Coordination Chemistry Reviews, 90 (1988) 1–27
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

1. CHROMIUM†

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CONTENTS

INTRODUCTION

The review on chromium chemistry this year deals mainly with the inorganic and coordination chemistry of the element which was cited in Chemical Abstracts, Volumes 102 and 103. Thus most of the work published in 1985 and some published towards the end of 1984 will be reviewed. Chromium organometallic chemistry, including carbonyl chemistry, is not formally included in this review but reference is made to some papers of general interest.

The organization of the review is similar to that of previous years. The various oxidation states are dealt with in turn with individual systems ordered in terms of the nature of the donor atoms. Chromium chemistry is dominated by the trivalent state so, for convenience, this large section of the review is divided into sections according to the nature of the ligands.

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† **NO REPRINTS AVAILABLE**

0010-8545/88/$09.45

1.1 CHROMIUM(VI)

The oxidation of lactic acid by chromium(VI) has been studied in detail and found to proceed in two separate and measurable steps, both of which give pyruvic acid

$$2Cr(VI) + 2CH_3CHOHCOOH \longrightarrow 2CH_3COCOOH + Cr(V) + Cr(III)$$

$$Cr(V) + CH_3CHOHCOOH \longrightarrow CH_3COCOOH + Cr(III)$$

The buildup and decay of chromium(V) intermediates accompanied the disappearance of Cr(VI). Mechanisms were deduced for each step and it was suggested that the intervention of chromium(V) may be widespread in chromium(VI) oxidations [1].

A study has been made of the interaction at physiological pH's of chromium(VI) with a series of low molecular weight cellular reductants and other model compounds since it is known that reduction to chromium(III) is involved in the carcenogenic properties of chromium(VI). It was found that only ascorbate and compounds containing a thiol group reduced Cr(VI) at an appreciable rate. Several mechanisms of interaction were observed, but with glutathione, which is the most abundant intracellular thiol, clear evidence was obtained for the formation of a chromium(VI) thioester in a rapid pre-equilibrium step. This was followed by a slower reduction step involving a further molecule of glutathione [2].

$CrOF_4$ has been prepared by the reaction of CrO_3 and fluorine at 140°C and 4 atm. pressure in a Monel autoclave with a watercooled lid. $CrOF_4$ is a powerful fluorinating agent and is rapidly hydrolyzed by water. A sample isolated in a nitrogen matrix showed a strong Cr=O stretch at $1028cm^{-1}$ and a doublet at $746,742cm^{-1}$ due the chromium-fluorine stretches. An analysis of the spectrum and comparison with similar data for $MoOF_4$ and WOF_4 suggested a square pyramidal structure with a O-Cr-F angle of 106°C. Reaction between $CrOF_4$ and CsF under nitrogen gave $Cs[CrOF_5]$ which has a Cr=O stretch at $955cm^{-1}$ and a broad band at $650-720cm^{-1}$ due to Cr-F stretches [3].

CrF_6 has been prepared under conditions considerably less extreme than those in the original report of this compound. Reaction between CrO_3 and fluorine in a Monel reactor fitted with a watercooled lid at 170°C and 25 atm. pressure followed by cooling to room temperature and then to -63°C led to the formation of CrF_6. Excess F_2 and CrO_2F_2 were pumped off to yield a mixture of red CrF_5 and yellow CrF_6. Matrix isolation IR studies showed the Cr-F stretch to occur at $759cm^{-1}$ [4].

Force fields and mean amplitudes of vibration have been calculated for MF_6

and MO_2F_2 (M Cr,Mo,W). The agreement between calculated and observed spectra was good [5].

1.2 CHROMIUM(V)

A review has appeared on the coordination chemistry of chromium(V) [6]. CrN(TTP) is known to have a distorted porphyrin core while MnN(TTP) has a regular core. These structural differences are reflected in their resonance Raman spectra. Whereas the Mn≡N stretch at 1052cm^{-1} is greatly enhanced in intensity, no such enhancement is observed for CrN(TTP) [7].

It has been shown that the most likely mechanism of the interaction between iodosylbenzene and ClCr(TPP) involves transfer of an oxygen atom to give Cr(V), which then reacts with further Cr(III) to give Cr(IV)

$$\mathrm{PhI{=}O + ClCr(TPP) \longrightarrow PhI + ClCr(O)(TPP)}$$

$$\mathrm{ClCr(O)(TPP) + ClCr(TPP) \xrightarrow{H_2O} 2Cr(O)(TPP) + 2H_2O}$$

but in the presence of excess of PhI=O the final product is Cr(V) [8]. The kinetics of the interactions of ClCr(TPP) with a number of percarboxylic acids and hydroperoxides were also investigated. The data indicated that all the reactions proceeded with similar mechanisms involving heterolytic fission of the O-O bond [8].

1-phenyl-1,2-ethanediol is oxidized by *p*-cyano-N,N-dimethylaniline N-oxide in the presence of ClCr(TPP) as catalyst. It was shown that photo-initiation of the reaction is necessary and the likely catalytic intermediate is ClCr(O)(TPP) [9].

One-electron oxidation of Cr(O)(TPP) by electrochemical techniques gave a Cr(V) oxoporphyrin which is stable on the coulometric timescale. It is reactive towards norbornadiene to give the epoxide in a 1:1 stoichiometric reaction. A 2:1 mixture of ClCr(TPP) and iodosylbenzene gave a product which was thought to be the Cr(IV) dimer $[ClCr(TPP)]_2O$ which disproportionates to Cr(III) and Cr(V) [10].

A number of substituted sal_2en complexes of oxochromium(V) have been isolated. The synthetic procedure involved reaction of Cr(III) triflate with the ligand and subsequent air oxidation to give $[(sal_2en)Cr(H_2O)_2]O_3SCF_3$. Oxidation with iodosylbenzene in MeCN yielded the air-stable $[(sal_2en)CrO]^+$ species. The crystal structure of $[(7,7'\text{-}Me_2sal_2en)CrO]^+$ revealed a square pyramidal structure with the oxo group apical and the Cr atom 0.53Å above the mean N_2O_2 plane. Bond distances are Cr=O = 1.545(2), Cr-O = 1.809(av) and Cr-N = 1.98Å(av). All the complexes reacted with a variety of donor ligands and the crystal structure of pyNO adduct showed that the additional ligand completed the octahedral coordination about the metal. EPR and magnetic data confirm the d^1 configuration of these complexes [11].

The catalytic epoxidation of various olefins with iodosylbenzene may be carried out in the presence of a series of Cr(III) cations $[Cr(sal_2en)]^+$ with or without the presence of pyNO. Kinetic studies showed that the Cr(V) species $[(sal_2en)CrO]^+$ and $[(sal_2en)Cr(O)(pyNO)]^+$, described above, are the active intermediates. The mechanism of the oxygen transfer involves the rate determining attack by the Cr(V) oxocation on the olefin [12].

It has been shown that the EPR signals for paramagnetic $[CrO_3]^-$ and $[CrO_4]^{3-}$ may be distinguished by a combination of g- and A-tensor analysis and the temperature dependence of the line widths. This arises because the electronic spin-lattice relaxation time for a species is dependent upon its coordination and point symmetry. The results indicate that several previous assignments distinguishing between these species need to be reviewed [13].

The relatively stable Cr(V) complex sodium bis(2-ethyl-2-hydroxybutanato)-oxochromate(V) has been the subject of several investigations. The chromium(V) complex disproportionates

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

and is most stable at pH 3-4 in the presence of a small amount of free 2-ethyl-2-hydroxybutanoic acid. Oxidation of organic substrates with this Cr(V) reagent have been studied and compared with similar oxidations using Cr(VI). Generally, oxidations with Cr(V) are faster than those with Cr(VI) (hence Cr(V) is not usually observed as an intermediate in Cr(VI) oxidations) except for the oxidation of pinnacol (faster with Cr(VI)) and ethylene glycol which is oxidized at about the same rate by the two reagents. The organic substrates investigated included oxalic acid, primary and secondary hydroxy acids, alcohols etc [14].

