_3)_6]^{3+}$ and $[Cr(NH_3)_5NCS]^{2+}$ (for this complex two reaction products were observed depending on whether NH_3or NCS^- was the departing ligand). In reactions involving the replacement of NH_3 by H_2O in $[Cr(NH_3)_6]^{3+}$ and $[Cr(NH_3)_5NCS]^{2+}$ the quantum yield Φ decreases significantly with increasing viscosity η. Although the viscosity dependence of Φ is generally interpreted as evidence for a solvent cage effect, the exact correlation between this effect and η is controversial. However these authors favour the following mechanism where S represents a solvent (water) molecule which competes with L for the sixth coordination site on chromium within the solvent cage. The photoaquation reactions involving substitution of CN^- or NCS^- do not exhibit strong cage recombination effects.

$$\begin{tikzcd}
\mathrm{CrL_6} \arrow[rr, shift left, "h\nu"] & & {}^{*}\mathrm{CrL_6} \arrow[ll, shift left, "k_5"] \arrow[d, "k_6"] \\
\mathrm{CrL_5(OH_2)} + \mathrm{L} & & \left[\mathrm{CrL_5}\,{}^{\mathrm{S}}_{\mathrm{L}}\right]_{\mathrm{cage}} \arrow[ll, "k_8"] \arrow[llu, "k_7"']
\end{tikzcd}$$

Ligand field irradiation of *trans*-$[Cr(NH_3)_4(dmf)Cl]^{2+}$ in acidic solution gives simultaneous loss of NH_3, dmf and Cl^-, but the major pathway is by loss of dmf. The aquation reaction is accompanied by isomerization as shown [18].

$$\begin{tikzcd}
 & cis\text{-}[Cr(NH_3)_4(H_2O)Cl]^{2+} + dmf \quad (93\%) \\
trans\text{-}[Cr(NH_3)_4(dmf)Cl]^{2+} + H_2O \arrow[ur] \arrow[r] \arrow[dr] & cis\text{-}[Cr(NH_3)_4(dmf)H_2O]^{3+} + Cl^- \quad (5\%) \\
 & [Cr(NH_3)_3(dmf)(H_2O)Cl]^{2+} + NH_3 \quad (2\%)
\end{tikzcd}$$

This scheme may be contrasted with the aquation in the ground state of *trans*-$[Cr(NH_3)_4(dmf)Cl]^{2+}$ which proceeds with retention of stereochemistry

$$\begin{tikzcd}
 & trans\text{-}[Cr(NH_3)_4(H_2O)Cl]^{2+} + dmf \quad (83\%) \\
trans\text{-}[Cr(NH_3)_4(dmf)Cl]^{2+} + H_2O \arrow[ur] \arrow[dr] & \\
 & trans\text{-}[Cr(NH_3)_4(dmf)H_2O]^{3+} + Cl^- \quad (17\%)
\end{tikzcd}$$

This system provides another example of the intrinsically different substitution chemistries of ground state and excited states of chromium(III).

Mercury(II) catalyses the aquation of chloro complexes by the reaction

$$[M\text{-}Cl]^{n+} + Hg^{2+} \overset{K}{\rightleftharpoons} [M\text{-}Cl\text{-}Hg]^{(n+2)+} \xrightarrow{k_1} M^{(n+1)+} + [HgCl]^{+}$$

The aquation rates of the $[Cr(NH_3)_5Cl]^{2+}$ and $[Cr(NH_3)_4(H_2O)Cl]^{2+}$ cations in water and in methanol-, ethanol- and acetonitrile-water mixtures show first order kinetics in the presence of excess Hg^{2+}. The products were identified as $[Cr(NH_3)_5H_2O]^{3+}$ and *cis*-$[Cr(NH_3)_4(H_2O)_2]^{3+}$ by their visible spectra. There is only a slight dependence of rate of aquation on solvent composition [19].

The reaction of $[Cr(NH_3)_5Cl]Cl$ with selenic acid led to the isolation of the first chromium complexes containing coordinated selanate groups by the reactions

$$\begin{tikzcd}[Cr(NH_3)_5Cl]Cl_2 + H_2SeO_4 \arrow[r, "70^{o}C"] & {[Cr(NH_3)_5SeO_4]HSeO_4.2H_2O} \arrow[dl, "X^-"] \\ {[Cr(NH_3)_5SeO_4]X \quad (X^- = ClO_4^-,\ NO_3^-,\ Cl^-,\ Br^-)} & \end{tikzcd}$$

All the complexes were 1:1 electrolytes and their IR spectra are consistent with monodentate (C_{3v} symmetry) coordination of the selenato group. The visible spectra of the compounds are typical of acidopentaamine chromium(III) complexes [20]. In the same paper a complex containing the dihydrogenarsenate ligand was also reported

$$[Cr(NH_3)_5H_2O](ClO_4)_3 \ + \ H_3AsO_4 \ \longrightarrow \ [Cr(NH_3)_5(H_2AsO_4)]^{2+}$$

The arsenate ligand is very labile, readily exchanging with water, as do similar salts containing IO_3^-, $HSeO_3^-$ etc due to lability of the non-metal-oxygen bond [20].

The kinetics of the oxidation by periodate of the hyperphosphite ion in $[Cr(NH_3)_5(H_2PO_2)]^{2+}$ have been investigated and compared with those for the free ligand. It was found that the coordinated ligand is distinctly more reactive. The mechanism involves a pre-equilibrium

$$[Cr(NH_3)_5(H_2PO_2)]^{2+} \ \rightleftharpoons \ [Cr(NH_3)_5(HPO_2)]^{+} \ + \ H^{+}$$

followed by transfer of an oxygen atom to phosphorus without rupture of the Cr-O bond to give a phosphato complex [21].

The study of the visible spectrum of $[Cr(NCS)_6]^{3-}$ in various solvents (H_2O, MeOH, EtOH, dmso, dmf, 7.7M NH_4CNS) has led to the conclusion that the previously accepted value for the crystal field splitting parameter for the thiocyanate ion on chromium(III) is incorrect. The new suggested value is 216.5(0.4)KJmole^{-1} (corresponding to λ_{max} = 554nm) rather than 212.7KJmole^{-1} (λ_{max} = 564nm) which had been derived from spectra in aqueous solutions for which it is now known that rapid aquation occurs even in the dark [22].

A study has been made of the low temperature magnetic ordering in $[Cr(NH_3)_5H_2O][Cr(CN)_6]$ (compound A) and $[Cr(urea)_6][Cr(CN)_6]$ (compound B) [23]. Compound A obeys the Curie-Weiss law over the temperature range 1-4 K, but at lower temperatures the susceptibility rises very sharply to a maximum at 0.380 K and then falls sharply at still lower temperatures. This behavior is typical of a powdered ferromagnetic material in which demagnetization effects become important. The susceptibility behavior of compound B is somewhat different in detail. The Curie-Weiss law is obeyed above 1 K, there is a sharp maximum in the susceptibility at 0.30 K and a broad maximum of unknown origin at 0.15 K. It was proved that superexchange between the cation and anion causes these phenomena since the compounds $[Cr(NH_3)_5H_2O][Co(CN)_6]$ and $[Co(NH_3)_5H_2O][Cr(CN)_6]$, both of which were shown by X-ray powder diffraction methods to be isostructural with A and B, do not show the effects. Thus the cooperative effects are not due to the cation or anion alone and this work demonstrates that superexchange can be enhanced when both the cation and anion are paramagnetic even when the ligands are such poor candidates for superexchange as in this case.

A theoretical study of the electronic structure of $[Cr(CN)_6]^{3-}$ has been made using discrete variational X_α calculations [24]. The calculated *d-d* excitation energies are in good agreement with the values obtained from the spectrum of the compound.

Crystal structure data has been reported for two difluorotetraammine complexes of chromium(III) [25]. *Trans*-$[Cr(NH_3)_4F_2]I.H_2O$ is monoclinic with Cr-F = 1.894(3)Å and Cr-N = 2.085(5) (av). *Cis*-$[Cr(NH_3)_4F_2]ClO_4$ is tetragonal; The Cr-F distance is 1.887(6)Å but there are two distinctly different Cr-N distances of 2.206(5) and 2.051(7)Å. The shorter Cr-N bonds are *trans* to the fluorines. The structure of *trans*-bis(methylnicotinate)aquatrichlorochromium(III) has been determined [26]. The compound is important as it may serve as a model for the proposed complex between nicotinic acid and chromium in glucose tolerance factor. The methylnicotinate ligands are bonded through nitrogen (av. Cr-N = 2.094(9)Å) and the angle N-Cr-N is 177.4(4)°. The average Cr-Cl and Cr-O bond lengths (2.317(4) and 2.011(9)Å respectively) are typical values.

The kinetics of the aquation of $[Cr(H_2O)_5(O_2CCCl_3)]^{2+}$(containing monodentate trichloroacetate) have been investigated over the temperature range 35-55°C at 1.00M ionic strength with $[H^+]$ = 0.01-1.00M. Possible parallel and competitive pathways for the reaction

$$[Cr(H_2O)_5(O_2CCCl_3)]^{2+} + H_2O + H^+ \longrightarrow [Cr(H_2O)_6]^{3+} + CCl_3COOH$$

have been considered [27]. The reaction follows the rate law

$$-d\ln[Cr]/dt = (a[H^+]^{-1} + b + c[H^+])/(1 + d[H^+])$$

where [Cr] is the stoichiometric concentration of the complex. Two types of mechanism are consistent with this rate law. The first involves aquation of species such as $[Cr(H_2O)_4(OH)(O_2CCCl_3)]^+$, $[Cr(H_2O)_5(O_2CCCl_3)]^{2+}$ and

$[Cr(H_2O)_5(HO_2CCCl_3)]^{3+}$ but analysis of this mechanism leads to the conclusion that the acid dissociation constant of Cl_3COOH increases only very slightly on coordination to chromium(III) in contrast to the generally observed result that coordination increases acidity by several orders of magnitude. An alternative mechanism, involving addition of water across the carbonyl group of the coordinated trichloroacetate, gives the same rate law and is the preferred mechanism [27].

The rates of exchange between solvent water and both $[Cr(H_2O)_5NH_3]^+$ and *mer*-$[Cr(H_2O)_3(NH_3)_3]^{3+}$ in acid 1M perchloric solution have been investigated [28]. The kinetics for both systems are characterized by two first order rate constants which at 25°C are

$[Cr(H_2O)_5NH_3]^+$ $(2.8 \pm 0.4) \times 10^{-5}\ s^{-1}$ and $(0.449 \pm 0.014) \times 10^{-5} s^{-1}$

mer-$[Cr(H_2O)_3(NH_3)_3]^+$ $(7.6 \pm 1.0) \times 10^{-5}\ s^{-1}$ and $(1.23 \pm 0.05) \times 10^{-5}\ s^{-1}$

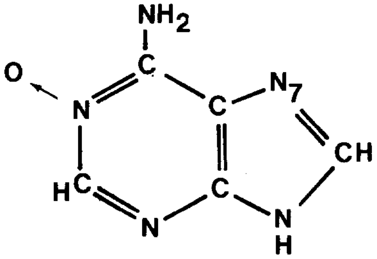
The two rates correspond to the two types of water ligand in the cations and the larger rate constant is associated with H_2O *trans* to NH_3. Both types of water in each complex exchange with retention of stereochemistry as shown by ^{18}O labelling experiments. Common features in the reaction patterns were rationalized on the basis of an associative interchange mechanism. Similar results were obtained under the same conditions for the exchange of solvent water and *cis*-$[Cr(H_2O)_4(NH_3)_2]^{3+}$ [29]. The two first order rate constants at 25°C are $(4.94 \pm 0.37) \times 10^{-5}\ s^{-1}$ and $(1.024 \pm 0.087) \times 10^{-5}\ s^{-1}$ and once again the exchange is stereoselective.

