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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 100 and 101. Thus most of the work published in 1984 and some published towards the end of 1983 will be reviewed. Although chromium organometallic chemistry is not formally included in this review, 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 and, for convenience, this large segment of the review is divided into sections according to the nature of the ligands.

[†] NO REPRINTS AVAILABLE.

1.1 CHROMIUM(VI)

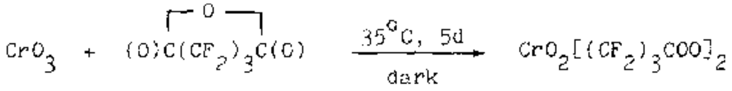
$Cs_2Mg(CrO_4)_2.6H_2O$ contains discrete regular tetrahedral $[CrO_4]^{2-}$ ions with $Cr{=}O = 1.650Å(av)$ [1]. Volumes of activation for the base hydrolysis of $[Cr_2O_7]^{2-}$ have been measured at 20°C using high pressure stopped flow spectrophotometry. The values of ΔV^* for OH^-, NH_3, H_2O and 2,6-lut as base are -17.9 ± 0.6, -19.2 ± 0.9, -24.9 ± 0.9 and -26.0 ± 0.7 respectively and are consistent with the (Ia) mechanism deduced from kinetic studies on the same systems [2]. The cyclic polyether 18-crown-6 solubilizes chromate in $CHCl_3$ to give a solution which is stable in the dark. However, light causes decomposition which has been followed spectrophotometrically. $[HCrO_4]^-$ and CrO_2Cl_2 were detected as intermediates in the decomposition to Cr(III) [3].

Chromyl chloride reacts almost quantitatively at 0°C with F-*tert*-butyl hypochlorite according to the equation

$$CrO_2Cl_2 \;+\; 2(CF_3)_3COCl \;\longrightarrow\; CrO_2[(CF_3)_3CO]_2 \;+\; 2Cl_2$$

to give chromyl F-*tert*-butoxide. This new chromium compound is a thermally stable orange liquid, although it is decomposed by light. It is extremely sensitive to water yielding a yellow Cr(VI) solution and CF_3COH [4].

The reaction between CrO_3 and excess perfluoroglutaric anhydride gives chromyl perfluoroglutarate in almost quantitative yield



$$CrO_3 \;+\; (O)C(CF_2)_3C(O) \xrightarrow[\text{dark}]{35^\circ C,\ 5d} CrO_2[(CF_2)_3COO]_2$$

It is a brown solid which readily hydrolyzes to H_2CrO_4. An analogous complex was obtained using perfluorosuccinic anhydride. The involatility of both compounds suggests a polymeric structure with the bifunctional group acting as a bridge between chromium centres. The IR spectrum of the glutarate complex showed Cr=O stretches at 970 and 950cm^{-1} [5]. Similarly, CrO_3, K_2CrO_4 and CrO_2Cl_2 all dissolve in chlorosulphuric acid to give $CrO_2(SO_3Cl)_2$. The dark green solid has been isolated and characterized by analytical, conductance and IR methods [6].

The reaction between aqueous $Na_2Cr_2O_7$ and galena (PbS) is commonly used in the froth flotation of galena from other metal sulphides. XPES studies reveal a combination of $PbCrO_4$ and $Cr_2O_3.nH_2O$ with a layer of chemisorbed CO_2 on the surface, thus forming a mixed complex of the type $Cr_2O_3.nH_2O,xCO_2$ [7].

The kinetics of the oxidation of formic acid by chromium peroxydichromate have been studied [8]. In solution this compound decomposes according to

$$Cr_2(Cr_2O_8)_3 \;\longrightarrow\; 2Cr^{3+} \;+\; 3[Cr_2O_7]^{2-} \;+\; 3O$$

The peroxy oxygen reacts rapidly with substrate formic acid, but the rate determining step is