Reduction of sodium bis(2-ethyl-2-hydroxybutanato)oxochromate(V) by $[VO]^{2+}$ has been investigated by spectrophotometric and EPR techniques [15]. In reactions with $[VO]^{2+}$ in less than 1:1 stoichiometry, the chromium appeared to be reduced to Cr(IV) and only after addition of further $[VO]^{2+}$ was subsequent reduction to Cr(III) observed. The EPR signal of Cr(V) decreased as $[VO]^{2+}$ was added until at 1:1 stoichiometry no signal was observed. The eight line spectrum of $[VO]^{2+}$ only appeared after 2 moles had been added. Kinetic measurements also indicated the intervention of Cr(IV) in the overall reaction scheme [15]. In a similar reduction by Fe(II), spectrophotometric evidence suggested transient formation of Cr(IV), but the observation was not so clear cut as in the vanadium system [16]. In the reduction of the Cr(V) species by

Ti(III), Cr(IV) was not detected even though the reduction must pass through this stage. Hence it was deduced that Cr(IV) must react with Ti(III) at least 20 times faster than Cr(V) [17].

Matrix isolation studies show that CrF_5 rapidly disproportionates in the gas phase to CrF_4 and CrF_6 [4]. This result therefore casts some doubt on the interpretation of electron diffraction data for CrF_5 reported in the review for 1984. CrF_5 reacts with $NF_4.HF_2$ to give $(NF_4)[CrF_6]$ and with NOF to yield $(NO)[CrF_6]$. The hexafluorochromate(V) anion was identified by analysis and IR and Raman spectroscopies [18].

1.3 CHROMIUM(IV)

The compound $CrH_4(dmpe)_2$ has been prepared in two ways; by the interaction of $CrCl_2(dmpe)_2$ with lithium butyl or by the photolysis of $Cr(N_2)_2(dmpe)_2$ in hexane. This is the first hydride of Cr(IV) and the first eight coordinate complex of Cr(IV). The structure is dodecahedral with bond distances Cr-P = 2.255(3) and Cr-H = 1.53(3)-1.60(3)Å [19].

The compounds Sr_2CrO_4, Ba_2CrO_4 and Ba_3CrO_5 have been prepared by high temperature reactions between the appropriate chromate and Cr_2O_3. All contain the tetrahedral $[CrO_4]^{4-}$ ion. Magnetic moments are close to spin-only values with small Weiss constants and weak antiferromagnetic ordering was indicated [20].

Chromyl chloride, CrO_2Cl_2, and chromyl acetate react with various alkylaromatics (toluene, ethylbenzene etc) to yield solids which, on the basis of IR and magnetic studies, contain Cr(IV) [21].

Chromium tetrafluoride has been isolated in a dilute matrix and displays bands at 784 and 303cm^{-1} which were shown to be due to monomeric CrF_4. On warming, changes occurred in the spectrum which are consistent with a monomeric to polymeric rearrangement [4].

1.4 CHROMIUM(III)

1.4.1 Complexes of simple ligands

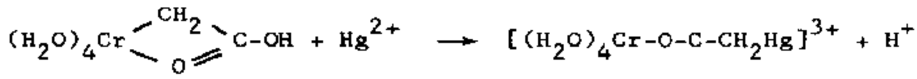
X-ray diffraction and structural refinement on $[Co(NH_3)_5(H_2O)][Cr(CN)_6]$ at 295 and 120 K showed it to be isomorphous with $[Co(NH_3)_6][Cr(CN)_6]$. The data for both compounds were refined using an aspherical valence electron population model. The metal configuration, the observed metal-ligand overlap populations and the ammonia lone pair populations could all be analyzed in terms of a single two parameter per bond σ-bonding LF model, using only metal *d* orbitals [22]. The spin distribution in the anion of $Cs_2K[Cr(CN)_6]$ has been determined by polarized neutron diffraction and analyzed in terms of atomic orbital populations [23].

There has been controversy in the literature as to whether the hydrolysis of aquo Cr(III)-α-hydroxyalkyl complexes proceeds through intervention of a water molecule *cis* to the alkyl group, or whether a solvent water molecule is involved. The hydrolysis of number of such complexes have been studied including $[(edta)Cr(CR_1R_2OH)]^{2-}$ (no coordinated water), and complexes of two quadridentate ligands (nta and [15]aneN_4) which have a coordinated water molecule and the α-hydroxyalkyl group *cis* and *trans* respectively.The results indicate that a water molecule *cis* to the alkyl group has no major role in the hydrolysis mechanism [24]. In addition, the specific rates of reaction of the free radicals $.CH_2OH$, $.CH(Me)OH$ and $.C(Me)_2OH$ with $[Cr^{II}(edta)]^{2-}$ and $[Cr^{II}(nta)]^-$ are reported [24].

The reaction

$$2Cr^{2+} + ICH_2CO_2H \longrightarrow [(H_2O)_5I]^{2+} + [(H_2O)_5Cr(CH_2CO_2H)]^{2+}$$

appears to give the expected products, but the Cr(III) complex has some unusual properties which are best explained by chelation of the organo group. For example, reaction with Hg(II) does not give $[Cr(H_2O)_6]^{3+}$ and an organomercurial as usual [25]. It is suggested that the reaction is



$$(H_2O)_4Cr\overset{CH_2}{\underset{O}{\langle\;\rangle}}C\text{-}OH + Hg^{2+} \longrightarrow [(H_2O)_4Cr\text{-}O\text{-}C\text{-}CH_2Hg]^{3+} + H^+$$

Substitution of $K_3[Cr(NCS)_6]$ with PEt_2Ph or $PEt_2(p\text{-}tol)$ gives the new series of complexes $[Cr(NCS)_4(PEt_2R)_2]^-$ [26]. The solvation of the $[Cr(NCS)_4(morpholine)_2]^-$ anion has been studied in water/methanol mixtures varying from 9.7 to 87.3 volume % MeOH at several temperatures. Mechanisms of substitution are discussed [27].

It has been shown that the coordinated trifluoromethane sulphonate in $[Cr(NH_3)_5(OSO_2CF_3)]^{2+}$ is readily replaced by a large number of *O* and *N* donor ligands including H_2O, MeOH, dmso, $OP(OMe)_3$, dma, MeCN, urea etc thus opening the way to the synthesis of may such derivatives [28].

The displacement of water by dmso in the second coordination sphere of $[Cr(NH_3)_5(dmso)]^{3+}$ has been investigated in dmso/H_2O mixtures by line broadening effects in ^1H NMR spectroscopy. The number of molecules in the second coordination sphere was found to be 10 and stepwise equilibrium constants for the replacement of H_2O by dmso were determined. The free energy increase per replacement is about 1.42 $KJmol^{-1}$ [29].

The determination of the equilibrium constant K for the reaction

$$[Cr(NH_3)_5(H_2O)]^{3+} + Br^- \rightleftharpoons [Cr(NH_3)_5Br]^{2+} + H_2O$$

several years ago by a kinetic method and by the method of mixtures gave two values which differed by an order of magnitude. The actual values have now been verified by new determinations [30]. The descrepancy arises because medium effects and/or other specific effects seriously influence the interpretation of the kinetic data and therefore the value from the method of mixtures is preferred.

The kinetics of the stepwise aquation of *trans*-$[Cr(NH_3)_4(CN)_2]^+$ to *trans*-$[CrCr(NH_3)_4(CN)(H_2O)]^{2+}$ and finally to *trans*-$[Cr(NH_3)_4(H_2O)_2]^{3+}$ have been studied spectrophotometrically in acid solution. Both aquation steps can be described in terms of an acid independent pathway (k_o) and an acid dependent one (k_H), the latter consequent to instantaneous and reversible (K) protonation of some of the reactant. Then

$$k_{obs} = (k_o + k_H K[H^+])/(1 + K[H^+])$$

and although the pattern for dependence for the two steps are different for the two species, both favour the acid assisted pathway. Comparisons with the kinetics of aquation of other cyano complexes of Cr(III) are discussed in detail [31].

The emission spectra of some CrN_4XY complexes (N_4 = 4py, 2en etc) have been examined as a function of glassy solvent at 77 K. When X or Y is F or OH, the splitting of the $^2T_1$ level is reduced in hydrogen bonding solvents. The solvent effect on the spectra depends upon whether the lowest component of $^2T_1$ ($^2E,^Q$) is above or below ^2E in all solvents. If it is above, the spectra are sharp and solvent independent while if it is below the spectra are broader and solvent dependent [32].