Complexes of adenosine triphosphate (ATP) with chromium(III) are thermally unstable [30]. Decomposition of $[Cr(H_2O)_4ATP]$ (containing bidentate ATP) at slightly elevated temperatures and alkali pH's gives predominantly free ATP with small amounts of the monophosphate (AMP) and diphosphate (ADP), but the amount of free ATP is pH dependent. In contrast, $[Cr(H_2O)_4ATP]$ (containing tridentate ATP), gives mainly ADP and only small amounts of ATP on hydrolysis. No AMP was detected in this reaction.

The chlorine K X-ray absorption spectrum of *trans*-$[Cr(H_2O)_4Cl_2]Cl.2H_2O$ gives more fine structure than previously seen in this type of spectrum [31]. Two peaks were observed which are separated by 1.8ev, which is close to the crystal field splitting for both $[Cr(H_2O)_6]^{3+}$ and $[CrCl_6]^{3-}$, so the peaks were interpreted as transitions from Cl to empty metal *d* orbitals.

IR spectroscopy has been used to investigate the modes of coordination of substituted ureas in complexes of chromium(III) [32]. The compounds studied were $[Cr(eu)_6](NO_3)_3$, $[Cr(eu)_5H_2O](NO_3)_3$, $[Cr(eu)_4Cl_2]Cl$, $[Cr(dmeu)_2(H_2O)_2Cl_2]Cl$ and $[Cr(etu)_4(H_2O)_2](NO_3)_3$ (eu = ethylene urea, dmeu = dimethylethylene urea, etu = ethylene thiourea). All of the urea complexes were thought to be *O*-bonded on the basis that ν_{CO} drops on coordination. In contrast, the thiourea complex is thought to be *N*-bonded as ν_{CS} rises on coordination of the ligand.

Chromium perchlorate dissolved in EtOH in the presence of triethylorthoformate reacts with adenine N(1) oxide (LH) *(2)* to give $[Cr(LH)_2(OClO_3)_2(EtOH)_2]ClO_4$.



(2)

Monodentate perchlorate was identified by IR and LH was thought to coordinate *via* N_7 [33].

$Cs_2CrP_2O_7$ is monoclinic and has the $KAlP_2O_7$ type structure containing CrO_6 octahedra and PO_4 tetrahedra derived from non-linear P_2O_7 groups (P-O-P = 125.9°) [34]. Solid solutions in the composition range $CaLa_{1-x}Y_xCrO_4$ ($0 \leq x \leq 1$) have been prepared. Depending on the yttrium content they are ideal or distorted K_2NiF_4 type structures [35]. Mostly they have two dimensional magnetic properties due to the layer structure, but for $x = 1$ there is some three dimensional magnetic behavior between chromium centres due to the covalent yttrium-oxygen bonds. Monoclinic $MCrSe_2O$ (M = La, Ce) was prepared by heating mixtures of $(MO)_2Se$ and Cr_2Se_3 at 100°C. The structure of the cerium compound consists of layers of $CeSe_6O_3$ polyhedra between layers of $CrSe_4O_2$ and $CrSe_6$in which the octahedral groups alternate regularly [36].

It has been found [37] that reduction of CrO_3 with hydrazine in the presence of excess MF in 40% HF gives M_3CrF_6 in high yield (M = NH_4, Li, Na, K, Rb). The crystal structure of $KPbCr_2F_9$has been determined [38]. Octahedral CrF_6 units share *cis* corners to form a chain while a third fluorine links to a second chain to give parallel double chains of $(Cr_2F_9)_n^{3n-}$ through the structure. Chromium-fluorine bond distances range from 1.872(7) to 1.927(5)Å. A series of compounds of the type $K_xMn^{II}Cr^{III}_{(1-x)}F_3$ have been prepared [39]. They are all based on Perovskite-like structures and their magnetic properties show an ordered ionic structure.

5.4.2 Complexes containing an organic group

Although the complexes described in this section are organometallic compounds and strictly are not to be included in the review, they have nevertheless been included because their properties are much more akin to ordinary chromium(III) complexes than to the lower oxidation state organometallic compounds of chromium.

There have been a number of papers concerned with the preparation and reactions of complexes of the general formula $[Cr(H_2O)_5R]^{2+}$ where R is an organic group and the complexes contain a direct chromium-carbon bond. Previous methods of preparation which involve reaction of chromium(II) with H_2O_2 in the presence of the appropriate alcohol are not efficient for the simpler alkyls, especially methyl. A new preparative route involving formation of Me radicals from dmso has been described [40]. The reaction is thought to proceed through the following steps

$$[Cr(H_2O)_6]^{2+} + H_2O_2 \longrightarrow [Cr(H_2O)_6]^{3+} + HO\bullet + OH^-$$

$$HO\bullet + (CH_3)_2SO \longrightarrow (CH_3)_2S(O\bullet)OH$$

$$(CH_3)_2S(O\bullet)OH \longrightarrow CH_3\bullet + CH_3SO_2H$$

$$CH_3\bullet + [Cr(H_2O)_6]^{3+} \longrightarrow [Cr(H_2O)_5CH_3]^{2+} + H_2O$$

The yield of the methyl complex (determined spectrophotometrically) was 80% compared with about 15% from previously reported methods. The reaction is probably of general applicability since it is known that corresponding radicals are formed from other sulphoxides.

The complex β-hydroxyethylpentaaquochromium(III) was prepared by the interaction of chromium(II) and the $\bullet CH_2CH_2OH$ radical which was generated by three separate photochemical methods [41]. The most fully investigated system utilized photochemical reaction of chromium(II) solutions with nitrous oxide and ethylene

$$[Cr(H_2O)_6]^{2+} \xrightarrow{h\nu} [Cr(H_2O)_6]^{3+} + e^-(aq)$$

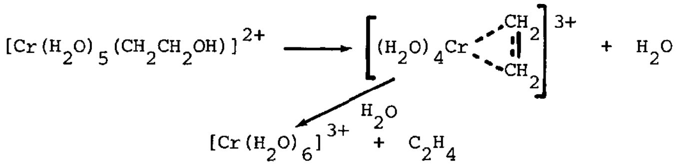
$$e^-(aq) + N_2O \xrightarrow{H^+} HO\bullet + N_2 + H_2O$$

$$HO\bullet + C_2H_4 \longrightarrow \bullet CH_2CH_2OH$$

Other sources of the radical included photolysis of cobalt complexes. Each of these methods depend upon the rapid reaction

$$[Cr(H_2O)_6]^{2+} + \bullet CH_2CH_2OH \longrightarrow [Cr(H_2O)_5(CH_2CH_2OH)]^{2+} + H_2O$$

to form the complex. $[Cr(H_2O)_5(CH_2CH_2OH)]^{2+}$ is extremely labile in acid solution to give $[Cr(H_2O)_6]^{3+}$ and it was detected only as a transient species by its absorption maximum at 380nm which decayed rapidly with first order kinetics [41]. Since the complex decays much more rapidly than the analogous alkyl derivatives it was suggested that decomposition may occur *via* a π-bonded ethylene complex



Chromium-carbon bonds are cleaved by both heterolytic (acidolysis) and homolytic mechanisms and an attempt has been made to determine the rates of these individual pathways [42]. The experimental method used was to add suitable reagents to suppress one mechanism so that the other rate could be measured independently. The rates of acidolysis and homolysis were measured for twelve $[Cr(H_2O)_5R]^{2+}$ complexes. The homolytic rate constants varied between $3.7 \times 10^{-5}S^{-1}$ for R = CH_2OH to $3 \times 10^2S^{-1}$ for R = $C(CH_3)(^tC_4H_9)OH$ at 25°C. Steric effects associated with groups on the α-carbon were a major contribution to this large range of rates, although it was thought not to be the only factor.

Pulse radiolysis has been used to study rates of homolysis of $[Cr(H_2O)_5(C\{CH_3\}_2OH)]^{2+}$, $[Cr(H_2O)_5(C\{CH_3\}_2CO_2H)]^{2+}$ and $[Cr(H_2O)_5(C\{CH_3\}_2CN)]^{2+}$. These workers also found that while steric effects are important, they are not the only factor effecting homolysis rates and they suggested that the resonance stabilization energy of the free radical is also important [43]. It was shown that aliphatic free radicals react with organochromium(III) species at very high rates.

$$[Cr(H_2O)_5R]^{2+} + \bullet R' \xrightarrow{H_2O} [Cr(H_2O)_6]^{2+} + R\text{-}R'$$

Kinetics and equilibrium data for the reaction between CNS^- with four $[Cr(H_2O)_5R]^{2+}$ complexes ($R = CH_2OH$, CH_2OCH_3, CH_2CN and $CH(CH_3)_2$) have been investigated [44]. All four complexes react readily with CNS^- and the reaction is thought to be

$$[Cr(H_2O)_5R]^{2+} + CNS^- \longrightarrow \textit{trans}\text{-}[Cr(H_2O)_4(NCS)R]^+ + H_2O$$

with the thiocyante *N*-bonded to chromium. In the experiments thiocyanate was present in large excess and the data conformed to a first order rate law. In two cases ($R = CH_2OCH_3$ and $CH(CH_3)_2$) the observed rate constant was given by

$$k_{obsd} = (A[CNS^-] + B)/(1 + C[CNS^-])$$

while for the other two complexes

$$k_{obsd} = A[CNS^-] + B$$

These general rate laws are consistent with either a limiting S_N1 (or D) mechanism or an ion pair (I) mechanism, but the former was thought to be the more likely [44].

The interaction between $[Cr(H_2O)_5(CH\{CH_3\}_2)]^{2+}$ with oxygen has been investigated [45]. The idealized stoichiometry is

$$[Cr(H_2O)_5(CH\{CH_3\}_2)]^{2+} + O_2 + H^+ \longrightarrow [Cr(H_2O)_6]^{3+} + (CH_3)_2CO$$

and the rate law is given by

$$-d\ln[[Cr(H_2O)_5(CH\{CH_3\}_2)]^{2+}]/dt = k[[Cr(H_2O)_5(CH\{CH_3\}_2)]^{2+}]^{3/2}$$

independent of $[O_2]$ and $[H^+]$. The value of k at 25°C and 1M ionic strength is $0.46 \pm 0.6M^{-1/2}s^{-1}$. The kinetics are consistent with a chain mechanism initiated by unimolecular homolysis of $[Cr(H_2O)_5(CH\{CH_3\}_2)]^{2+}$ with $(CH_3)_2CH\bullet$ and $CH_3CHOO\bullet$ as the chain carrying intermediates.