$$2HCOOH + [Cr_2O_7]^{2-} \longrightarrow 2CO_2 + 2[HCrO_3]^- + H_2O$$

The resulting Cr(IV) species disproportionates to Cr(III) and Cr(V) which also reacts with HCOOH [8]. Similar oxidations by chromium peroxydichromate in dilute H_2SO_4 of D-galactose, D-xylose and L-arabinose have also been studied. The reactions are all first order with respect to substrate, oxidant and sulphuric acid concentrations [9]. The reaction between $[CrO_4]^{2-}$ and L-cysteine at neutral pH has been studied. A 3:1 stoichiometry was established and the rate law is

$$-d[Cr(VI)]/dt = a[L\text{-}cys]^2[Cr(VI)]/(1 + b([L\text{-}cys])$$

where $a = 140 \pm 13M^{-2}s^{-1}$ and $b = 220 \pm 25M^{-1}$ at 288 K. Several mechanisms are possible, but the favoured one involves initial formation of a chromate thio ester, a two-electron reduction of Cr(VI) with formation of L-cystine, and following steps to complete the stoichiometry [10].

A new preparation of CrF_6 has been reported in which CrO_3 is reacted with F_2 at 170°C and 25 atm pressure [11]. The lemon yellow solid, which gives a bright yellow vapour, is readily separated from CrF_5, which is also formed in the reaction, by sublimation at room temperature. The IR spectrum of CrF_6 in a N_2 matrix gives a Cr-F stretch at $758.9cm^{-1}$ and the chromium isotope pattern confirms the O_h symmetry.

Part of the laser induced fluorescence spectrum ($17,900 - 18,600cm^{-1}$) of CrO_2F_2 has been obtained at an instrumental resolution of better than $0.001cm^{-1}$. This spectrum, together with that of dispersed fluorescence, allows identification of the (0,0) band of the absorption spectrum and several progressions in the lowest bending frequency [12].

The reactions between $ClCrO_2^+$ (generated by 95eV electron impact in a selected ion flow tube) and alkenes have been studied in the gas phase [13]. Reaction with ethylene gives two products arising from oxygen transfer, $C_2H_3O^+$ (75%) and $ClCrO^+$ (12%) and one, $ClCrOCH_2^+$ (13%), containing both carbon and chromium. The favoured mechanism for the reaction is insertion of the alkene into the Cr=O bond to give an oxametallocyclobutane which then undergoes reductive elimination of CH_2O to give $ClCrOCH_2^+$ in accordance with the theory of Goddard and Rappe which was described in the 1982 review.

Cr(VI) is widely used as a selective oxidant for organic systems, but little is known of the chromium reduction products. It has been shown that when $(pyH)[CrO_3Cl]$ is used to oxidize *n*-octanol, the chromium product is (pyH)[CrO_2Cl]. The identity of the Cr(IV) complex was confirmed by the disproportionation

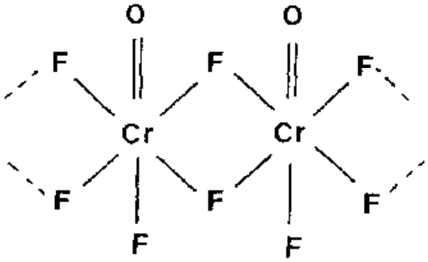
$$3Cr(IV) \longrightarrow Cr(VI) + 2Cr(III)$$

by oxidation experiments and by magnetic measurements. In contrast, reduction of (pyH)[Cr_2O_7] with hexanol gave a solid which appears, on similar experimental evidence, to be Cr_2O_5 [14].

1.2 CHROMIUM (V)

During the course of the oxidation of *cis*-[Cr(phen)$_2$(H_2O)$_2$] to Cr(VI) by periodate ion, a long lived intermediate was observed which could be isolated. The red-brown solid proved to be [Cr(phen)$_2$(IO_6)] and the EPR spectra of the solid and of a glassy solution were similar to those of other Cr(V) species. The magnetic moment of the complex was found to be 1.94 BM. The $[IO_6]^{5-}$ conformation of the periodate ion is only observed with highly charged metal centres, and the structure of the complex is thought to be square pyramidal with the $[IO_6]^{5-}$ ligand monodentate in the axial position [15].