The crystal structures of *trans*-$[Cr(NH_3)_4(H_2O)Cl]Cl_2$ and *trans*-$[Cr(NH_3)_4Cl_2]I$ have been determined [33]. Important bond distances are

	$[Cr(NH_3)_4(H_2O)Cl]^{2+}$	$[Cr(NH_3)_4Cl_2]^+$
Cr-Cl	2.298(1)	2.325(1)
Cr-N	2.064(3)-2.086(3)	2.071(2)
Cr-O	2.023(2)Å	

The water exchange between solvent and $[Cr(H_2O)_6]^{3+}$ and $[Cr(H_2O)_5(OH)]^{2+}$ has been investigated by ^{18}O tracer studies at various pH's as a function of pressure. For $[Cr(H_2O)_6]^{3+}$, ln k is a linear function of pressure to 400MPa implying no solvational change in the activation process [34]. The rate of aquation of $[Cr(H_2O)_5F]^{2+}$ has been determined in relatively concentrated

(1-10M) $HClO_4$ solution and compared with the corresponding data for $[Cr(H_2O)_5(N_3)]^{2+}$ [35].

A series of complexes $CrCl_3(py.3COOR)_3$ (R = Me,Et,Pr,Bu) have been prepared with the esters of nicotinic acid being used to prevent coordination of nictinic acid through its carboxylate group. IR studies indicate that all the compounds have the ligand coordinated through nitrogen in a *meridiianal* configuration [36].

1.4.2 Complexes of bidentate ligands

Reactions of substituted biguanidines (Rbiq) and $[Cr(NCS)_6]^{3-}$ in 3:1 molar proportions in refluxing EtOH gave $[Cr(Rbiq)_3](CNS)_3$ [37].

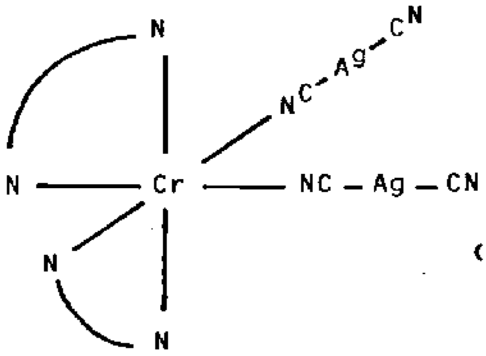
The kinetics have been determined for the quenching of the long lived excited states of $[Cr(L\text{-}L)_3]^{3+}$ (L-L = bipy, phen), and the corresponding ruthenium complexes, by the copper proteins plastocyanin, azurin and stellacyanin. The kinetic behaviour of the reaction with plastocyanin was discussed in terms of model in which the chromium complex binds to the protein at a site remote from the copper atom [38].

The reaction of $[Cr(en)_3]Cl_3$ with KCN in dmso at 80°C gave good yields of *cis*-$[Cr(en)_2(CN)_2]Cl$. The stereochemistry of the cation was elucidated by ion exchange studies, vibrational spectroscopy and by resolution [39].

Irradiation of solid $[Cr(en)_3]_2(C_2O_4)_3.3H_2O$ in the region of the LF $^4A_{2g} \longrightarrow {}^4T_{2g}$ bands gave conversion to $[Cr(en)_2(ox)][Cr(en)(ox)_2]$. The yield was high and the kinetics of the reaction were studied. The products were isolated by ion exchange techniques and fully characterized [40]. The photoaquation of $[Cr(1,3\text{-}pn)_3]^{3+}$ has been studied in both acid and alkali solution by absorption spectroscopy, pH measurements and phosphorescence intensity measurements. It was concluded that two main products, $[Cr(pn)_2(pnH)(H_2O)]^{4+}$ and $[Cr(pn)_2(H_2O)_2]^{3+}$, were formed [41].

Room temperature circular dichroism (CD) spectra have been measured in the spin forbidden $^2E_g, {}^2T_{1g} \longleftarrow {}^4A_{2g}$ transition for diastereoisomers of a number of complexes of Cr(III) containing (R)- or (S)-propylenediamine or (1R,2R)- or (1S,2S)-1,2-*trans*-cyclohexanediamine. The compounds studied were of the types $[Cr(en)_x(diamine)_{3-x}]^{3+}$ (x = 0,2), *cis*-$[Cr(NH_3)_2(diamine)_2]^{3+}$ and $[Cr(NH_3)_4(diamine)]^{3+}$. The differences in the observed CD spectra between each pair of diastereoisomers were accounted for by the separability and additivity of the configurational and vicinal CD effects [42].

Cis-$[Cr(en)_2(CN)_2]^+$ has been shown to interact in solution with other cations such as Hg(I), Ag(I) and Cd(II) and the association constants have been measured. Isolation of the silver salt formed by addition of AgCN and determination of its structure revealed the interesting stereochemistry shown in (1) which shows that linkage isomerism has occurred at the chromium atom. Bond distances were not reported [43].



(1)

A series of complexes of the type $[Cr(Rbiq)_2(NCS)_2](CNS)$ (Rbiq = substituted biguanidine) have been prepared by the interaction of the ligands with $[Cr(NCS)_6]^{3-}$ in 2:1 proportions in refluxing EtOH [44].

Hydrolysis of $[Cr(en)_2(S\text{-}XCOO)]^+$ (X = CH_2, CH_2CH_2, CMe_2) involves an acid catalyzed Cr-S bond cleavage as the first step. The product, $[Cr(en)_2(H_2O)(OOC\text{-}X\text{-}SH)]^{2+}$, can then react in three ways:- (i) the pendant thiol can coordinate to regenerate the starting material (ii) the pendant thiol can anchimerically assist Cr-O bond cleavage to release the complete ligand or (iii) the pendant thiol can assist Cr-N bond cleavage to give further reactive products. The relative rates of these reactions are influenced by the ring size of the chelated ligand and steric effects in the comparisons between X = CH_2 and CMe_2 [45].

A number of mixed chelate complexes of Cr(III) containing en, 1,3-pn and fluoride have been prepared from *trans*-$[Cr(en)F_2(H_2O)_2]Cl$ in refluxing EtOH by the following reaction scheme **(2)**. Heating *trans*-[Cr(en)(pn)FCl]Cl or *cis*-$[Cr(en)(pn)F(H_2O)]Br_2$ gave a mixture of products including *cis*-[Cr(en)(pn)FX]X which on reaction with NH_4F gave *cis*-$[Cr(en)(pn)F_2]^+$ which was resolved [46]. The complete series of fluoro complexes of the type $[Cr(aa)(bb)F_2]^+$ (where aa, bb are diamines such as en, pn, chxn) have been synthesized using the general reaction

$$[Cr(aa)F_2(H_2O)_2]Br + bb \longrightarrow [Cr(aa)(bb)F_2]Br + 2\ H_2O$$

The compounds were all *trans* except for *cis*-$[Cr(en)(pn)F_2]Br$ [47]. The

$$\begin{tikzcd}
\textit{trans}\text{-}[Cr(en)F_2(H_2O)_2]Cl \arrow[d, "1,3\text{-}pn"] & \\
\textit{trans}\text{-}[Cr(en)(pn)F_2]Cl \arrow[d, "HClO_4"] & \\
\textit{trans}\text{-}[Cr(en)(pn)F(H_2O)](ClO_4)_2 \arrow[r, "KCl"] \arrow[d, "NH_4X\ (X = F,Cl,NCS)"] & \textit{trans}\text{-}[Cr(en)(pn)F(H_2O)]Cl_2 \arrow[d, "dry"] \\
\textit{trans}\text{-}[Cr(en)(pn)FX]^+ & \textit{trans}\text{-}[Cr(en)(pn)FCl]^+
\end{tikzcd} \qquad (2)$$

different stereochemistries for $[Cr(en)(pn)F_2]^+$ reported in these two papers may well be correct and due to the different conditions of preparation.

The solid phase thermal dehydration of *trans*-$[Cr(en)_2F(H_2O)][M(CN)_4]$ (M = Ni, Pd, Pt) to give *trans*-$[Cr(en)_2(F)NCM(CN)_3]$ has been investigated by non-thermal DSC together with isothermal and non-isothermal TG methods. The proposed mechanism is S_N1 involving a square pyramidal activated complex and elimination of water as Frankel defects [48].