The complexes $[Cr(edta)(CR'R''OH)]^{2+}$ ($R',R'' = H$ or CH_3), containing pentadentate $edta^{4-}$, were prepared [46] by reaction of $[Cr(H_2O)_6]^{2+}$ with $edtaH_4$ in the presence of H_2O_2 and the appropriate alcohol according to the equation

$$[Cr(edta)H_2O]^{2-} + H_2O_2 + H^+ \longrightarrow [Cr(edta)H_2O]^- + \bullet OH + H_2O$$

$$HCR'R''OH + \bullet OH \longrightarrow \bullet CR'R''OH + H_2O$$

$$[Cr(edta)H_2O]^{2-} + \bullet CR'R''OH \longrightarrow [Cr(edta)(CR'R''OH)]^{2-} + H_2O$$

The complexes were characterized spectrophotometrically by a shoulder at 270-295nm ($\varepsilon \simeq 2000M^{-1}cm^{-1}$) and a band at about 390nm ($\varepsilon \simeq 300M^{-1}cm^{-1}$) similar to the spectra of other organochromium(III) derivatives. The complexes were readily aquated to give $[Cr(edta)H_2O]^-$ without any intermediate products being observed. The aquation follows first order kinetics with the rate law

$$-d\ln[[Cr(edta)(CR'R''OH)]^{2-}]/dt = k_{obsd} = k_o + k_1[H^+]$$

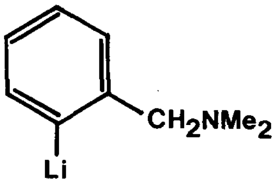
except for $[Cr(edta)(CH\{CH_3\}OH)]^{2-}$ for which

$$k_{obsd} = (k_o + k_1[H^+])/(1 + Q[H^+])$$

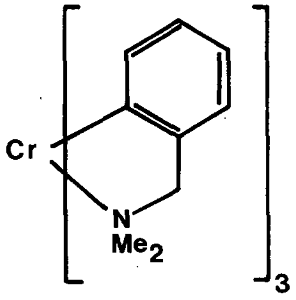
The rates for the acid independent path of aquation (k_o values) are quite similar to those of the $[Cr(H_2O)_5R]^{2+}$ compounds, so therefore replacement of four water molecules by $edta^{4-}$ shows little effect on the rate of cleavage of the chromium-carbon bond. However, the rates for the acid dependent pathway are 10^4 - 10^6 times greater than for $[Cr(H_2O)_5R]^{2+}$.

5.4.3 Complexes of bidentate ligands

One of the products of reaction of $Cr_2(O_2CCH_3)_4$with Li(C_6H_4-*o*-CH_2NMe) (LiLL') *(3a)* is the complex $Cr(LL')_3$ *(3b)* [47].



(3a)



(3b)

The complex crystallizes in a hexagonal unit cell with a *fac* arrangement of ligands with Cr-C = 2.075Å, Cr-N = 2.356(4)Å, N-Cr-N' = 96.8(1)^{o} and C-Cr-C = 93.9(2)^{o}. The complex is stable, contrary to an earlier report, but the mechanism of its formation is not known.

There have been a number of studies on the thermal decomposition and isomerization of chromium(III) complexes containing diamine ligands. The deamination of the unitary, binary and ternary tris(diamine) complexes $[Cr(aa)_3]X_3.nH_2O$, $[Cr(aa)_2(bb)]X_3.nH_2O$ and $[Cr(aa)(bb)(cc)]X_3.nH_2O$ (aa, bb and cc = en, *d,l*-1,2-propanediamine (pn) and 1,3-propanediamine (tn); X = Cl, CNS$^-$; n = 0-3) was investigated in the solid phase [48]. All the compounds lose one mole of a diamine to give $[CrX_2(diamine)_2]$ but the isomer formed depends upon the identity of X. All chloro compounds give *cis*-$[CrCl_2(diamine)_2]$ although these readily give the *trans* isomer on further heating. On the other hand, the thiocyanate complexes all gave *trans*-$[Cr(NCS)_2(diamine)_2]$ directly. In the binary and ternary tris(diamine) complexes the diamine which escapes is the one of lower boiling point. All the products were identified by IR, UV-visible and TLC studies [48].

In a second paper [49] the isomerization of $[CrX_2(aa\ or\ bb)_2]X.nH_2O$ and $[CrX_2(aa)(bb)]X.nH_2O$ in the solid state was investigated further (aa, bb = en, pn, tn, 2,4-pentanediamine (ptn) and *d,l*-1,2-cyclohexanediamine (chxn), n = 0-2). The direction of the isomerization depends on the identity of the diamines. Initial *trans* → *cis* isomerizations occur on heating for complexes containing diamines which form five-membered rings on coordination (en,pn,chxn) although further heating at higher temperatures may cause further changes [49], but the complexes of those diamines which give six-membered rings on coordination (tn,ptn) gave *cis* → *trans* isomerizations on heating. All complexes containing two different diamines show *trans* → *cis* isomerizations even when one of the diamines is tn or ptn. The activation energies of these changes are in the range 150-190 KJmole^{-1} which suggests a bond rupture mechanism. Support for this mechanism is found in another very similar paper by the same authors [50] in which they studied the isomerization of *trans*-$[CrX_2(aa)_2]X.nH_2O$ (aa = bn,chxn) and *cis*-$[CrCl_2(aa)_2]Cl.2H_2O$ (aa = ptn). They showed that dehydration preceeds isomerization which then proceeds through a common *mer* complex containing one bidentate and one monodentate diamine,which was isolated in one case, as shown in the following scheme. Russian workers have reported [51] similar results on the isomerization of *trans*-$[Cr(en)_2Br_2]Br.2H_2O$ although

$$\begin{tikzcd}
\textit{cis}\text{ or }\textit{trans}\text{-}[CrX_2(aa)_2]X \arrow[r] & \textit{mer}\text{-}[CrX_3(aa)_2] \arrow[dl] \\
\textit{cis}\text{ or }\textit{trans}\text{-}[CrX_2(aa)_2]X &
\end{tikzcd}$$

in this case isomerization also occurs on dehydration

$$\textit{trans}\text{-}[Cr(en)_2Br_2]Br.2H_2O \longrightarrow \textit{cis}\text{-}[Cr(en)_2Br_2]Br \longrightarrow \textit{trans}\text{-}[Cr(en)_2Br_2]Br$$

The second isomerization is similar to that described above [48] for the corresponding chloro complex. However, heating *cis*-$[Cr(en)_2Br_2]Br.2H_2O$ was reported to give quite different results [51].

$$\begin{tikzcd}
\textit{cis}\text{-}[Cr(en)_2Br_2]Br.2H_2O\text{ or }\textit{cis}\text{-}[Cr(en)_2Br(H_2O)]Br_2.H_2O \arrow[d] \\
\textit{cis}\text{-}[Cr(en)_2Br(H_2O)]Br_2 \arrow[d, "90\text{-}130^\circ"] \\
\textit{cis}[Br(en)_2Cr\text{-}OH\text{-}Cr(en)_2Br]Br_3
\end{tikzcd}$$

The reactions which occur on heating *cis* and *trans*-$[Cr(en)_2L_2]Br_3$ (L = NH_3, $MeNH_2$) have also been investigated [52] and the results are summarized in the scheme

$$\begin{tikzcd}
\textit{trans}\text{-}[Cr(en)_2(NH_3)_2]Br_3 \arrow[r, "150^\circ"] & \textit{trans}\text{-}[Cr(en)_2(NH_3)Br]Br_2 \arrow[d] \\
\textit{cis}\text{-}[Cr(en)_2(NH_3)_2]Br_3 \arrow[r] & \textit{trans}\text{-}[Cr(en)_2Br_2]Br \\
\textit{trans}\text{-}[Cr(en)_2(MeNH_2)_2]Br_3 \arrow[ru] & \\
\textit{cis}\text{-}[Cr(en)_2(MeNH_2)_2]Br_3 \arrow[r, "200^\circ"] & \textit{cis}\text{-}[Cr(en)_2(MeNH_2)Br]Br_2 \arrow[uu, "230^\circ"']
\end{tikzcd}$$

Thus, although there appears to be wide range of stereochemistries and stoichiometries possible for intermediates, all workers seem to agree that *trans*-$[Cr(en)_2X_2]X$ (X = Cl,Br) is the ultimate product formed at higher temperatures on heating almost any halo ethylenediamine complex of chromium.

Somewhat different, although in one sense complementary, results were obtained [53] by heating *trans*-$[Cr(aa)_2(H_2O)F][M(CN)_4]$ complexes (aa =en, tn; M = Ni,Pd,Pt). In all cases a binuclear complex $[(aa)_2FCrNCM(CN)_3]$ involving a bridging cyano group was formed, but for en the stereochemistry about chromium is *cis* and for tn it is *trans*, thus reinforcing the trends shown in the previous examples. In all cases the bridging group was detected by IR and the stereochemistry about chromium was determined both from visible and IR (δ_{NH_2}) spectroscopic studies. Thermal decomposition of *trans*-$[Cr(tn)_2(H_2O)F]S_2O_6$ proceeds first of all *via* an anation step to give *cis*-$[Cr(tn)_2F(S_2O_6)]$. A second step preceeding total decomposition involves the change

$$cis\text{-}[Cr(tn)_2F(S_2O_6)] \longrightarrow cis\text{-}[Cr(tn)_2F(SO_4)] + SO_2$$

but this product is always contaminated by further decomposition products [54].

Although the rates of aquation of *cis*-$[Cr(en)_2(H_2O)X]^{2+}$ (X = Cl,Br) were determined some years ago there is no previous report of the activation energies of these processes. Studies have now been carried out [55] at 30, 35 and 40°C at 0.1 and 1.0M acid concentration. There is no apparent variation with acid concentration of the rate of aquation of the chloro complex but the bromo compound does show a slight effect with a smaller rate constant at the higher concentration. Activation parameters at 1M acid are

$\Delta H^{\#}$ (KJmole^{-1})	$\Delta S^{\#}$ (JK^{-1}mole^{-1})	
92.1 ± 1.8	-25.7 ± 0.6	(chloro)
75.2 ± 0.5	-65.5 ± 1.5	(bromo)

which are similar to those for many other aquation reactions of chromium(III) under similar conditions. The photocalorimetric method has been used to determine the enthalpies of aquation at low acid concentrations at 25°C of a number of chromium(III) complexes [56]. The method is most useful for those complexes which show clean photochemical reactions in good quantum yield.

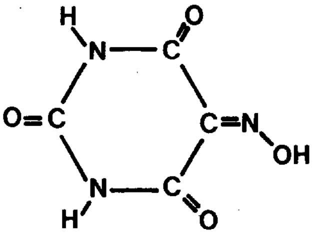
Convenient preparations of racemic $[Cr(aa)_2(ox)]ClO_4$ salts (aa = en, tn) have been described [57]. The complexes were resolved by racemic modification using the monohydrogendibenzoyl + tartrate ion. The less soluble diastereoisomerides were assigned the Δ absolute configuration on the basis of CD spectra.

It has been found [58] that laser irradiation of aqueous solutions of $[Cr(ox)_2phen]^-$ or $[Cr(ox)(phen)_2]^+$ in their ligand field transition regions in the presence of *d* or *l* cinchonine hydrochloride leads to a rapid shift in the chiral equilibrium between their two enantiomers which is opposite in direction to that induced by the usual Pfeiffer effect in the dark. The non-mixed chelates $[Cr(ox)_3]^{3-}$ and $[Cr(phen)_3]^{3+}$ do not show the effect.

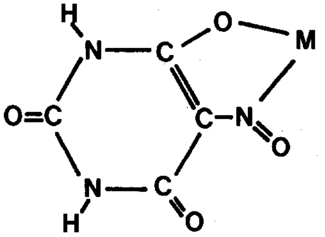
A comprehensive review of fluoro-diamine complexes of chromium(III) has appeared [59]. It includes surveys of synthetic methods and applications of various physical techniques to these systems. It has been found that there are changes in the visible spectra of some fluoro complexes of chromium(III) as the solvent is varied [60]. The complexes studied were *trans*-$[Cr(en)_2F_2]^+$, *trans*-$[Cr(en)_2(NCS)F]^+$ and $[Cr(NH_3)_5F]^{2+}$. The largest effects occurred on changing the solvent from water to dmf with smaller effects between water and MeOH and EtOH. It was shown that the phenomenon is characteristic of fluoro complexes only and it is thought to be due to strong hydrogen bonding between F and the solvent molecules.