The reaction between CrO_3 and BrF_3 is known to give the adduct $CrOF_3.0.3BrF_3$ and this has now been shown to give pure $CrOF_3$ upon heating in fluorine at 120°C [16]. The IR spectrum indicates terminal oxygen ($\nu_{Cr=O}$ = 990cm^{-1}) and both bridging and terminal fluorine atoms, so a polymeric structure of the type (1) is proposed.



(1)

Several methods of preparing oxofluoro anions of Cr(V) were investigated; all gave $[CrOF_4]^-$ and no evidence was obtained for the formation of $[CrOF_5]^{2-}$ in the solid state. Cs[$CrOF_4$] shows $\nu_{Cr=O}$ = 1005cm^{-1} in addition to bands assigned to both bridging and terminal fluoro groups [16]. Salts of $[CrOCl_4]^-$ were prepared by reducing CrO_3 with acetyl chloride followed by addition of pyridine, bipy or phen in glacial acetic acid [17]. Alternatively, reduction of CrO_3 in glacial acetic acid by gaseous hydrogen chloride in the presence of base led to the salts $[CrOCl_5]^{2-}$ [18]. Neutral adducts $CrOCl_3(L\text{-}L)$ (L-L = bipy, phen) were isolated by reducing CrO_3 in $SOCl_2$ followed by addition of the ligand in MeCN [17].

CrF_5 is monomeric in the gas phase and should show a Jahn-Teller distortion from ideal D_{3h} symmetry. Electron diffraction studies show that a C_{2v} model (increase in one equatorial angle and displacement of one axial fluorine towards this gap), and also an unrealistic four distance model, both showed better fits with the experimental data than the exact D_{3h} structure. The actual structure could not be determined, but one possibility is a dynamic Jahn-Teller distortion averaging to a C_{2v} structure. No evidence could be found for a contribution from the C_{4v} structure [19].

1.3 CHROMIUM(IV)

A theoretical study of the electronic structure of $[CrF_6]^{2-}$ has been carried out using several methods of calculation. The best calculated spectrum agrees with the one observed for Rb_2CrF_6 within 1.5kK [20].

1.4 CHROMIUM(III)

1.4.1 Complexes of simple ligands

The crystal structures of $[Cr(CNPh)_6]^{+,2+,3+}$ have been determined and together with the previously reported structure for $[Cr(CNPh)_6]^0$ represent a unique example of structural data for a metal which attains four oxidation states with the same ligation. In all cases the metal stereochemistry is octahedral although there is considerable angular distortion in the Cr(II) complex and a slight axial elongation (Jahn-Teller?) for Cr(I). There is, surprisingly, a gradual increase in Cr-C bond lengths in the sequence Cr(0) to Cr(III), and a corresponding decrease in the C≡N distance. This probably results from decreased back bonding to the ligands [21].

Ab initio SCF calculations have been carried out for $[Cr(CN)_6]^{3-}$ in its ground state, for a selected set of ligand field excited states and for the average of the ligand field states (av. d^3). Unfortunately, the SCF results are only moderately successful from a quantitative point of view [22]. The crystal structure of the elpasolite $Cs_2K[Cr(CN)_6]$ has been determined, the anion is almost perfectly octahedral with Cr-C = 2.072(2)A [23]. In the complex $[Cr(urea)_6][Cr(CN)_6].(dmso)_2(EtOH)_2$ both cation and anion have regular stereochemistry [24] with

$$\begin{aligned} Cr\text{-}O &= 1.960(2) - 1.982(1)Å \\ Cr\text{-}C &= 2.074(2) - 2.081(2) \end{aligned}$$

$[Cr(CN)_6]^{3-}$, $[Cr(CN)_5OH]^{3-}$ and $[Cr(CN)_3(OH)_3]^{3-}$ all produce $[CrO_4]^{2-}$ upon exposure to UV irradiation in alkaline solution. It is thought that the initial step is reduction to a short lived Cr(II) species which is subsequently oxidized to Cr(VI) [25]. In contrast, although the complexes $[Cr(CN)_{5-x}(H_2O)_xNO]^{x-3}$ (n = 0, 3 or 5) do form some Cr(VI) under irradiation in alkali solution, the reaction is not quantitative. Two reaction pathways were demonstrated, one leading to Cr(VI) and the other to displacement of CN^-, but the product remaining as Cr(III)

$$[Cr(CN)_{5-x}(H_2O)_xNO]^{x-3} \xrightarrow[O_2,\,OH^-]{h\nu} \left\{ \begin{array}{l} [CrO_2(H_2O)_x]^- + NO_2^- + (5-x)CN^- \\ [CrO_4]^{2-} + NO_2^- + (5-x)CN^- \end{array} \right.$$

with the formation of $[CrO_4]^{2-}$ being the minor pathway (<20%) [26].