The crystal structure of *trans*-$[Cr(en)_2F(NH_3)](ClO_4)_2$ has been determined. As expected, the stereochemistry is octahedral with bond distances Cr-F = 1.862(3), Cr-NH_3 = 2.093(6) and Cr-N = 2.057(8)-2.088(6)Å [49].

It has been found that *l*-*cis*-$[Cr(en)_2Cl_2]Cl$ undergoes thermal racemization at 158°C without any *cis* to *trans* conversion. This result is in accord only with the rhombic twist mechanism originally proposed for $[M(aa)_3]^{3+}$ complexes, since the alternative trigonal twist would give both racemization and isomerization [50].

Trans-$[Cr(en)_2Br_2]Br.H_2O$ undergoes efficient photoaquation in the solid state to give *cis*-$[Cr(en)_2Br(H_2O)]Br_2$. The chloride behaves similarly, but no other complex of the type *trans*-$[Cr(en)_2X_2]^+$ was found to be photosensitive [51].

The compounds $(aa\text{-}H_2)[Cr(aa)F_4]Cl$ (aa = en, chxn) have been prepared by the interaction of $CrCl_3.6H_2O$, HF and the ligand. The crystal structure of the en complex showed an octahedral stereochemistry for the anion with Cr-F = 1.885(10)-1.930(4) and Cr-N = 2.079(6)Å(av). The compounds hydrolysed in HBr solution to give $[Cr(aa)F_2(H_2O)_2]$ [52].

$CrCl_3$ reacts with guanine (LH) in refluxing EtOH/triethylformate to give $CrCl_3(LH)_2$. IR evidence suggested that the ligand was not bonded through the exocyclic groups (CO and NH_2) and that all the chlorines were terminal. A polymeric octahedral structure with one chelated and one bridging LH ligand was postulated [53].

The kinetics of the reaction between $[Cr(H_2O)_6]^{3+}$ and L-cysteine have been investigated. A simple first order process was observed which suggests that ring closure is rapid. The results are strikingly similar to those of an earlier study of the glycine/Cr(III) system which suggests that a *N,O* complex is formed initially [54]. The stability of glycine (HG) complexes of Cr(III) have been determined by paper electrophoresis to be $[CrG]^{2+}$ $10^{8.07}$, $[CrG_2]^+$ $10^{14.32}$ and CrG_3 $10^{19.23}$ [55].

The solubility of $Cr(acac)_3$ has been measured in $H_2O/{}^tBuOH$ and $H_2O/MeOH$ mixtures as a function of temperature and the thermodynamic parameters of solution calculated [56]. New complexes of the types $[Cr(acac)_{3-x}(L\text{-}L)_x]^{n+}$ (L-L = $bipyO_2$, 3,3'-Me_2bipyO_2) have been prepared. The number of conformational isomers differed in the two series as a result of the steric interactions of the methyl groups in the latter ligand. The isomers were resolved with visible and CD spectra being recorded. Isomerization occurred via an intermolecular conformation inversion of the $bipyO_2$ ring and racemization occurred via an intermolecular twist mechanism [57].

CrO_3 reacts with SO_2 in dmso to give $Cr_2(S_2O_7)_3.24dmso$ which is the first disulphate of Cr(III) [58].

The chiral octahedral complex tris((-)cyclic O,O'-1(R)2R dimethylethylenedithiophosphato)chromium(III) has been prepared in EtOH solution. CD spectra in various solvents show a configurational inversion occurs which gives the diastereoisomeric equilibrium [59]

$$\Lambda\text{-}(R,R)(R,R)(R,R) \rightleftharpoons \Delta\text{-}(R,R)(R,R)(R,R)$$

The sodium salt of N-benzoylglycine (hippuric acid, hipH) reacts with $CrCl_3(thf)_3$ in refluxing MeOH to give $Cr(hip)_3$ with the ligand acting as a bidentate. Mixed carboxylates $Cr(hip)_{3-x}(carboxylate)_x$ were also synthesized together with some adducts $Cr(hip)_3.2L$ (L = py, thf etc) in which one hippuric acid group is displaced as free anion [60].

It has been found that Pb^{2+} strongly catalyzes the aquation of $[Cr(ox)_3]^{3-}$ to *cis*-$[Cr(ox)_2(H_2O)_2]^-$. The catalysis is greater than would be expected on the basis of a previously determined relationship (for some transition metals) between the rate of catalysis and K_{M-ox}, the formation constant for the first oxalato complex [61].

The electronic structure of *trans*-$[Cr(ox)_2(py)_2]^-$ has been calculated by the spin polarization SCF-Xα-SW method. The ground state for Cr^{3+} is $^4B_{1g}$ and the calculated electronic spectrum associated with *d-d* and pyridine $\pi\text{-}\pi^*$

transitions agrees well with the experimentally observed spectrum. However, the calculated energies of ligand to metal charge transfer transitions show poor agreement [62].

The complexes *cis* and *trans*-H[Cr(mal)$_2$(nic-N)$_2$] were synthesized starting from Cr(II) solutions and their stereochemistries determined using ^{2}D NMR studies [63]. Complexes of sulphosalicylic acid (SsalH$_3$) have been prepared for a number of M(III) ions including Cr(III). The species [Cr(Ssal)(H$_2$O)$_4$] and Cs$_3$[Cr(Ssal)$_2$(H$_2$O)$_2$] were isolated and characterized by electrophoresis, IR and ion exchange studies. It was concluded that the ligand bonds through the carboxylate and phenolate oxygen atoms [64].

The 1:1 charge transfer adducts between Cr(dtc)$_3$ compounds and iodine have been investigated and compared with those formed between thiuramdisulphides and iodine. The latter form slightly stronger complexes, reflecting the lower basicity of the sulphur atoms on coordination [65].

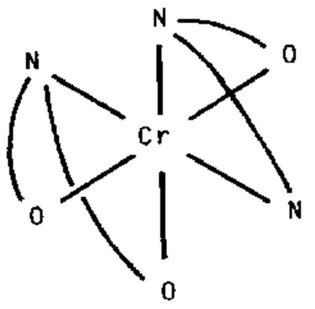
Complexes of dibenzoyldisulphide (L) with a number of transition metal halides have been reported and CrCl$_3$ reacts to give CrCl$_3$L. IR spectra indicate chelation of the ligand through its two oxygen atoms with sulphur taking no part in the coordination. A polymeric structure with chlorine bridges was proposed to give an octahedral arrangement about chromium [66].

1.4.3 Complexes of polydentate ligands

CrCl$_3$(thf)$_3$ reacts with K[HB(pyz)$_3$] in dichloromethane to give [CrCl$_3$(HB{pyz}$_3$)]$^-$, isolated as the (AsPh$_4$)$^+$ salt. This anion reacts with nitrogen bases L (such as py, pyz) to easily replace one halogen to give CrCl$_2$(HB{pyz}$_3$)L and a crystal structure determination on the py compound showed the donor atoms of the tridentate ligand to be arranged in the *facial* arrangement. Bond distances are Cr-Cl = 2.311(1), Cr-N(py) = 2.108(3), Cr-N = 2.043(3)-2.065(3)Å [67].

The complex (L-alanine-N-acetato)(L-histidinato)chromium(III) monohydrate has been synthesized and its crystal structure determined by X-ray diffraction. The L-alanine ligand coordinates as the dianion through two oxygens and one nitrogen while the histidine ligand coordinates through two nitrogens and one oxygen. Each ligand coordinates in a *facial* geometry, but the arrangement of donor atoms about the metal is *meridional* as shown in (3) [68].

The crystal structure of bis(salicylaldehydethiosemicarbazonato(1-)) chromium(III) perchlorate, [Cr(C$_8$H$_8$N$_3$OS)$_2$](ClO$_4$).3H$_2$O, has been determined. The cation has a bis tridentate *(S,N,O) meridional* ligand arrangement with the *S* and *O* donor atoms of the ligands *cis* to each other and the nitrogen atoms *trans*. Bond lengths are Cr-O = 1.937, Cr-S = 2.416 and Cr-N = 2.038Å [69].