The crystal structure of *trans*$[Cr(en)_2F_2]ClO_4$ has been determined [61]. The triclinic unit cell contains two crystallographically independent cations of very similar dimensions. The Cr-N bond lengths fall in the range 2.05-2.10Å with the average Cr-F distance being 1.88(1)Å. The diamine is in the *gauche* form. *Cis*-$[Cr(tn)_2(NCS)_2][Sb_2(tart)_2]_2$ is orthorhombic [62]. The Cr-N (NCS) bonds are 1.996(7) and 2.003(6)Å long and the ligands are close to linear. The Cr-N (tn) bond lengths fall in the range 2.086(7) - 2.097(7)Å and the diamines are in the chair form. The absolute configuration is Λ.

Violuric acid H_3V *(4a)* readily loses only one proton (on oxygen) to give the strong ligand H_2V^- which chelates to metals *via* N and O *(4b)*.



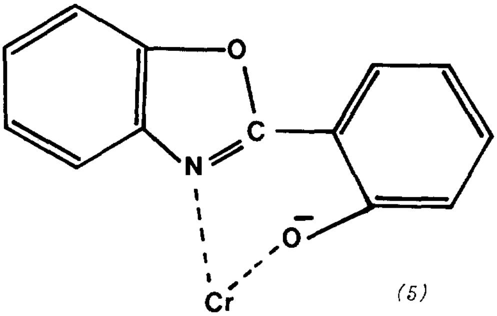
(4a)



(4b)

The complexes $[Cr(H_2V)_3]5H_2O$ and $Na[Cr(H_2V)_2(OH)_2]4H_2O$ were isolated and solution measurements (Job's method of continuous variations) confirmed the stability of 1:3 and 1:2 complexes in solution. On coordination, one of the imine protons is labilized and three successive proton losses to give $[Cr(H_2V)_2(HV)]^-$, $[Cr(H_2V)(HV)_2]^{2-}$ and $[Cr(HV)_3]^{3-}$ can be observed by titration methods [63].

A series of complexes of deprotonated 2-(*o*-hydroxyphenyl)benzooxazole (L) *(5)* have been prepared [64].



(5)

The complexes were CrL_3, $[Cr(bipy)(tu)_2L]Cl_2$, $[Cr(phen)(tu)_2L]Cl_2$ and $[Cr(phen)L_2]$ and all were prepared from $Cr(tu)_3Cl_3$.

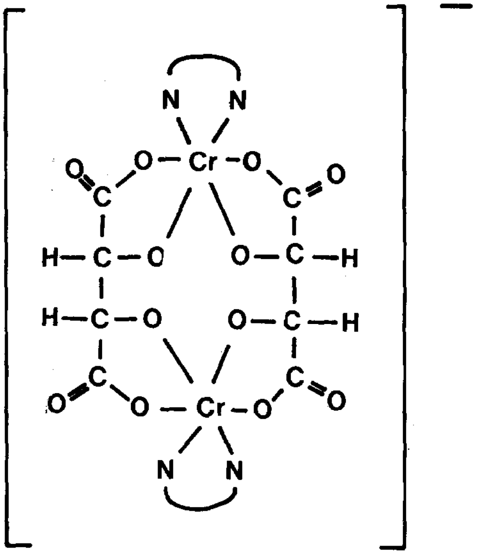
Stability constants have been determined for binary complexes of the types CrAH, CrA, CrA_2H_2, CrA_2H, CrA_2 and CrA_3 in the chromium(III) imindiacetic acid (H_2ida), -*L(+)*-aspartic acid (asp), -*L(+)*-glutamic acid (glu) and -*L(+)*-cysteine (cys) systems, and also for ternary systems containing two of the above ligands [65]. The results suggest that H_2ida and asp act as tridentate ligands in the binary complexes CrA and CrA_2 and in the ternary complexes CrAB. However, glu appears to be tridentate in CrA, but only bidentate in CrA_2 and CrAB. The potentially tridentate ligand cys acts only as a bidentate towards chromium(III).

Although chromium (V) disproportionates in aqueous solution, it has been found that $[bipyH_2][CrOCl_5]$ is reduced in MeCN to give chromium(III) as $CrCl_3(bipy)NCMe$ [66]. It is paramagnetic as expected and although the IR spectrum suggests N-bonded MeCN the stereochemistry (*fac* or *mer*) could not be determined. The nitrile group can be readily replaced by other ligands to give $CrCl_3(bipy)L$ (L = py, Ph_3PO etc). In contrast, nitriles other than MeCN gave a product formulated as $[CrCl_3(bipy)]_n$.

Complexes CrL_3 have been prepared for L = three substituted phenyldithiophosphinates [67]. EPR spectra were observed and the optical spectra indicate that these complexes are lower in the spectrochemical series than most dithio ligands. Tris(substituted malonate) complexes of chromium(III) have been reported [68] using Etmal, Me_2mal and Bzmal as ligands. In addition, *cis* and *trans*-$[Cr(mal)_2(H_2O)_2]^-$ were prepared. In a subsequent paper [69] the aquation of these complexes was investigated. Between 25-40°C the aquation of $[Cr(Memal)_3]^{3-}$ and $[Cr(Me_2mal)_3]^{3-}$ follows a two term rate law, one of which is acid dependent. All the other substituted malonate complexes aquate according to a one term rate law which is first order wrt acid concentration, similar to the malonate complex itself.

The ^1H NMR spectra of chromium(III) complexes such as malonates are broad due to the paramagnetic centre, but it has been found that the corresponding ^2D resonances are much sharper and allow resolution of the lines [70]. Thus, the ^2D NMR spectra of labelled malonate complexes allows determination of the stereochemistry of compounds such as $[Cr(mal\text{-}d_2)_2(py)_2]^-$ as easily as ^1H NMR does for cobalt(III) complexes. There is much obvious potential for the future use of this technique.

The crystal and molecular structure of sodium hydrogen bis(μ-*ms*-tartrato)-bis(2,2'-bipyridyl)dichromate(III) heptahydrate has been determined [71]. The structure *(6)* contains the first example of a *ms*-tartrate bridged complex. The crystal contains a racemic mixture of β-ΛΛ-(RS,RS) and β-ΔΔ-(RS,RS) isomers. The Cr-Cr distance is 4.799(2)Å, Cr-N distances fall in the range 2.053(5) - 2.069(5)Å with the longer bonds being associated with the carboxyl oxygen atoms. There is a close approach (2.418(6)Å) between the hydroxyl oxygen atoms of two different tartrate groups and it is thought the hydrogen atom forms a very strong symmetrical hydrogen bond between them.

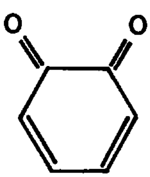


(6)

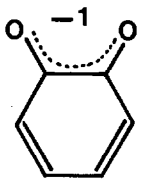
The anion $[Cr(HP(O)O_2)_3]^{3-}$ was prepared by dissolving freshly precipitated $Cr(OH)_3$ in a boiling solution of phosphorous acid followed by evaporation to give the free acid [72]. The IR spectrum showed P-H and P=O vibrations suggesting that the ligand is coordinated through two O^- groups. The visible spectrum was similar to those of other chromium(III) complexes, but the magnetic moment was very high (4.93BM).

A series of complexes $Cr(LL)_3$ (LLH = pyridine 2,3-dicarboxylic acid, 4-hydroxypyridine 2,6-dicarboxylic acid and pyridine 2,4,6-tricarboxylic acid) have been reported [73].

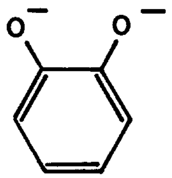
The ligands *(7a-c)* form a series of chromium complexes with overall charge +2 to -3, but because these are 'non-innocent' ligands, defining the oxidation state of the metal is difficult. A study has been made [74] of some of the chromium complexes using a molecular orbital theory treatment and the results of the calculations compared with the known EPR parameters. The previously reported reaction between tetrachloro-*o*-semiquinone and $Cr(CO)_6$ could not be repeated under the stated conditions, but the reaction was found to proceed rapidly under UV irradiation. The product is $Cr(O_2C_6Cl_4)_3$ and the reaction provides a good example of photochemical oxidative substitution [75].



(7a)
o-quinone



(7b)
o-benzosemiquinone

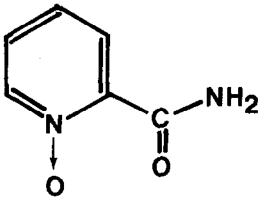


(7c)
catecholate

Greatly improved separation of optical isomers of metal complexes can be achieved on montmorillonite clay pretreated with Δ-$[Ni(phen)_3]^{2+}$ and this has been illustrated by the resolution of $Cr(acac)_3$ [76]. The effect arises because the bound nickel complex makes the clay stereoselective towards adsorption of a complex of another kind. A 2.5cm column gave a molecular rotation of 3000 for $Cr(acac)_3$ compared with about 630 for a large column of *D(+)* lactose.

The energies of the intermolecular association between the molecules of a chiral solvent and those of a racemic compound are generally unequal for the two enantiomers of the racemate. In the case of an optically labile racemate, the different energies of the intermolecular association result in a time dependent antiracemisation in which the concentration ratio of the enantiomeric solutes differ from unity. This process allows energy discrimination between the enantiomers and has been applied to $[Cr(ox)_3]^{3-}$ salts in chiral α-hydroxy ester solutions [77].

Complexes of 2-pyridinecarboxamine N-oxide (pco) *(8)* with several



(8)

transition metals, including chromium(III), have been reported [78]. IR evidence suggests that the complex $[Cr(pco)_3]Cl_3.2H_2O$ contains the ligand chelated through both oxygen atoms and this is supported by the visible spectrum which is similar to other chromium(III) compounds with the CrO_6 chromophore.

In order to test the angular overlap (AO) model of ligand field transitions of chromium(III) for bidentate oxygen ligands a number of new fluorooxalato and fluoromalonato complexes were prepared [79]. These were of the types *cis* and *trans*-$[CrF_2(O\text{-}O)_2]^{3-}$ (O-O = ox or mal) which were separated by ion exchange techniques, *cis*-$[CrF_2(ox)(en)]^-$ and *trans*-$[CrF_2(mal)(en)]^-$ which were the only isomers observed in these systems. The *d-d* spectra were recorded and discussed in terms of the AO model.