It is rare for a polyatomic molecule with many normal modes of vibration to show significant intensity in its Raman overtones. However, $[Cr(CN)_5NO]^{3-}$ does show such overtones and this has led to the first successful calculation of the displacement of a potential surface along a given mode for such a multimode polyatomic complex from the intensity of its overtones [27].

The bimetallic complex $[(NC)_5Co(\mu\text{-}CN)Cr(NH_3)_5]$ was prepared in solution by the interaction of $[Cr(NH_3)_5(H_2O)]^{3+}$ and $[Co(CN)_6]^{3-}$. Such a complex provides an ideal case for studying intermolecular energy transfer as the spectra of the two independent transition metals are quite different. Irradiation at 313nm gives bridging cyanide labilization and formation of $[Co(CN)_5(H_2O)]^{2-}$. Good evidence for intermolecular energy transfer was obtained by the observation of sensitized acceptor emission [28].

$[Cr(NH_3)_5(NCO)]^{2+}$ hydrolyzes in acid solution (0.04 - 0.6M $HClO_4$) to give CO_2, $[Cr(NH_3)_6]^{3+}$ and other unidentified Cr(III) products which are probably a mixture of triammines and diammines. The proportion of $[Cr(NH_3)_6]^{3+}$ formed decreases with $[H^+]$ and increases with increasing temperature [29]. The observed rate law is of the form

$$-d[Cr(NH_3)_5(NCO)^{2+}]/dt = k_{obs}[Cr(NH_3)_5(NCO)^{2+}]$$

$$\text{where } k_{obs} = a[H^+]^2/(1 + b[H^+]^2)$$

and at 55°C a = $0.36 M^{-1}s^{-2}$ and b = $6.9 \times 10^{-3} M^{-1}s^{-1}$.

The thermal decompositions in air of a number of imidazole, N-methylimidazole and 2-methylimidazole derivatives of Cr(III) of the types $[CrL_6]^{3+}$, $[CrL_5X]^{2+}$ and *cis* and *trans*-$[CrL_4X_2]^+$ have been investigated. All eventually give Cr_2O_3, but differences in the reaction pathways can be related to the *trans* effects of the halogens in the compounds [30].

The kinetics of the reaction between $[Cr(NH_3)_5(H_2O)]^{3+}$ and azide ion have been investigated at pH 2.5 - 4.5 [31]. The first order rate constants for the formation of $[Cr(NH_3)_5(N_3)]^{2+}$ show a dependence on total azide concentration, $[N_3^-]_T$, of the form

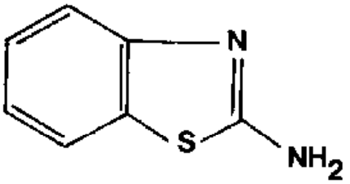
$$K_{obs}/[N_3^-]_T = (k_1K_a - k_2[H^+])/(K_a + [H^+])$$

where K_a is the acid dissociation constant for HN_3 (which is the dominant form of azide under these conditions) and k_1 and k_2 are the rate constants for the reactions of $[Cr(NH_3)_5(H_2O)]^{3+}$ with $[N_3]^-$ and HN_3 respectively. This mechanism differs from one previously reported which failed to take into account the possibility of HN_3 involvement.

Photoinduced ionizations and photochemical ammine ligand aquation for the complete series of $[Cr(NH_3)_x(H_2O)_{6-x}]^{3+}$ complexes have been examined and the quantum yields determined. The reactivities of the tetraammines and triammines are dominated by photoionization [32].