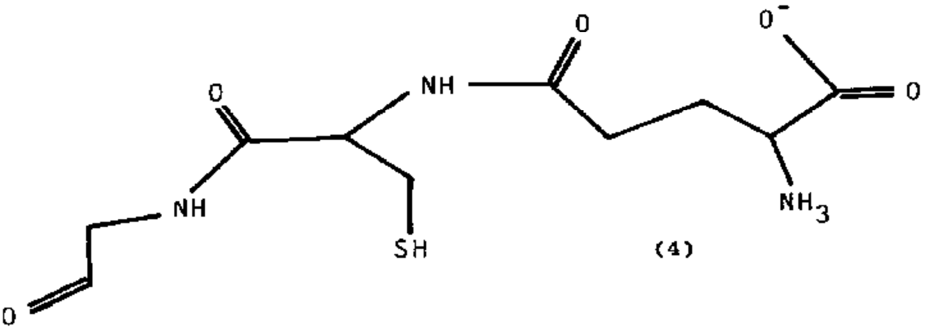


(3)

Bond distances are

(alanine ligand)		(histidine ligand)	
Cr-O(acetyl)	= 1.960(3)	Cr-N(amine)	= 2.062(4)
Cr-O	= 1.946(4)	Cr-N(imid)	= 2.036(5)
Cr-N	= 2.078(5)	Cr-O	= 1.957(4)Å

The compounds $K_2[Cr(H_3L)(H_2L)].3H_2O$ and $K_2[Cr(H_2L)(A)].nH_2O$ have been prepared (where H_5L = glutathione (4) and A = anion of amino acids such as L-cysteine, L-glutamic acid and L-aspartic acid). All show intense charge transfer bands associated with Cr-S bonds. Comparison with the IR spectra of other compounds suggests that glutathione is coordinated through a deprotonated sulphur and the terminal glycine *(N,O)* group with the glutamic acid residue also interacting with chromium [70].



(4)

The magnetic properties of the linear chain molecules $[Cr(Pc)F]_n$ and $[Cr(Pc)(CN)]_n$ have been measured over the temperature range 4.2-225 K. The fluoro compound shows antiferromagnetic exchange with $J = -12.2 cm^{-1}$ and g = 2.00 whilst the data for $[Cr(Pc)(CN)]_n$ indicates ferromagnetic exchange with

$J = 0.2cm^{-1}$ and $g = 1.98$. This is the first example of ferromagnetic coupling in a linear chain Cr(III) compound. The differences between the systems were discussed in terms of the electronegativities of the bridges and the orbitals which transmit the superexchange interactions [71].

The interactions of Cr(TPP)Cl with various nitrogen bases in dichloromethane have been investigated spectrophotometrically. It was found that axial ligation is rapid and that a correlation exists between ln K for the equilibrium

$$\mathrm{Cr(TPP)Cl} + \mathrm{L} \xrightleftharpoons{K} \mathrm{Cr(TPP)(Cl)L}$$

and pK_a for the ligand, thus suggesting a predominantly σ-bonding interaction in the adducts [72].

Reaction between Cr(TPP)Cl with various thioglycollate esters in chloroform in the presence of NMe_4OH gave intensely coloured green solutions which are thought to contain bis(thiolate)Cr(III)(TPP) species [73]. The Soret band in the near UV spectrum was split in a manner similar to that of cytochrome P_{450} in the reduced state in the presence of carbon monoxide.

It has been found that oxidative cleavage of 1-phenyl-1,2-ethanediol to give benzaldehyde stoichiometrically occurs in the presence of Cr(TPP)Cl and the exogeneous oxidant 4-cyano-N,N-dimethylaniline-N-oxide. This carbon-carbon lyase reaction is analogous to one step in the removal of the side chain of cholesterol by cytochrome $P\text{-}450_{SCC}$. The process involves transfer of an oxygen atom from the N-oxide to chromium to give Cr(TPP)O followed by reaction of this species with the diol, regenerating Cr(TPP)Cl [74].

Cr(TPP) reacts with oxygen to give Cr(TPP)O and these species interact to give (TPP)Cr-O-Cr(TPP) as a blue, very air sensitive material which reacts with excess oxygen to give Cr(TPP)O. The magnetic moment of the dimer at room temperature is 1.61 BM per chromium atom and its variation with temperature indicates antiferromagnetic coupling. An IR band at $860cm^{-1}$ is assigned to the Cr-O-Cr linkage [75]. Similar hetero dinuclear complexes (P)Cr-O-Fe(P') were prepared by the interaction of $Cr^{IV}(P)O$ and $Fe^{II}(P')$ where P and P' are the dianions of different porphyrins. These dinuclear complexes react with only one mole of heterocyclic bases and a partial structural determination of the py adduct showed the base to be coordinated to chromium. The magnetic properties of the complexes were interpreted in terms of strong antiferromagnetic coupling between Cr(III) ($S = 3/2$) and Fe(III) ($S = 5/2$) centres with $J = -130$ to $-150cm^{-1}$ [76].

Complexes of 1,4,7,10-tetraazacyclotridecane, [13]aneN_4, (L), have been prepared for a number of first row transition metals including Cr(III). Reaction of $CrCl_3.3H_2O$ and L in a mixture of dmf and 2,2-dimethoxypropane gave violet crystals of *cis*-$[CrCl_2L]Cl.H_2O$, the *cis* configuration being confirmed by the electronic spectrum [77]. There is a trend in the stereochemistries of Cr(III) complexes from $[12]aneN_4$ to $[15]aneN_4$ with the [12] and [13] ligands giving *cis* complexes exclusively, [14] gives a mixture of *cis* and *trans* while $[15]aneN_4$ gives only *trans* complexes. This trend is related to the size of the cavity in the ligand.

Cis-$[Cr(NCS)_2(tetb)]CNS$ has been resolved using potassium antimonyl(+)tartrate and then converted back to the thiocyanate salt (tetb = (RR);(SS)-C(5,12)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane. It was found that the chiroptical properties show extensive solvent dependence. This was attributed to the fact that the 5 and 6 membered rings are of opposite helicity and the solvent properties depend upon which ring pair is dominant in a particular solvent [78].

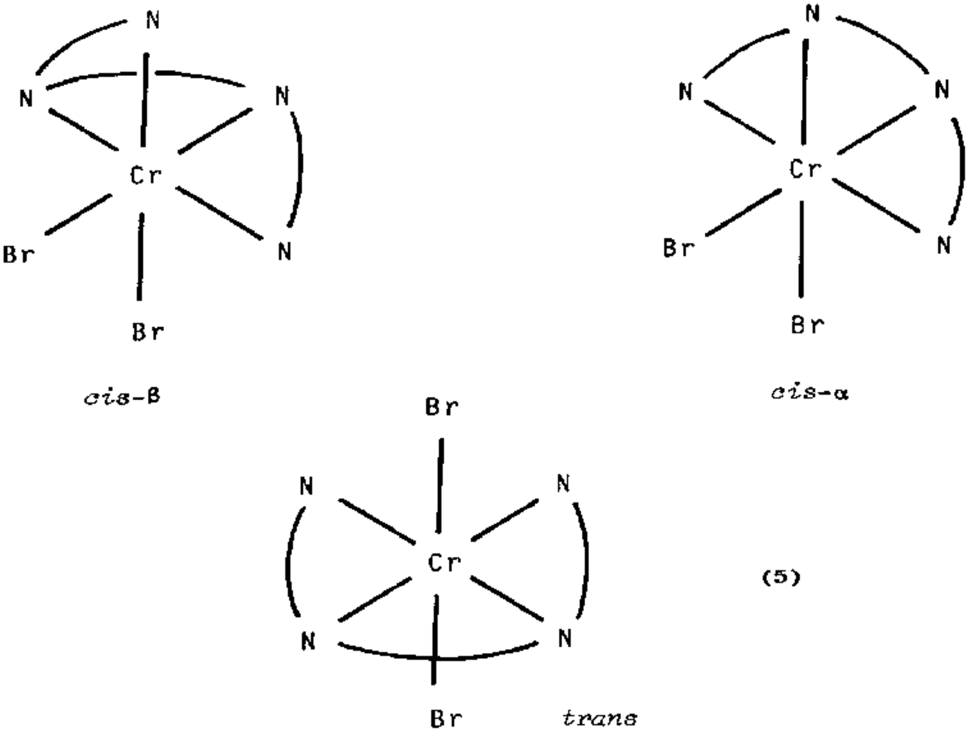
The crystal structure of *trans*-$[Cr(L)(H_2O)Cl](NO_3)_2$ (L = 5,5,7e,12,12,14e-hexamethyl-1,4,8,11-tetraazacyclotetradecane) has been determined. The macrocyclic ligand is planar and the *sec* NH protons adopt the *meso* R(SSR) configuration and the Me groups at the 7 and 14 positions adopt an equatorial orientation. Bond distances are Cr-Cl = 2.307(2), Cr-O = 2.090(6) and Cr-N = 2.074(11)-2.102(7)Å [79].