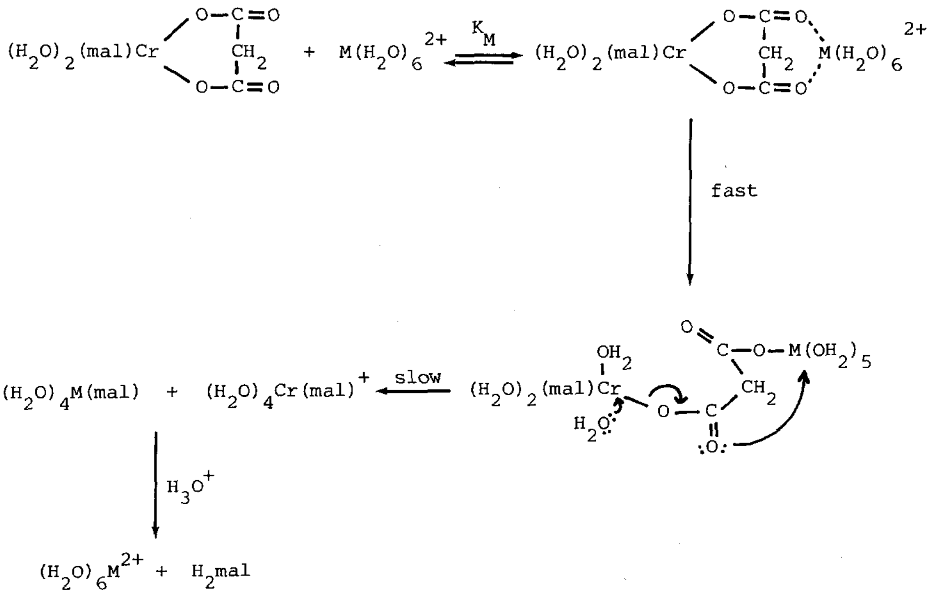
The kinetics and mechanism of the reaction

$$cis\text{-}[Cr(H_2O)_2(mal)_2]^- \longrightarrow [Cr(H_2O)_4(mal)]^+$$

has been studied [80] in perchloric acid in the presence of Cu(II), Ni(II), Co(III) and Zn(II) which catalyse the reaction to various extents, so that the overall rate expression takes the form

$$k_{obs} = k_H[H^+] + k_{cat}[M^{2+}]$$

The metals exert a substantial catalytic effect and the values of k_{cat} follow the sequence Cu(II)>Ni(II)>Co(III)>Zn(II) which follows the values for the formation constants of monomalonato complexes. The proposed mechanism is



The kinetics of the reaction

$$[Cr(H_2O)_4(acac)]^{2+} \longrightarrow [Cr(H_2O)_6]^{3+}$$

in various concentrations (1-5M) of perchloric acid have been studied [81]. It is found that there is an increase in the heat of aquation in the sequence $[Cr(H_2O)_4acac] > [Cr(H_2O)_2(acac)_2] > Cr(acac)_3$.

The interaction of $Cr(CO)_6$ with $Hg(S_2CNEt_2)_2$ ($Hgdtc_2$) gives the chromium(II) dialkyldithiocarbamate as the initial product which was identified by its visible and EPR spectra [82]. However, the product isolated after working up the mixture in air was $Crdtc_3$.

A series of complexes of the type *cis*-$[Cr(L\text{-}L)X_4]^-$ have been prepared by the reaction

$$CrCl_3(thf)_3 + n\text{-}Pr_4NCl + L\text{-}L \longrightarrow [Pr_4N][Cr(L\text{-}L)Cl_4]$$

Where L-L = dppe, dppee, diars [83]. The complexes were all 1:1 electrolytes in solution, all showed four Cr-Cl stretches in their IR spectra and all had magnetic moments of about 3.88BM. It was confirmed that the complex $Cr(diars)_{1.5}Cl_3$ is actually *trans*-$[Cr(diars)_2Cl_2][Cr(diars)Cl_4]$.

5.4.4 Complexes of polydentate ligands

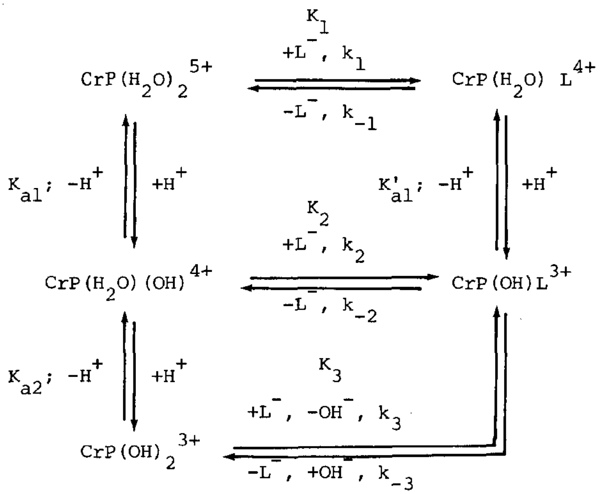
The compound $[Cr(terpy)_2](ClO_4)_3$ crystallizes in the monoclinic space group Cc with four molecules in the unit cell [84]. The complex adopts the expected *mer* configuration about chromium although there is significant distortion from the idealized geometry. The mean Cr-N distances are 2.06(1)Å (terminal N) and 1.97(1)Å (central N). The three pyridyl rings of each ligand are not coplanar with twists of up to 7.8° being observed. One factor causing these distortions is thought to be the strong attraction between the chromium(III) atom and the perchlorate anions, some of which are wedged inside the interligand pockets.

Reaction of thiocyanate ion with *cis*-$[Cr(2,3,2\text{-tet})Cl_2]^+$ was expected to give *cis*-$[Cr(2,3,2\text{-tet})(NCS)_2]^+$, but the product had a visible spectrum and emission properties which suggested it was the *trans* isomer. An X-ray structural determination has confirmed that the product is *trans*-(R,S)-$[Cr(2,3,2\text{-tet})(NCS)_2]CNS$ [85]. The four nitrogens of the tetraamine ligand are coplanar (mean Cr-N = 2.071(2)Å) and the chromium atom is just out of the plane of the nitrogen atoms. The three ligand rings are in the *gauche*, chair and *gauche* configurations. The two *N*-bonded thiocyanate groups are almost collinear and complete a slightly distorted octahedral arrangement about chromium.

A kinetic and equilibrium study of the reaction of CN^- and CNS^- with *meso*-tetra(4-N-methylporphine)diaquochromium(III), $[CrP(H_2O)_2]^{5+}$ has been made at various temperatures in the pH range 1-13 [86]. The results are described by the scheme given below. The presence of the porphine greatly enhances the lability of chromium(III) towards substitution, especially in basic solution.

The crystal structure of *trans*-$[Cr(cyclam)(OCONH_2)]ClO_4.1.5H_2O$ has been determined [87]. The monoclinic unit cell contains two centrosymmetric complex ions which are almost identical except for the orientations of the monodentate carbamate groups. The macrocyclic tetraamine has its 5 membered rings in the *gauche* and its 6 membered rings in the chair configurations. The average Cr-N distance is 2.060Å and the average Cr-O distance is 1.960Å.

The preparations of a number of chromium(III) complexes of 3,2,3-tet have been reported [88]. ΔΛ-*cis*-β-(RR,SS)-$[Cr(ox)(3,2,3\text{-tet})](ClO_4).H_2O$ was



isolated and resolved using dibenzoyl-*d*-tartaric acid. *Cis* and *trans*-[CrCl$_2$(3,2,3-tet)]$^+$ and *trans*-[Cr(NCS)$_2$(3,2,3-tet)]$^+$ were also isolated.

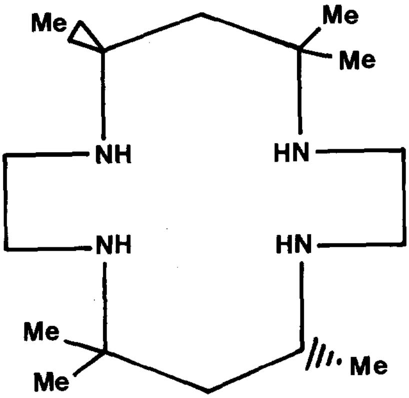
Cis-[CrCl$_2$(3,2,3-tet)]$^+$ slowly hydrolyses in acid solution to give *cis*-[CrCl(3,2,3-tet)(H$_2$O)]$^{2+}$ with no evidence for isomerization or Cr-N bond rupture. Addition of Hg^{2+} causes smooth hydrolysis to *cis*-[Cr(3,2,3-tet)(H$_2$O)$_2$]$^{3+}$.The *trans* dichloro compound is much more resistant to hydrolysis and a temperature of 70°C is required to replace the first chloride. The second step is complicated by isomerization and Cr-N bond rupture. Base hydrolysis leads to stepwise formation of [CrCl(3,2,3-tet)OH]$^+$ and [Cr(3,2,3-tet)(OH)$_2$]$^+$ with the *trans* isomer again being less reactive than the *cis* [88].

The complex *trans*-[CrCl$_2$(teta)]NO$_3$ has been prepared [89] and its hydrolysis reactions have been studied (teta = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetrazacyclotetradecane *(9)*). For base hydrolysis two moles of OH$^-$ are consumed for every mole of complex (pH 7.8-9.4) and the final visible spectrum is identical to that of *trans*-[Cr(teta)(OH)$_2$](ClO$_4$)$_3$ dissolved in 0.1M NaOH [89]. Thus the two reactions

$$\textit{trans}\text{-}[\mathrm{CrCl_2(teta)}]^+ + \mathrm{OH}^- \xrightarrow{k_1} \textit{trans}\text{-}[\mathrm{CrCl(teta)(OH)}]^+ + \mathrm{Cl}^-$$

$$\textit{trans}\text{-}[\mathrm{CrCl(teta)(OH)}]^+ + \mathrm{OH}^- \xrightarrow{k_2} \textit{trans}\text{-}[\mathrm{Cr(teta)(OH)_2}]^+ + \mathrm{Cl}^-$$

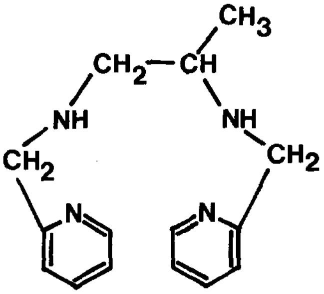
proceed at comparable rates.



(9)

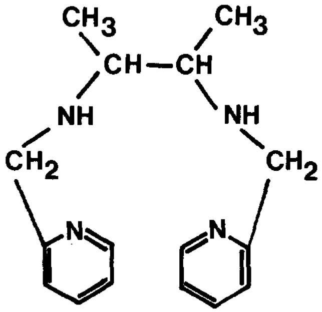
In acid solution *trans*-$[CrCl_2(teta)]^+$ aquates smoothly with excellent isobestic points to give *trans*-$[CrCl(teta)(H_2O)]^{2+}$ over the temperature range 55-70°C [90].

A number of complexes of the types $[CrX_2(N_4)]$ (X = F,Cl,Br) and $[Cr(OH)(N_4)]_2{}^{4+}$ have been prepared [91,92] where N_4 is one of the quadridentate nitrogen donor ligands *(10a-c)*. SS-picbn and SS-picchxn give the novel Λ(SS)-*cis*-α diastereomer of the dichloro complex, in which the terminal chelate ring is formed by coordination of an equitorially orientated substituent on the secondary nitrogen. It is suggested that steric repulsions account for the stereoselective formation of these isomers and similar explanations are given for the stereoselective formation of a limited number of isomers of the dinuclear μ-dihydroxo complexes of all the



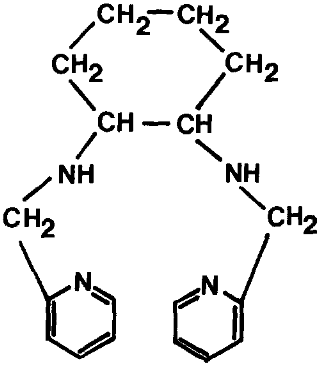
(10a)

(S)-NN'bis(2-pyridylmethyl)1,2-propylene
diamine (S-picpn)



(10b)

(SS)-NN'(2-pyridylmethyl)2,3-butanediamine
(SS-picbn)



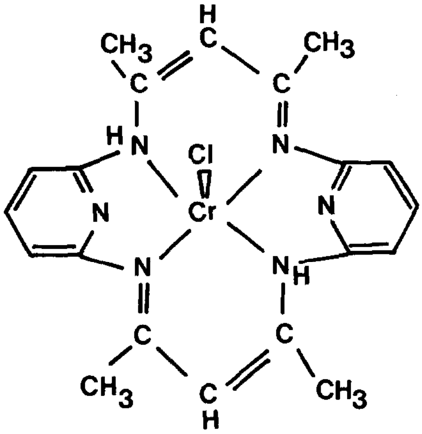
(10c)

(SS)-NN'-bis(2-pyridylmethyl)-1,2-cyclohexanediamine
(SS-picchxn)

ligands [91]. The complexes show CD spectra of a dispersion type in the region of pyridine ring absorption [92].