Volumes of activation for the aquation of $[Cr(NH_2CH_3)_5Cl]^{2+}$ and for several Co(III) complexes have been determined [33]. The aquation rates for the cobalt complexes increase with pressure, but that of the Cr(III) complex is independent of pressure. The data for $[Cr(NH_2CH_3)_5Cl]^{2+}$ is not fully consistent with an I_a mechanism and differs from the data for $[Cr(NH_3)_5Cl]^{2+}$. It is suggested that there is a change in the importance of bond making and breaking between the two chromium complexes.

A number of complexes of 2-amino-benzothiazole (L) (2)



(2)

of the types $CrCl_3L_3$. $Cr_2L_3(SO_4)_3$, $CrL_3(NO_3)_3$ etc. have been prepared [34]. IR evidence suggests that the ligand is coordinated through the amine nitrogen, in contrast to complexes of this ligand with Zn(II), Hg(II), Cu(I) and Ag(I) in which coordination is thought to occur through the endocyclic nitrogen [34].

The kinetics of the substitution of aquo ligands in $[Cr(H_2O)_5OH]^{2+}$ by DL-phenylalanine have been investigated and activation parameters have been evaluated. The mechanism is thought to involve outersphere association between $[Cr(H_2O)_5OH]^{2+}$ and phenylalanine (in the Zwitter ionic form) followed by an associative interchange mechanism [35].

The second order rate constant for the reaction

$$Cr^{2+} + PhCH_2^{\cdot} \longrightarrow [CrCH_2Ph]^{2+}$$

has been determined to be $(8.5\pm0.6) \times 10^7 M^{-1}s^{-1}$ in 0-2M MeCN in water, 0.05M $HClO_4$ at $\mu = 0.10M$ at 23°C. This value is based on flash photolysis determinations of both the photohomolysis of $[CrCH_2Ph]^{2+}$ and the photodecomposition of $(PhCH_2)_2CO$ in the presence of Cr^{2+} [36]. The rates of the reversible alkyl group transfer between Cr^{2+} and $[Co(II)(dmgBF_2)_2(H_2O)_n]$

$$Cr^{2+} + RCo(dmgBF_2)_2 \rightleftharpoons RCr^{2+} + Co(dmgBF_2)_2$$

have been investigated in both directions and show a dependence on steric effects consistent with a S_H2 mechanism [37].

The kinetics of the hydrolysis of $[(H_2O)_5Cr(CMe_2OH)]^{2+}$ in the pH range 0 - 5.6 have been investigated. The rate of hydrolysis increases at pH 2 although the kinetic law indicted that the mechanism does not change from hydrolysis to homolysis. The reason for the acceleration of the reaction is due to the equilibrium

$$[(H_2O)_5Cr(CMe_2OH)]^{2+} \rightleftharpoons [(H_2O)_4(OH)Cr(CMe_2OH)]^{+} + H_3O^{+}$$

and the rate of hydrolysis of the hydroxo complex is faster than that of the parent compound [38].

Complexes of the extensive family $[(H_2O)_5CrR]^{2+}$ (R = CH_2OMe, CH(Me)OEt, $CHMe_2$, CH_2Ph) all react with hydroxyl radicals to give Cr-C bond cleavage via a chain reaction, although the process involves only short chain lengths due to efficient chain terminating reactions [39].

$[(H_2O)_5Cr(CMe_2OH)]^{2+}$ may be used as a source of $CMe_2OH^{\cdot}$ radicals. These in turn react with alkyl iodides, RI, to give the alkyl radicals which may then interact with Cr^{2+} to give the overall reaction

$$[(H_2O)_5Cr(CMe_2OH)]^{2+} + RI \longrightarrow [(H_2O)_5CrR]^{2+} + I^- + H^+ + (CH_3)_2CO$$

thus effectively giving a conversion of one organochromium complex to another. The kinetics of this reaction for several alkyl iodides have been examined and found to be pseudo first order and the identities of the organochromium products were established [40].