The crystal structure determination of *trans*-$[Cr(L)(NCS)(H_2O)])CNS)_2$ (L = $[15]aneN_4$) shows that the ligand forms an equatorial belt about the metal atom with all four N-H bonds orientated to one side of the metal, away from the water ligand and towards the thiocyanato ligand. Bond distances are Cr-O = 1.997(4), Cr-NCS = 1.976(4) and Cr-N = 2.050(7)-2.108(6)Å [80].

In anhydrous solvents Cr(III) reacts with 1,5,9,13-tetraazacyclohexadecane (L) to give species containing the CrL unit which appear to exist in one *cis* and at least two *trans* forms [81].

Linear aliphatic tetraamines $NH_2(CH_2)_nNH(CH_2)_mNH(CH_2)_nNH_2$ (denoted as n,m,n-tet) have been reacted with $[Cr(NH_3)_6]Br_3$ and the products identified as $[Cr(tet)Br_2]Br$. The ligands used were 1,4,7,10-tetraazadecane (2,2,2-tet), 1,4,8,11-tetraazaundecane (3,2,3-tet) and 1,5,8,12-tetraazadodecane (3,2,3-tet). With 2,3,2-tet all three possible isomers of $[Cr(tet)Br_2]Br$ shown in **(5)** were isolated although *cis*-α is the thermodynamically stable isomer. In the solid state *cis*-β converts to *cis*-α at 20°C and the *trans* isomer converts to *cis*-α at 200°C [82].

Reaction of Cr(III) salts with *m*-phenylenediamine and 2,3-butanedione in refluxing MeOH gave greyish green compounds which, on the basis of IR, magnetic and electronic spectral data, were formulated as containing the macrocyclic ligand **(6)** bound to chromium with the anions (Cl,Br,NCS) completing the octahedral geometry about the metal [83].

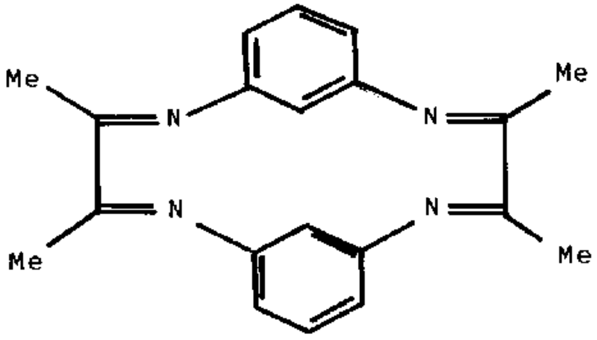


cis-β

cis-α

trans

(5)



(6)

The decomposition reaction of H_2O_2 in the presence of $[Cr(edta)(H_2O)]^-$ proceeds via two pathways in which both the aquo and the hydroxy-edta complexes act as catalysts. Substitution controlled mechanisms were proposed for the reactions [84].

The studies of ^2D NMR of Cr(III) complexes reported in previous reviews have been extended to include fully and partially deuterated edta and related ligands. The hexadentate coordination of cdta (= 1,2-cyclohexanediamine-N,N,N',N'-tetraacetate) and pdta (the 1,2-propanediamine analogue) was demonstrated by ^{2}D NMR spectroscopy. For the first time assignments of the contact shifted ^{2}D resonances were made whereas in previous studies structures had been deduced simply from the number of resonances and the possible molecular symmetries [85].

1.4.4 Dinuclear complexes

New dinuclear complexes of the types $[(NH_3)_5MNCCr(CN)_5]$ (M = Rh,Ir) and $[(NH_3)_5MNCCr(NO)(CN)_4]$ (M = Co,Rh,Ir) have been prepared by heating in the solid state the double salts $[M(NH_3)_5(H_2O)][Cr(CN)_6]$ and $[M(NH_3)_5(H_2O)][Cr(NO)(CN)_5]$ respectively. The solid state deaquation-anation reactions were followed by TG measurements. Activation energies were in the range (101.4±5 - 127.8±5)KJmol^{-1} and these low values were taken as an indication that an S_N1 dissociative mechanism with a square pyramidal intermediate was operating [86].

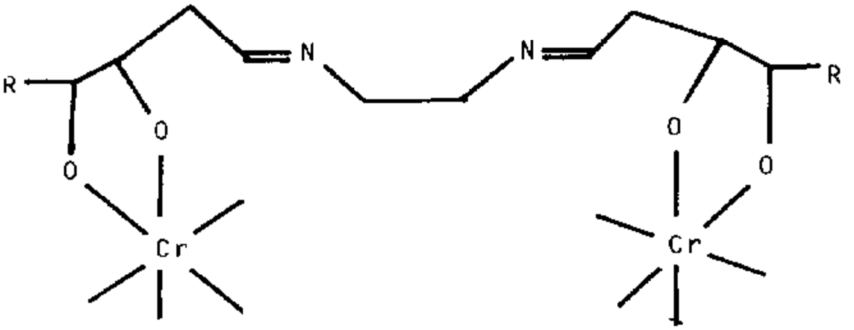
Single crystal EPR spectra have been observed over a wide temperature range for the complexes $[LCr(OH)_3CrL]X_3{\cdot}nH_2O$ (X = I, n = 3; X = ClO_4, n = 1; L = 1,4,7-trimethyl-1,4,7-triazacyclononane). The zero field splittings of each excited state (S = 1,2,3) in the exchange coupled system (-2J = 128cm^{-1}) were derived [87].

The magnetic susceptibility of di-μ-hydroxobis[{(S)alaninato}chromium(III)] trihydrate has been measured over the temperature range 1.8-290 K. The molecule is known to contain a highly distorted Cr_2O_2 unit and so provides a stringent test of the proposed correlation between J and the geometry of the bridging groups. The experimental data show that a simple averaging of parameters for the two bridges is not sufficient and further theoretical work is required to fully understand the interactions in this type of system [88].

It has been found that perchlorate catalyses the oxo-bridge cleavage in $[(H_2O)_5Cr\text{-}O\text{-}Cr(H_2O)_5]^{4+}$ almost as well as chloride and bromide ions. Furthermore, anation of Cr(III) is not the operative mechanism since only $[Cr(H_2O)_6]^{3+}$ is observed as the product in all cases and none of the inert $[Cr(H_2O)_5Cl]^{2+}$ was observed even under conditions when the chloride catalysed pathway predominates. The proposed mechanism involves bending of the originally linear Cr-O-Cr unit followed by protonation of the emergent lone pair on the μ-oxo group [89]. It has been found that both strong and weak reductants, such as $[Cr(H_2O)_6]^{2+}$ and ascorbic acid, also catalyse the acid hydrolysis of $[(H_2O)_5Cr\text{-}O\text{-}Cr(H_2O)_5]^{4+}$ to give only $[Cr(H_2O)_6]^{3+}$. Electrochemical studies on the aquo dimer show an irreversible one-electron reduction ($E_{1/2}$ = +0.52V vs SHE) which is about 0.93V more positive than for $[Cr(H_2O)_6]^{3+}$. This may be understood in terms of electron acceptance into the essentially non-bonding $e_g(\pi)$ MO of the linear Cr-O-Cr system which disrupts $2p_\pi(O) - 3d_\pi(Cr)$ overlap, leading to bridge rupture [90].

Chromium(III) catalyses the oxidation of EtOH by chloranilic acid (2,5-dihydroxy-3,6-dichlorobenzoquinone = H_2L). Kinetic and spectrophotometric studies indicated formation of a binuclear complex Cr_2L as the active catalytic species [91].