Reaction of $CrCl_3$ in MeOH with acetylacetone and 2,6-diaminopyridine in the presence of a small quantity of KOH gave directly the five coordinate complex $CrClN_6$ *(11)*. The corresponding nitrate and *N*-thiocyanate were also prepared [93]. The complexes were non-electrolytes, IR evidence suggested that the pyridine nitrogens were not coordinated and that the NO_3 and NCS were monodentate. A Cr-Cl stretch was identified in the spectrum of the chloro complex. All this evidence is consistent with a five coordinate square pyramidal structure similar to those found for other five coordinate chromium(III) complexes.

In coordinating solvents Cr(TPP)Cl ($TPPH_2$ = 5,10,15,20-tetraphenylporphyrin) forms the complex (S)Cr(TPP)Cl from which the solvent may be



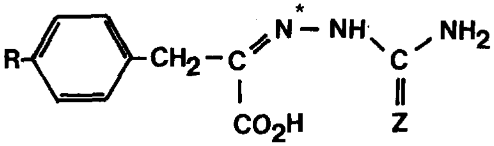
(11)

displaced by ligands (L) such as pyridine and N-methylimidazole to form (L)Cr(TPP)Cl. The kinetics of the reaction

$$\text{(L)Cr(TPP)Cl} + \text{X} \rightleftarrows \text{(X)Cr(TPP)Cl} + \text{L}$$

(where X = py, N-methylimidazole, PPh_3, $P(CH_2CH_2CN)_3$ and $P(O^iPr)_3$) have been studied [94] and clearly indicate a dissociative mechanism *via* five coordinate Cr(TPP)Cl. The phosphorus ligands cannot compete well with the nitrogen ligands indicating that the chromium centre in Cr(TPP)Cl is quite hard. However, in all cases the ligand *trans* to chlorine is significantly labilized relative to most chromium(III) complexes.

Complexes $[Cr(L\text{-}H)_2]X$ (L is one of the ligands *(12)*; X = Cl,Br,I,NO_3)



(12)

a) R = H Z = O
b) R = H Z = S
c) R = CH_3 Z = O
d) R = CH_3 Z = S

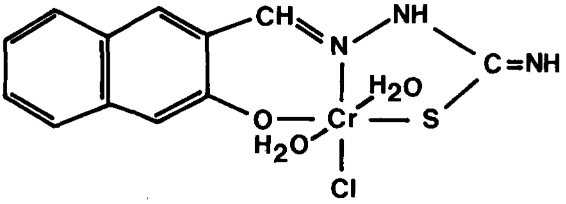
have been reported [95]. The IR spectra suggest that the deprotonated ligands coordinate through N* and two O's (or O and S) to give octahedral chromium(III) cations. Magnetic moments and visible spectra are consistent with these formulations.

Potassium (2S,4S)-2,4-pentanediaminetetraacetochromate(III) monohydrate, which contains a *cis*-$[Cr(N)_2(O)_4]$ stereochemistry similar to $[Cr(edta)]^-$, has been prepared [96]. The complex is formed stereospecifically with a Λ(ΛΔΛ) absolute configuration. The CD spectra in the forbidden transitions were measured along with those of known analogues and discussed in terms of theoretical relationships involving rotational strengths of spin-forbidden and spin-allowed transitions in trigonal and tetrahedral fields.

Kinetic studies on reactions of the Schiff base complexes $[Cr(salen)(H_2O)_2]^+$ and $[Cr(acacen)(H_2O)_2]^+$ (acacen = NN'-ethylenebis-(acetylacetonimine)) revealed high aquo ligand substitution rates with ligands such as CNS^-, N_3^-, py, imidazole and nicotinic acid [97]. Similar reactions have been investigated independently for nicotinic acid and other 3-substituted pyridine bases with $[Cr(salen)(H_2O)_2]^+$ [98]. It was found [97] that the forward rate constants for reactions of $[Cr(salen)(H_2O)_2]^+$ and $[Cr(acacen)(H_2O)_2]^+$ were independent of the nucleophile which suggests a rate determining dissociation step for substitution of the aquo cations. In contrast, the forward rate constants for substitution of the conjugate base of $[Cr(salen)(H_2O)_2]^+$ did show a marked dependence on the nature of the incoming nucleophile.

Reaction of Hg(salen) with $Cr(CO)_6$ in refluxing toluene gave an insoluble brown product $[Cr(salen)]_2O$ [99]. In addition to bands characteristic of salen the IR spectrum showed bands at 858 and 870cm^{-1} which are similar to those due to the Cr-O-Cr vibrations in $[\{Cr(NH_3)_5\}_2O]^{4+}$. The EPR spectrum confirmed the presence of chromium(III) but the magnetic moment was low at 2.2BM per chromium atom. It was suggested that the material is a μ-oxo complex.

The doubly charged anion of 3-hydroxy-2-naphthaldehydethiosemicarbazone acts as a tridentate ligand in the complex *(13)* [100].



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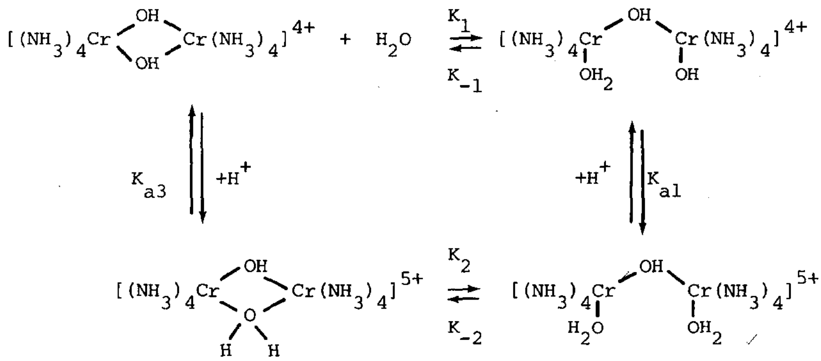
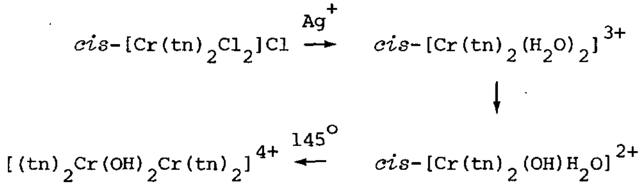
5.4.5 Dinuclear complexes

The binuclear ion $[(NH_3)_4Cr(OH)_2Cr(NH_3)_4]^{4+}$ equilibrates in aqueous solution according to the scheme



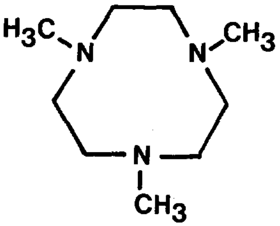
giving both acid catalyzed and uncatalyzed pathways [101]. The compounds $[(NH_3)_4Cr(OH)_2Cr(NH_3)_4]X_4.4H_2O$ and $[en_2Cr(OH)_2Cren_2]X_4.2H_2O$ (X = Cl,Br) all show strong linear dichroism as a result of unusually intense spin allowed *d-d* transitions polarized perpendicular to the $Cr_2(OH)_2$ plane [102]. The exchange coupling is antiferromagnetic with $2J \approx 1cm^{-1}$ for the NH_3 compounds and $\approx 30cm^{-1}$ for the en compounds. These differences are due to the different positions of the H atoms of the bridging OH groups. In the en complexes, the H's lie in the Cr_2O_2 plane, but in the NH_3 complexes they are forced out of the plane by hydrogen bonding. The p_x orbital in the en complexes is fully available for π-bonding between the chromium atoms, but not in the NH_3 compounds. This difference leads to significantly altered ligand fields at chromium sufficient to produce changes in the optical spectra. Superexchange through the bridging hydroxy groups is also thought to be the dominant mechanism for $^4A_{2g}\,^4A_{2g} \rightarrow \,^2E_g\,^4A_{2g}$ pair excitations in the single crystal absorption spectra of the same complexes [103]. The complex cation $[(tn)_2Cr(OH)_2Cr(tn)_2]^{4+}$ (tn = 1,3-propanediamine) has been prepared [104] by the reaction scheme



It has properties similar to those of the NH_3 and en analogues.

The magnetic properties of a series of di-μ-hydroxy complexes $[CrLm(H_2O)_nOH]_2$ (Lm = gly, mal, en, phen) have been discussed in terms of the extended Hückel MO formalism [105]. Singlet-triplet splittings which arise from superexchange correlate with the ratio Φ/r where Φ is the angle at the bridging oxygen and r is the Cr-O (bridging) distance. The magnetic properties of the complex di-μ-hydroxo-S,S,S,S-tetrakis(*L*-prolinato)dichromium(III) also fit this theoretical model [106].

The synthesis of the cyclic amine 1,4,7-trimethyl-1,4,7-triazacyclononane (L) *(14)* has been reported [107]. Reaction with $CrCl_3$ followed by $NaClO_4$ in

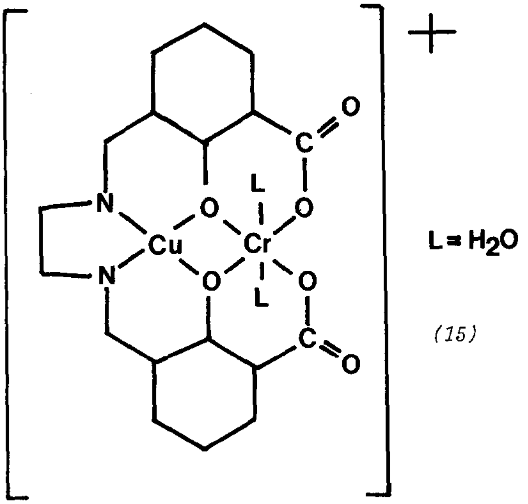


(14)

alkali solution gave $[Cr_2L_2(OH)_3]^{3+}$. The crystal structure of the iodide salt revealed *facial* coordination of the ligand and three bridging hydroxyl groups. Bond distances are Cr-N 2.089(4) and Cr-O 1.972(6)Å. The Cr-Cr distance of 2.642(2)Å is the shortest so far discovered for chromium(III) dimers.

The complex $[(acac)_2Cr(OMe)_2Cr(acac)_2]$ has been prepared to explore the relationship between structural factors and magnetic properties [108]. The alkoxide gives a better determination of the dihedral angle at the bridging oxygen than the corresponding hydroxy complex. The average Cr-OMe bond length is 1.962Å and the average Cr-O (acac) bond distance is1.971(4)Å. The Cr-Cr distance is 3.028(2)Å. The magnetic properties over the temperature range 4-260 K are similar to those of other methoxy bridged complexes and fit the previously developed theoretical model.