The volumes of activation, ΔV^*, for the acid independent heterolysis of $[(H_2O)_5Cr(CMe_2OH)]^{2+}$ and $[(H_2O)_5Cr(CHMe_2)]^{2+}$ in $HClO_4$ have been measured and the results (0.3±0.2 and $-0.2\pm2cm^3mol^{-1}$) are consistent with the separation of propanol and propane respectively as the rate determining step. For the concurrent homolytic pathway leading to $Cr^{2+}(aq)$, ΔV^*'s are $+15.1\pm1.6cm^3mol^{-1}$ (independent of pressure) and $+26\pm2cm^2mol^{-1}$ respectively, values which suggest extensive breaking of the solvent cage with the free radical separation from Cr^{2+} [41].

Although Cr(III) forms many relatively stable alkyl complexes $[(H_2O)_5CrR]^{2+}$, those containing β-OH groups readily decompose. It has previously been proposed, based on UV-visible spectra, that elimination of water from $[(H_2O)_5Cr(CH_2CMe_2OH)]^{2+}$ gives either $[(H_2O)_5Cr(CH_2CMe{=}CH_2)]^{2+}$ or $[(H_2O)_5Cr(CH{=}CMe_2)]^{2+}$ (both containing Cr-C σ bonds) before the final elimination of 2-methylpropene by protonation. New evidence, based on the mass spectrometric examination of the 2-methylpropene produced in deuterated solution, now shows that the intermediate is a surprisingly long lived alkene complex $[(H_2O)_5Cr(CH_2{=}CMe_2)]^{3+}$ whose UV-visible spectrum is deceptively similar to those of the alkyl complexes [42].

^{57}Fe and ^{151}Eu Moessbauer measurements on the Perovskites $EuFe_{(1-x)}M_xO_3$ (M = Al, Ga, Sc, Cr, Mn, Ni) have been investigated in detail and the principal result is to establish that the Fe(III)-O-Cr(III) superexchange coupling in orthoferrite and orthochromate solid solution is antiferromagnetic [43]. The IR spectra of some triple orthovanadates $TlM(II)Cr_2(VO_4)_3$ have been observed. The bands due to the CrO_6 groups in the lattice reflect the different types of condensed CrO_6 units in these compopunds [44].

The absorption, emission and excitation spectra of Cr(III) were obtained for transparent glass ceramics containing β-quartz and petalite-like phases. Emission from ^2E and $^4T_2$ levels were observed simultaneously at room temperature [45].

In a series of papers [46-48] the solubilities of a number of salts of the $[Cr(urea)_6]^{3+}$ cation have been determined in water/methanol mixtures; these were then used to derive transfer chemical potentials for the anions.

Oriented single crystal Raman spectra have been determined for a number of transition metal alums $CsM(SO_4)_2{\cdot}12H_2O$ which contain the hexa-aquo metal cations. The totally symmetric stretching modes are higher than previously reported from measurements on aqueous solutions, and they vary with the reciprocal of the metal-water bond lengths. For chromium, the band appears at

540cm^{-1} [49]. A basic chromium selenite $2Cr_2(SeO_3)_2.Cr(OH)_3.18H_2O$ has been reported. The IR spectrum and the insolubility of the compound suggest a polymeric structure and its electronic spectrum and magnetic moment suggest octahedral Cr(III) [50].

The complex $[(H_2O)_5Cr(NCMe)]^{3+}$ has been prepared in solution by two methods and the kinetics of its hydrolysis to $[Cr(H_2O)_6]^{3+}$ and MeCN have been determined. A key factor in the characterization of the complex is that the kinetics of hydrolysis of the products of the two very different preparative routes were in fact the same [51].

Rate parameters for the electroreduction of a number of Cr(III) complexes adsorbed onto Ag electrodes through CNS^-, N_3^-, Cl^- or Br^- bridging ligands have been evaluated. Unimolecular rate constants for electron transfer were determined by rapid sweep voltammetry. When the data were compared with similar measurements at a mercury electrode, marked differences were apparent showing that the metal surface exerts a significant influence on the electron transfer step [52].