The condensation of the triketone 2,2-dimethyl-3,5,7-octatrione, H_2PAA, with en gave $(H_2PAA)_2en$. Reaction of this ligand with $Cr_2(OAc)_4$ and recrystallization of the product from pyridine gave $Cr_2[(HPAA)_2en]_3.6py.H_2O$ which was examined by X-ray crystallography. Remarkably, the ligand is in the unfolded form with the two 1,3-diketonate moities bonded to different chromium atoms as shown in **(7)** [92].



(7)

Three such ligands are coordinated in this manner to give a Cr-Cr separation of 10.3A!.

The structure of monoclinic $NaBaCr_2F_9$ has been determined. The lattice is built of tilted double *cis* chains of $[Cr_2F_9]_n^{3n-}$, containing octahedrally coordinated chromium, linked by the Na^+ and Ba^{2+} ions. Bond distances are Cr-F(t) = 1.86 and Cr-F(b) = 1.92-1.95Å [93].

The energy dispersion of the singlet-triplet dimer exciton in $Cs_3[Cr_2Cl_9]$ has been studied by inelastic neutron scattering at temperatures down to 1.3 K. Three exchange parameters were determined; intradimer, interdimer-intrasublattice and interdimer-intersublattice. The systematic variation of the exchange parameters with substitution of chloride by bromide and iodide were discussed [94].

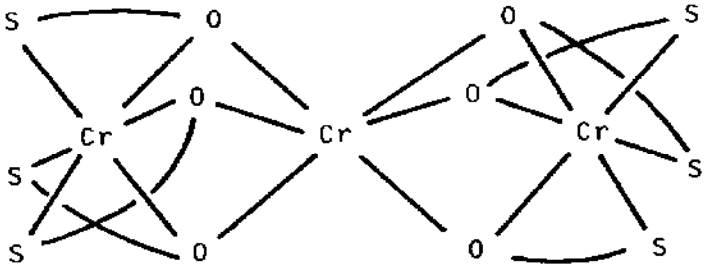
1.4.5 Polynuclear complexes

It has been suggested previously that dynamic rather than static distortions best explain the magnetic susceptibility data for $[Cr_3O(OAc)_6(H_2O)_3]^+$. However, it has now been shown [95] that the complex undergoes a phase transition at 211.4 K and optical spectral data clearly show the presence of two types of trimer in the solid state at low temperatures. Hence the distortions at low temperature must be static.

The complexes $[Cr_nFe_{3-n}O(glycinate)_6(H_2O)_3]^{3+}$ (n = 1,2,3) have been prepared in EtOH/H_2O media at pH 2. The composition of the $CrFe_2$ complex was confirmed by a structure determination. At low pH's glycinate can be made to coordinate through the two oxygens of the carboxylate because the amino acid is in the Zwitterion form [96].

Reaction of $Cr_2(OAc)_4$ with metal acetates in pyridine solution in air gives the complexes $[Cr_2MO(OAc)_6(py)_3]$ (M = Mg,Co,Ni) which have basically the same geometrical structure as the $[Cr_3O(OAc)_6(H_2O)_3]^+$ cations. The trimetallic complexes $[CrFeMO(OAc)_6(py)_3]$ (M = Mn,Fe) were also prepared and the magnetic interactions between the metal ions were investigated in detail. They exhibit antiferromagnetic exchange and the strength of the Cr(III)-Cr(III) and the Cr(III)-Fe(III) interactions are largely independent of the nature of M(II), but approximately double those in the $[Cr_3O]^+$ cation. This suggests that the central oxygen provides the main superexchange pathway in these compounds [97].

Reaction of $CrCl_3(thf)_3$ with 2-hydroxyethanediol ($hetH_2$) in the presence of base yielded $Cr_3(het)_6$. A crystal structure determination revealed the interesting structure of a linear trimer with ligands chelating to the outer chromium atoms and the alkoxide groups acting as μ_2-bridges to give an octahedral array of O_3S_3 about the outer chromiums and an O_6 array about the inner chromium as shown in (8) [98].



(8)

There has been a re-appraisal of the structures of $[Cr_3(OH)_4]^{5+}$ and $[Cr_4(OH)_6]^{4+}$ which are early members of the series leading to the complete polymerisation of $[Cr(H_2O)_6]^{3+}$ solutions as the pH is raised. It is now suggested that the unusual formulations for the aquo species (see Review for 1983) are unnecessary, as the acidic character of the complexes can be explained in terms of internal hydrogen bonding. A series of structures involving more usual μ_2-OH bridges and hydrogen bonding is now proposed [99].

$Cr_2(mhp)_4$ (mhp = anion of 6-methyl-2-hydroxypyridine) in warm thf or diglyme gave a dark green solution from which was isolated $Cr_4(OH)_4(mhp)_8$. A crystal structure determination revealed a distorted cubane-type $Cr_4(OH)_4$ core, arranged such that there are two long Cr-Cr diagonals of 2.974(1)Å across two Cr_2O_2 faces and four short Cr-Cr diagonals of 2.829(1)Å. Four of the mhp ligands bridge the short diagonals between chromium atoms, whilst the remaining four bond to chromium atoms through oxygen and H-bond to a μ_3-OH group through nitrogen [100].

1.4.6 Photochemistry

Phosphorescence lifetimes and their temperature dependencies have been determined for $[Cr(NH_3)_5(CN)]^{2+}$ and *cis* and *trans*-$[Cr(NH_3)_4(CN)_2]^+$ in a variety of solvents. The lifetimes are in the 10-100μs range, which is relatively long for Cr(III) acidoammines. Considerable solvent effects were observed and the results are discussed in terms of the various processes effecting the lifetime of the doublet state [101].

The emission lifetimes of a number of Cr(III) complexes such as $[Cr(NH_3)_6]^{3+}$, $[Cr(ND_3)_6]^{3+}$, $[Cr(en)_3]^{3+}$ and *trans*-$[Cr(en)_2F_2]^+$ etc have been examined in aqueous solution as a function of pressure up to 207MPa. The apparent volumes of activation range from 0.1mLmol^{-1} for *trans*-$[Cr(cyclam)(CN)_2]^+$ to +6.9mLmol^{-1} for $[Cr(NH_3)_5(NCS)]^{2+}$. The effects of applied pressure on the LF absorption bands of some compounds and the doublet state emission spectrum of $[Cr(NH_3)_6]^{3+}$ were also examined [102].

The compounds *cis* and *trans*-$[Cr(cyclam)(NH_3)_2]^{3+}$ have been prepared from the corresponding dinitrato complexes in liquid NH_3. Both isomers exhibit strong phosphorescence in solution at room temperature. The emission of the *trans* isomer is very intense and long lived (136μs in dmso at 20°C) and shows a 12-fold enhancement on N-H deuteration. The *cis* isomer has a much shorter emission lifetime and shows only a weak deuterium isotope effect. Possible rationalizations of these effects are discussed [103].

Electronic absorption and emission spectra, lifetimes and phosphorescence yields of the lowest lying doublet states have been measured for the hexamine Cr(III) cage complexes $[Cr(sar)]^{3+}$ and $[Cr(diasar)]^{3+}$ (sar = 1,4,8,11,15,18-hexaazabicyclo[666]icosane; diasar = 3,6,10,13,16,19-hexaazabicyclo[666]-icosane). The photophysics were found to be markedly different to those of $[Cr(en)_3]^{3+}$. This has led to a questioning of the mechanism of relaxation of the excited states in this type of molecule. The earlier work with $[Cr(sep)]^{3+}$ was interpreted as favouring surface crossing to a reactive ground state intermediate with higher coordination number, but this work favours back intersystem crossing from the doublet state to an excited quartet state [104].