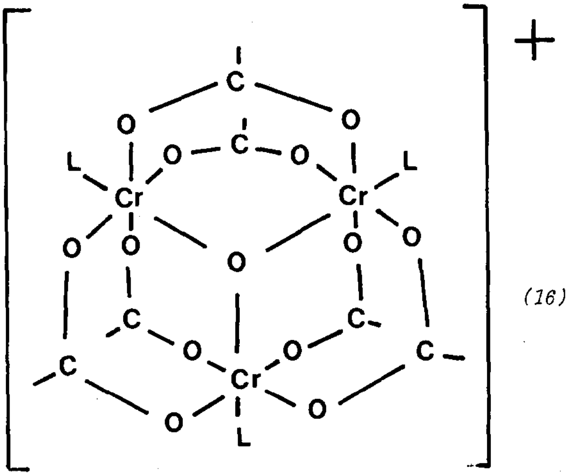
A heteronuclear complex $[Cu\{(fsa)_2en\}Cr(H_2O)_2]Cl$ *(15)* has been prepared [109] where $(fsa)_2en$ is a bichelate ligand derived from the Schiff base 3,3'-ethylenebis(nitrilomethylidyne)disalicylic acid. The copper coordination is square planar N_2O_2 whilst the chromium(III) coordination is $O_4(H_2O)_2$. The unpaired electron on copper is in the d_{xy} orbital and those on chromium are in $d_{x^2-y^2}$, d_{xz} and d_{yz} and the orbitals of the metal atoms are orthogonal. The magnetic susceptibility shows a maximum at 45 K and indicates ferromagnetic interaction between the metal centres.



(15)

5.4.6 *Polynuclear complexes*

The structural properties of $[Cr_3O(CH_3COO)_6(H_2O)_3]Cl.6H_2O$ were studied at 190 K by X-ray diffraction [110]. There is a phase change at 211 K and the unit cells of both phases are orthorhombic with the low temperature cell twice as long in the *c* direction as the high temperature cell, with *a* and *b* unchanged. In the LT structure there are two inequivalent sets of triangular clusters each with the structure shown *(16)* (L = H_2O).



(16)

Measurements on the luminescence spectra, decay curves and time-resolved spectra in the temperature range 7-83 K revealed that there is no excitation energy transfer between the inequivalent clusters at 7 K although it does occur at higher temperatures [110].

A very detailed IR and Raman study has been made of complexes of the type $[Cr_3O(OOCR)_6L_3]X$ *(16)* ($L = H_2O$, py, γ-pic; R = H, CH_3, CD_3; X = ClO_4, NO_3, Cl,Br). The vibrational modes of the central Cr_3O and surrounding CrO_4 units were identified [111]. Cr-N stretching vibrations and $Cr\text{-}OH_2$ modes were assigned. 'Basic chromium(III) formate' was shown to be $[Cr_3O(OOCH)_6(H_2O)_2(OOCH)]$ similar to *(16)* with one monodentate formate group replacing water. The same authors [112] also studied the vibrational spectra of the trinuclear complexes $[Cr_{3-n}Fe_nO(OOCR)_6L_3]^+$ (n = 1,2; R = H, CH_3; L = H_2O, py). Although there is greater complexity in the spectra due to the lowering of the symmetry, the data does show that these complexes are also similar to *(16)*. Despite the fact that these complexes have been known for many years little is known of their structure, but this work confirms they are genuine compounds and not simply mixtures of Cr_3 and Fe_3 complexes.

Two examples of a new type of trinuclear complex $Cr_3O(OOCCF_2H)_6L_3$ (L = py, 4-CNpy) which formally contain two chromium(III) atoms and one chromium(II) atom have been prepared [113]. They were made by heating a chromium(II) carbonato complex with difluoracetic acid in ether to give an intermediate believed to be $Cr_2(OOCCF_2H)_4.2(C_2H_5)_2O$ which was then reacted with py or 4-CNpy. The crystal structures of both complexes were determined and although they are not isomorphous with each other or with *(16)* they both have molecular geometries which are very similar to that of *(16)*. Both have three fold symmetry and there is no sign of valence trapping, that is, all the chromiums are equivalent and at least one electron is delocalized over the Cr_3 moiety. Average bond lengths are

	py complex	4-CNpy complex
Cr-Cr	3.356(2)	3.336(1)
$Cr\text{-}\mu_3O$	1.938(1)	1.926(1)
Cr-O	2.03(4)	2.03(2)
Cr-N	2.158(7)	2.155(5)

Extended Hückel MO calculations have been performed on the $Cp_4Cr_4O_4$ complexes which have a cubane-like Cr_4O_4 core. The ordering of the levels is not the same as suggested in previous papers and the latest scheme is more in accord with the experimental magnetic properties [114].

5.4.7 Photochemistry

There have been two reviews on the photochemistry and photophysics of chromium(III) complexes [115,116]. There has been some discussion as to whether the ligand field excited states in chromium(III) are responsible for the photosubstitutional behavior of Cr(III) complexes. Irradiation of $[Cr(en)_3]^{3+}$ has been carried out at various wavelengths and the quantum yield for the reaction

$$[Cr(en)_3]^{3+} \longrightarrow [Cr(en)_2(en\text{-}H)(H_2O)]^{4+}$$

was measured [117]. Irradiation at 404nm (1st quartet ligand field band) caused Cr-N bond breaking with $\Phi \approx 0.37$ (Φ = quantum yield) but excitation of the doublet state increased the quantum efficiency by 40-60%. If $^4T_{2g}$ were the only precurser of substitution then Φ should be constant, so it was suggested that the ^2E_g state is also involved.

Under high intensity pulsed laser excitation the doublet states of $[Cr(4,7\text{-}Me_2phen)_3]^{3+}$ and $[Cr(phen)_3]^{3+}$ decay with mixed first order and second order kinetics [118]. The kinetics depend upon laser intensity, the presence of quenchers and on the ionic strength of the solutions and demonstrate the occurrence of a doublet-doublet annihilation process in competition with uni-molecular doublet decay [118]. The intersystem crossing efficiency in $[Cr(en)_3]^{3+}$ was measured to be 0.68 ± 0.1 by comparison of the phosphorescence yield on quartet and doublet excitation [119]. The photochemical yield is the same at the two excitation wavelengths. The results allowed modelling of the quenchable photochemistry either by direct reaction or by reverse intersystem crossing and quartet reaction, although the latter mechanism was preferred.

^2E decays of $[Cr(NH_3)_{6-n}(H_2O)_n]^{3+}$ (n = 0-6) have been measured as a function of temperature in water/alcohol mixtures. Low temperature limiting decay behavior was reached above 77 K for all compounds except $[Cr(H_2O)_6]^{3+}$. The low temperature $^2E \rightsquigarrow {}^4A_2$ non-radiative relaxation rate increases monotonically with the number of water ligands, but pairs of isomers relax at the same rate. No fluorescence was found at any temperature, but the results indirectly support $^2E \rightsquigarrow {}^4T_2$ back transfer as the dominant high temperature decay mode [120].

Further studies [121] on the mechanism of quenching of triplet states of organic molecules (e.g. benzophenone, 2-acetonaphthone, acridine) by $Cr(acac)_3$ and $Cr(bzac)_3$ show that the mechanism is *via* energy transfer to doublet and quartet states of chromium(III).

5.5 CHROMIUM(II)

5.5.1 Simple compounds of chromium(II)

Aqueous chromium(II) reacts with KCN to give $Cr(CN)_2.2H_2O$ as an olive green compound which can be dehydrated to give brown $Cr(CN)_2$ [122]. Both compounds have two unpaired electrons corresponding to low spin chromium(II) and their IR spectra both show the presence of bridging cyanide groups. Chromium(II) with excess cyanide gives a red solution previously thought to contain $[Cr(CN)_6]^{4-}$ and this has now been proved by isolating some alkali metal salts of this anion. Their IR spectra show only terminal cyanide groups. They are easily oxidized and their magnetic moments (3.14-3.48BM) are higher than the spin only value. Reduction of $[Cr(CN)_6]^{4-}$ with an alkali metal in liquid ammonia gives diamagnetic $[Cr(CN)_6]^{6-}$ which is spontaneously inflammable. Its IR spectrum shows the presence of only terminal cyanide groups [122]. Ethanolic solutions of chromium(II) react with alkyl isocyanides RNC (R = ^{t}Bu, C_6H_{11}) in the presence of KPF_6 to give $[Cr(CNR)_6](PF_6)_2$. These are paramagnetic low spin (μ = 2.9BM) complexes. Further reaction with neat RNC yields the diamagnetic seven coordinate $[Cr(CNR)_7]^{2+}$ species, but this reaction is reversible on dissolving them in organic solvents [123]. The six coordinate complexes show a reversible electrochemical reduction to chromium(I) and two reversible oxidations, each of one electron, but the reaction products could not be isolated. In contrast, the seven coordinate species give an irreversible oxidation and the solution quickly shows evidence of the presence of $[Cr(CNR)_6]^{2+}$ formed either by loss of RNC directly (above) or subsequent to electrochemical oxidation. Both types of complex react with PR_3 (R = Et, ^{n}Pr, ^{n}Bu) to give paramagnetic *trans*-$[Cr(CNR)_4(PR_3)_2]^{2+}$ and with dppe to give *cis*-$[Cr(CNR)_4(dppe)]^{2+}$. This latter complex reacts with neat RNC to yield $[Cr(CNR)_5(dppe)]^{2+}$ [123].

The crystal structure of the complex $[Cr(CN^{t}Bu)_7](PF_6)_2$ has been determined [124]. The geometry of the cation is best described by the 4:3 *(Cs)* piano stool distribution of ligands about chromium. The chromium atom lies 0.98Å from the tetragonal plane and 1.33Å from the trigonal plane; the angle between the planes is only 3.7° which is very close to the idealized value of 0°. Cr-N bond lengths range from 1.966(8) to 2.016(6)Å. The corresponding Mo and W complexes both adopt the capped trigonal prismatic stereochemistry and it is suggested that the smaller size of chromium is responsible for it adopting the different structure.

The X-ray photoelectron spectrum of $[Cr(CNR)_6]^{2+}$ and $[Cr(CNR)_7]^{2+}$ (and their Mo and W analogues) have been observed [125]. The satellite structure associated with the N *1s* and C *1s* binding energies in the spectra probably arises from M(*d*) $\longrightarrow$ π^*(CNR) excitations accompanying the primary photoemission process.

Electrohydrodynamic mass spectrometry is used to study directly the nature of complexes in solution. It is a very soft ionization technique which does not cause fragmentation, and it has been applied to chromium(II) bipy complexes [126]. $[Cr(bipy)_3]^{2+}$ was dissolved in NaCl as supporting electrolyte in a glycerol (G) solution. Exchange reactions occur due to the lability of the complex and the mass spectrum showed peaks due to $[Cr(bipy)_3]^{2+}$, $[Cr(bipy)_2Cl]^+$, $[Cr(bipy)_2Cl_2]^+$ and $[Cr(bipy)_2(G-2H)]^+$ and $[Cr(bipy)_2Cl(G-H)]^+$. In contrast, the non-labile $[Ru(bipy)_3]^{2+}$ gave only one peak corresponding to the parent ion.