It is known that $Cr(C_6H_6)_2$ may be absorbed into the lamellar compound $FePS_3$ at about 130°C to give $FePS_3\{Cr(C_6H_6)_2\}_{0.32}$ without noticeable decomposition of the guest compound. However, it is now reported that at 150°C, when a de-oxygenated toluene solution of $Cr(C_6H_6)_2$ is reacted with $FePS_3$, decomposition of $Cr(C_6H_6)_2$ occurs within the interlamellar space to give a material $FeSP_3Cr_xC_y$ $(x \simeq y)$. X-ray powder diffraction shows that the interlamellar distance is about 6.42A, the same as for $FePS_3$ itself, but a detailed structural determination was not possible because of numerous defects in the lattice. EXAFS studies on $FeSP_3Cr_{1.1}C_{1.1}$ showed a Cr-S bond of 2.37 ± 0.02A, suggesting the presence of Cr(III) and also Fe-S and Fe-C bonds [53].

A detailed study has been made of the quaternary spinel systems $Cd_{1-x}Cu_xCr_2S_4$, $Cd_{1-x}Cu_xCr_2Se_4$ and $Mn_{1-x}CuCr_2S_4$ by X-ray diffraction at high temperature and also on quenched samples [54]. The hexagonal bronze-like system Rb_xCrF_3, prepared by the interaction of the appropriate quantities of RbF, CrF_2 and CrF_3 at 350°C, spans the composition range x = 0.18 - 0.29. Detailed studies of the structural and magnetic properties are reported [55]. The structures of the mixed oxidation state compounds $Cs_4Cr_5F_{18.24}$ and $Cs_4CoCr_4F_{18}$ have been determined by single crystal X-ray diffraction. They exhibit a new triple layer arrangement of octahedra, with average Cr-F distances of 1.920 and 1.929A respectively, with the smaller average value being due to the greater proportion of Cr(III) in the structure [56].

The equilibrium constants for Cr(III) and Cr(II) inner and outer sphere complexes with Cl^-, Br^- and I^- have been determined [57] by electrochemical methods. The IR, Raman and fluorescence spectra of Cr(III) in a $Cs_2NaScCl_6$ host lattice have been reported. The quenching of the $^4T_{2g} \longrightarrow {}^4A_{2g}$ fluorescence is temperature dependent [58]. The IR and low temperature Raman spectra of $Cs_2CrCl_5.4H_2O$ have been measured; a previous X-ray study has shown the compound to contain the *trans*-$[CrCl_2(H_2O)_4]^+$ ion. A normal coordinate analysis was carried out on this compound and the same structure was deduced for the corresponding bromo complex. The important band assignments are [59]

	R	IR
$\nu_{Cr=O}$	490	515cm^{-1}
ν_{Cr-Cl}	289	368
ν_{Cr-Br}		304

A series of complexes $CrCl_3L_3$ (L = imidoazolethione) has been prepared and spectroscopic evidence (especially IR) suggests the ligand is coordinated through sulphur [60]. As part of study of glycine derivatives of several transition metals, the complex $[CrCl_3(glyH)_2(H_2O)]$ was prepared in aqueous solution at pH 2-3. The IR spectrum suggested the ligand was coordinated through the amine function [61]. $CrCl_3(thf)_3$ reacts with one mole of NaOR in ROH to give soluble $CrCl_2(OR).2ROH$ (R = Me, Et, ^{i}Pr, ^{n}Bu) which when heated give unstable $CrCl_2(OR)$ compounds. The alcoholates are octahedral and hence dimeric in the solid state, probably with bridging OR groups, although they are monomeric in ROH solution. The ROH groups may be readily exchanged with different alcohols, but not the OR groups [62].

1.4.2 Complexes of bidentate ligands

The CD spectra of a number of optically active dinitritobis(diamine)-chromium(III) complexes have been measured in the visible and near UV region and the stereochemical and conformational (rotational) isomerism of the coordinated nitro groups are discussed on the basis of the solvent dependent CD spectra of the intraligand band localized on the nitro groups [63].