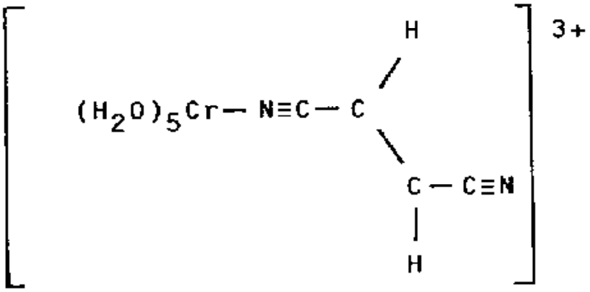
1.5 CHROMIUM(II)

1.5.1 Simple compounds of chromium(II)

The reaction of Cr(II) with the fumaronitrile complexes of Co(III) and with fumaronitrile itself have been investigated in detail. The reaction between $[(NH_3)_5Co(NCCH{=}CHCN)]^{3+}$ (A) and Cr(II) follows the rate law

$$-d\ln[A]/dt = k[Cr^{2+}]$$

with $k = (1.9\pm0.2) \times 10^5 M^{-1}s^{-1}$ (25°C, 0.50M $LiClO_4/HClO_4$). The products of the reaction after separation by ion exchange were $[Co(H_2O)_6]^{2+}$, $[Cr(H_2O)_6]^{3+}$ and fumaronitrile in equimolar proportions. When the reaction was carried out with a slight deficiency of Cr(II) an intermediate was detected spectrophotometrically which, based on its absorption spectrum and its rate of aquation to $[Cr(H_2O)_6]^{3+}$ was thought to be (9).

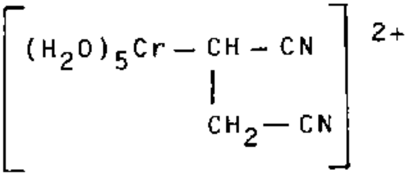


(9)

Cr(II) reacts with fumaronitrile with a complex series of colour changes from blue to red (20 mins) to blue green (200 mins) so that the reaction is not simply

$$2Cr^{2+} + 2H^+ + NCCH{=}CHCN \qquad NCCH_2CH_2CCN + 2Cr^{3+}$$

although the final product was shown to be succinamide. It was shown that 2mol of Cr^{2+} per mole of fumaronitrile are involved in the first stage of the reaction and that no further Cr^{2+} is involved in the latter part of the reaction. Several intermediates were separated by ion exchange techniques and all were thought to contain Cr-C linkages, one example being (10) [105].

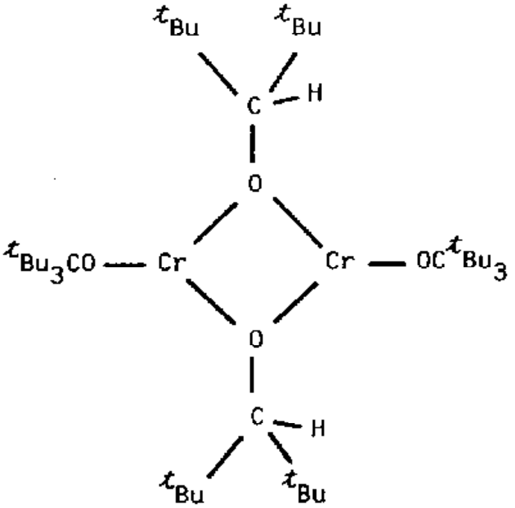


$$\left[(H_2O)_5Cr-CH(CN)-CH_2-CN\right]^{2+}$$

(10)

The reductions of Co(III) cysteinesulphonato and cysteinesulphinato derivatives containing en by Cr(II) have been investigated by stopped flow spectrophotometry [106].

When the green complex $[Cr\{OC^{t}Bu_3\}_2.LiCl.(thf)_2]$ (described in the Review for 1983) is dissolved in warm hexane LiCl is precipitated and a blue green complex is obtained. An X-ray structural analysis showed it to be $[Cr(\mu\text{-}OCH^{t}Bu_2)(OC^{t}Bu_3)]_2$ containing roughly trigonal three coordinate Cr(II) as shown in (11). The bridging ligands are derived from tri-*t*-butylmethoxide by elimination of C_4H_9 which was detected by CG/MS analysis [107].



(11)

Bond distances are

Cr-Cr = 3.075(1)

Cr-μO = 1.974(av)   Cr-O = 1.838(3)Å

Electron diffraction studies on $CrCl_2$ at 895°C suggested the compound exists as a bent monomeric species with about 30% of a dimeric form with two bridging chlorine atoms also present [108]. The geometrical parameters derived from the analysis are

	monomer	dimer
Cr-Cl(t)	2.207(10)	2.208(8)
Cr-Cl(b)		2.353(10)Å
Cl(t)-Cr-Cl(t)	72°	
Cl(b)-Cr-Cl(b)		82°

There has been a detailed study of the optical spectrum of single crystals of the two dimensional ferromagnet $(MeNH_3)_2[CrCl_4]$ in the region of the quartet to triplet LF transitions at 5330 and 6270Å from 1.6-9 K. Below 2 K there is evidence for cold band intensity arising from a small amount of spin canting [109].

The thf adduct of $CrCl_2$ reacts with dmpe to give *trans*-$CrCl_2(dmpe)_2$. Bond distances are Cr-Cl = 2.348(av) and Cr-P = 2.368Å(av). It reacts with LiMe to give *trans*-$CrMe_2(dmpe)_2$ which has bond distances of Cr-C = 2.168(4) and Cr-P = 2.345Å(av) [110].

$(NMe_4)[CrBr_3]$ has been prepared by the addition of NMe_4Br to a solution obtained by the reaction of chromium metal with HBr gas in glacial acetic acid. X-ray powder diffraction patterns are similar to those of the fully characterized chloro analogue. The magnetic susceptibility data at low temperatures was analyzed in terms of the linear chain model and it shows the compound to be antiferromagnetic [111].

1.5.2 Metal-metal bonded species

Generalized moleclar orbital and CI calculations on $Cr_2(O_2CH)_4$ and $Cr_2(\{NH\}_2CH)_4$ at various Cr-Cr bond lengths have been reported. The calculations show that the Cr-Cr bond length in the aminoiminato complex is 0.48Å shorter than in the formato complex. This is due to the stronger donor $(NH)_2CH$ causing the chromium orbitals to expand, thus giving better Cr-Cr overlap. Although axial ligation effects the Cr-Cr distance, these theoretical studies show that the nature of the bridging group does effect it also [112]. Hartree-Fock-Slater calculations have been performed on $M_2(O_2CH)_4$ and $[M_2(O_2CH)_4]^+$ (M = Cr,Mo,W) to yield the M-M bond distances and force constants. For the cations, the three alternatives of the electron being removed from σ,π and δ orbitals were considered [113].

The kinetics of the reaction between $Cr_2(O_2CMe)_4$ and $[I_3]^-$ have been studied in HOAc in the presence of NaI. The reaction is rapid and the spectrum of the final Cr(III) product closely resembles that of $[Cr_3O(OAc)_6(H_2O)_3]^+$. The kinetics support a mechanism of diiodide adduct formation (presumably axial) before dissociation into monmeric species and subsequent oxidation to Cr(III) [114].

1.6 CHROMIUM(I) AND CHROMIUM(0)

The electronic and geometric structures CrH^+, $CrCH_3{}^+$, $CrCH_2{}^+$ and $CrCH^+$ have been investigated by *ab-initio* MCSCF and CI methods. The ligands CH_3, CH_2 and CH form single, double and triple bonds respectively with Cr^+ [115].

Reduction of *trans*-$CrCl_2(dmpe)_2$ under N_2 by Na/Hg in thf gave red *trans*-$Cr(N_2)_2(dmpe)_2$, although if the time taken for the reaction was limited some brown crystals were isolated which are thought to be of the *cis* isomer. A crystal structure determination of *trans*-$Cr(N_2)_2(dmpe)_2$ gave the bond distances Cr-N = 1.874(3), Cr-P = 2.2970(5) and N-N = 1.122(3)Å. The shortness of the Cr-P bonds compared with those in *trans*-$CrMe_2(dmpe)_2$ suggests that some back bonding to phosphorus occurs in the dinitrogen complex [115].

Cr atoms were co-condensed with water in an argon matrix at 15 K. An adduct was formed resulting in a decrease of the ν_2 bending mode of water by 13.1cm^{-1}. Photolysis of the adduct caused insertion of chromium to give HCr(OH) which is non-linear [116].

ACKNOWLEDGEMENT

I thank Penny Panagiotidou for carefully proof reading the manuscript.

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