The aquation of $[Cr(L-L)_3]^{2+}$ (L-L = bipy, phen) is considered to occur through three equilibria

$$[Cr(L-L)_3]^{2+} + 2H_2O \rightleftharpoons [Cr(L-L)_2(H_2O)_2]^{2+} + L-L$$

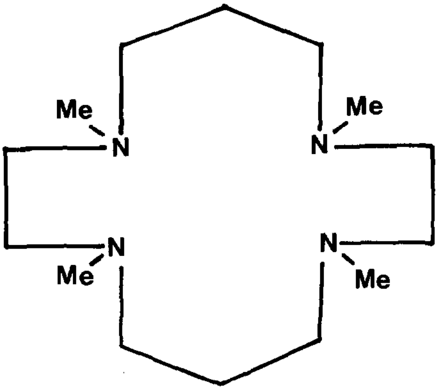
$$[Cr(L-L)_2(H_2O)_2]^{2+} + 2H\ O \rightleftharpoons [Cr(L-L)(H_2O)_4]^{2+} + L-L$$

$$[Cr(L-L)(H_2O)_4]^{2+} + 2H_2O \rightleftharpoons [Cr(H_2O)_6]^{2+} + L-L$$

The reactions have been followed in the presence of excess Zn^{2+} as a scavenger for released bipy or phen so that only the forward reactions need be considered [127]. The first step is rate determining and the ligand dissociation rate constants were found to be $0.39S^{-1}$ (bipy) and $0.064S^{-1}$ (phen). In a similar set of experiments [128] with other $[Cr(L-L)_3]^{2+}$ complexes (L-L = 4,4'-dimethylbipy and 5,5'-dimethylbipy) similar results were obtained except that the ligand dissociation rates were greater than for bipy itself.

A series of chromium(II) complexes with Me_4cyclam (L) (1,4,8,11-tetramethyl 1,4,8,11-tetraazacyclotetradecane *(17)* have been prepared by direct interaction [129]. The complexes CrX_2L (X = Br,I) are non-electrolytes in CH_2Cl_2 and hence are thought to be six coordinate and on the basis of the visible spectrum they appear to be *cis* with the ligand in a folded configuration. However, in dmf solution the bromo complex is a 1:1 electrolyte and the iodo complex is a 1:2 electrolyte and the visible spectra of these solutions are identical to those of $[CrBrL]^+$ and $[Cr(dmf)L]^{2+}$ (below) respectively. It is proposed that in dmf the following reactions occur

$$[CrBr\ L] \xrightarrow{dmf} [CrBrL]^+ + Br^-$$



(17)

$$[CrI_2L] \xrightarrow{dmf} [Cr(dmf)L]^{2+} + 2I^-$$

The five coordinate complexes [CrXL]BPh$_4$ (X = Cl, Br, I, NCS) and [Cr(solv)L](BPh$_4$)$_2$ (solv = dmf, CH$_3$CN) are all high spin (μ = 4.6-4.75BM) and are 1:1 or 1:2 electrolytes as expected. The geometry of the five coordinate complexes could not be determined.

The monomeric chromium(II) complex $(Me_2C_5H_3N)_2Cr(OOCCF_3)_2$ was made from 2,6-dimethylpyridine and CrCl$_3$ by the following route [130]

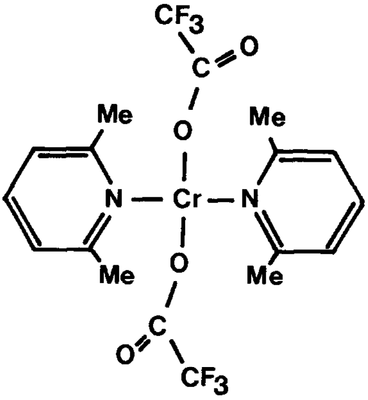
$$CrCl_3 \xrightarrow{NaBH_4} [thf.Cr(BH_4)_2] \xrightarrow{CF_3COOH} [thf.Cr(OOCCF_3)_2]_2 \xrightarrow{2,6\text{-}Me_2py} (Me_2C_5H_3N)_2Cr(OOCCF_3)_2$$

A single crystal X-ray structural determination showed the complex to be the first square planar chromium(II) compound *(18)*. Bond distances are Cr-O 2.028(3), Cr-N 2.111(3)Å. The second oxygen of the trifluoroacetate ligands are not coordinated (Cr-O ≈ 2.976(3)Å).

A SCF-MO calculation of the optical spectrum of chromium(III) in a distorted octahedral array of F's in CrF_3^- structures has been presented [131].

The adduct CrF$_2$.AsF$_5$ was prepared as a green solid by reaction of the constituents in anhydrous HF [132]. The compound is not isostructural with the corresponding Fe(II), Cu(II), Zn(II) and Sn(II) compounds. The magnetic moment of 4.68BM is consistent with high spin chromium(II). The IR and Raman spectra were recorded but no structural assignments were made.

Chromium metal dissolves in a mixture of anhydrous HF and a Lewis acid



(18)

(BF_3, AsF_5, SbF_5) to give a stable solution of chromium(II). The electronic spectrum of chromium(II) in HF gives only one band similar to that observed in aqueous solution and in molten $AlCl_3$ and suggests a similar octahedral arrangement about chromium. The species in solution is thought to be $[Cr(HF)_6]^{2+}$ [133].

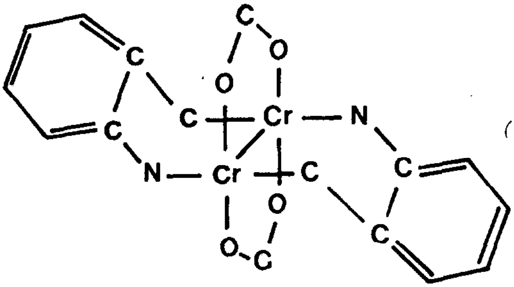
A number of alkylammonium tetrachlorochromates(II), $(C_nH_{2n+1}.NH_3)_2CrCl_4$, ($n$= 3,5,12) have been prepared and characterized by analysis and X-ray powder diffraction [134]. The effect of increasing the alkyl chain length is to separate the layers of metal octahedra, but not to influence separations within a layer of the structure. All the compounds are ferromagnetic and their magnetic properties at low temperatures are similar. Complementary studies have been made on some tetrabromochromates(II) which are also ferromagnetic with Curie temperatures in the range 57-59 K [135].

5.5.2 Metal-metal bonded species

From calorimetric measurements at 25°C of the enthalpies of oxidative hydrolysis, the standard enthalpies of formation of $Cr_2(mhp)_4$ and $Cr_2(dmp)_4$ were found to be -948.2 ± 9 and -961 ± 22 $KJmole^{-1}$ respectively [136], (mhp is the anion of 2-hydroxy-6-methylpyridine; dmp is the anion of 2,6-dimethoxybenzene). The electron distribution between chromium atoms in $Cr_2(mpm)_4$ has been studied by theoretical methods and for $Cr_2(mhp)_4$ by high resolution low temperature X-ray methods [137], (mpm is the anion of dimethylphosphoniumylidenedimethylide). The compounds have similar structures with 'super-short' Cr-Cr bond lengths. There is strong charge density accumulated between the chromium atoms extending over the σ and π regions comparable to that between multiple bonded first row elements.

Electrochemical oxidation of $Cr_2(map)_4$ (map is the anion of 2-amino-6-methylpyridine) revealed two reversible one-electron oxidations at -0.53 and -0.09V (vs $Ag/AgNO_3$) [138]. This is the first time that cationic and dicationic species derived from quadruple bonded complexes have been observed.

Reaction of $Cr_2(O_2CCH_3)_4$ with $[o\text{-}NMe_2C_6H_4CH_2]^-$ gave $Cr_2(O_2CCH_3)_2(o\text{-}NMe_2C_6H_4CH_2)_2$ *(19)* [139]. The Cr-Cr distance of 1.870Å is in



(19)

the 'super-short' range with the $o\text{-}NMe_2C_6H_4CH_2^-$ ligands oppositely orientated in a *trans* configuration; the $Cr_2(O_2CCH_3)_4$ portion of the molecule is planar. The species $Cr_2(o\text{-}NMe_2C_6H_4CH_2)_4$ could not be formed even under forcing conditions. Note that $o\text{-}NMe_2C_6H_4CH_2^-$ is an isomer of the anion in *(3b)* and the different modes of bonding of the two ligands is noteworthy.

The gas phase X-ray photoelectron spectrum of $Cr_2(O_2CCH_3)_4$ has been examined [140]. Two peaks were observed in the C 1*s* region corresponding to the two types of carbon atom. The same group of workers also carried out *ab initio* MO calculations on $Cr_2(O_2CCH_3)_4$ to discuss bonding in both ground and ionic states, particularly those features arising from metal *d* ionizations [141]. Correlation effects must be included to interpret the 3*d* ionizations of this molecule.

A spectrophotometric study has been made of the equilibria between $Cr_2(O_2CCH_3)_4$ and various chelating ligands [142]. Formation constants for mononuclear chromium(II) complexes were determined as follows: malonate, $\log \beta_2 = 6.0 \pm 0.2$; N-methyliminodiacetate, $\log \beta_2 = 12.3 \pm 0.5$; ethylenediamineNN'-diacetate, $\log K_1 = 9.1 \pm 0.2$ at 25°C, I = 1.0M ($NaClO_4$).

The interaction of $Cr_2(O_2CCH_3)_4$ and $Li(C_6H_4\text{-}o\text{-}CH_2NMe_2)$ *(3a)* in 1:2 proportions yields a complex $Cr_4O(C_6H_4\text{-}o\text{-}CH_2NMe_2)_4(O_2CCH_3)_2$ [47]. This molecule contains a central μ_4-O atom between two pairs of directly bonded chromium atoms (Cr-Cr = 2.554(2)Å). The two acetates bridge between two chromium atoms, one in each directly bonded pair,while the C_6H_4-*o*-$CH_2NMe_2^-$ groups are each chelated to one chromium atom. Thus each chromium is surrounded by an approximate square of ligands at right angles to the metal-metal bond comprising of the μ_4O, C and N of C_6H_4-*o*-$CH_2NMe_2^-$ with N *trans* to the μ_4O, and one oxygen of a bridging acetate group. The exact nature of the bonding within the Cr_2 units is not obvious [47].

5.6 CHROMIUM (I) AND MISCELLANEOUS SYSTEMS

Cyclic voltammetry has been used to study the system $[Cr(CNR)_6]^{0,1,2,3}$ for a series of arylisocyanides in various solvents [143]. The introduction of bulky *ortho* substituents on the aryl ring dramatically influences $E^{o3+/2+}$ and the substitutional lability of the chromium(III) complexes, which is attributed to a weakening of the Cr-C bond in chromium(III) by steric forces.

There have been several papers published concerning hydroxylamine reduction of higher oxidation state chromium compounds to give products containing the $CrNO^{2+}$ group. Thus, reaction of hydroxylamine with CrO_4^{2-} in the presence of CNS^- ion gives good yields of $[CrNO(NCS)_5]^{3-}$ which was isolated as the Ph_4P salt [144]. This paramagnetic salt has a magnetic moment of 1.8BM. Reaction with bidentate ligands such as bipy and phen gives complexes formulated as $Cr(NO)(NCS)_2(L-L)$. The corresponding cyanide complex $[CrNO(CN)_5]^{3-}$ reacts with en to give a number of dimeric species such as $[Cr_2(NO)_2(CN)_4en_3]$ which are thought to contain a bridging en group with NO *trans* to the bridge [145]. Derivatives of $[CrNO(H_2O)_5]^{2+}$ with dialkyldithiocarbamates and *O-O*-diakyldithiophosphates have been examined by EPR methods [146]. Generally, the spectra were triplets due to coupling to ^{14}N, but the dithiophosphates gave additional coupling due to phosphorus which aided in determining the stereochemistry of the complexes. Reduction of sodium bis(2-ethyl-2-hydroxybutyrato)oxochromium(V) with hydroxylamine gave the chromium(I) species $CrNOL_2$ (L = 2-ethyl-2-hydroxybutyrato) [147].

It has been reported that the neutral $Cr(bipy)_3$ and $Cr(phen)_3$ complexes are conveniently prepared by Na/Hg reduction of $CrCl_3$ or $Cr_2(O_2CCH_3)_4$ in the presence of the ligands [148].

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