A carbonyl-bound nicotinic acid complex *trans*-$[Cr(1,3\text{-}pn)_2(nic\text{-}O)_2]Cl$ has been prepared and it is stable at the physiological pH range [64]. The coordination of the nicotinic acid through oxygen was confirmed by ^{2}D NMR (it was reported in the review last year that ^{2}D NMR may be used to determine the stereochemistry of paramagnetic Cr(III) complexes). Labelling of nicotinic acid by D at the 2 positions gave a ^{2}D NMR signal at +9.9ppm which on coordination through the carbonyl gave only a small shift to +9.1ppm. In contrast, previously known complexes of Cr(III) with the ligand coordinated through the pyridyl nitrogen gave a dramatic shift to about -70ppm, thus providing an NMR method of determining nicotinic acid coordination in solution. The complex is thought to be stable towards hydrolysis because of the effects of the bulky

1,3-pn groups [64].

Reaction of *cis*-$[Cr(X(H_2O)(en)_2]X_2$ (X = Cl,Br) with $H_2[M(CN)_4]$ (M = Pd, Pt) gives the double salts *cis*-$[CrX(H_2O)(en)_2][M(CN)_4]$ which, on standing in a desiccator, yield the cyanobridged complexes *cis*-$[X(en)_2Cr{-}NC{-}M(CN)_3]$. Reaction of *cis*-$[CrX(H_2O)(en)_2]$ with $[Ni(CN)_4]^{2-}$ gave the corresponding bridged complexes directly [65]. The presence of the cyano bridges was confirmed by IR spectroscopy. Some further examples of cyano bridged species, in this case between two chromium atoms, have been prepared by heating the appropriate doubly complexed species

$$\textit{trans}\text{-}M[CrF(H_2O)(aa)_2][Cr(CN)_6] \rightarrow \textit{cis}\text{-}M[(aa)_2FCrNCCr(CN)_5]$$

$$\textit{trans}\text{-}[CrF(H_2O)(aa)_2][Cr(NO)(CN)_5] \rightarrow \textit{cis}\text{-}M[(aa)_2FCrNCCr(NO)(CN)_5]$$

$$M = K,\ Na,\ NH_4^+; \quad aa = en,\ 1,3\text{-}pn$$

and their magnetic properties have been investigated [66]. The reactions

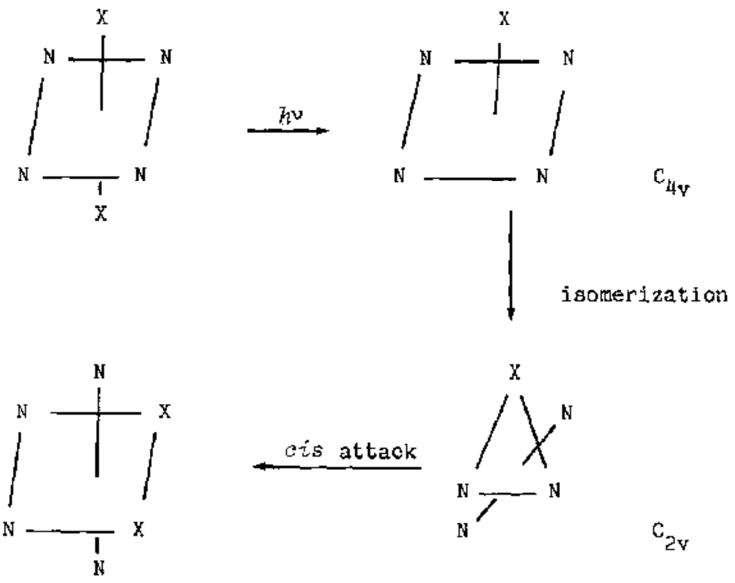
$$\textit{trans}\text{-}[CrF(H_2O)(aa)_2]I_2 \rightarrow [CrF(aa)_2I]I$$

$$(aa)_2 = (en)_2,\ (1,3\text{-}pn)_2 \text{ or } (en)(1,3\text{-}pn)$$

have also been investigated by thermogravimetric methods and their kinetics and activation parameters determined. The activation energies are low and suggest a S_N1 type mechanism with a square pyramidal activated complex [67].

The ligand field absorption CD spectra have been measured for a series of new complexes *trans*-$[CrF_2(diammine)_2]^+$ (where the two diamines may be the same or different) in an attempt to separate the various contributions to the CD effect. The additivity of the CD contributions for the individual chiral diamines was substantiated in most cases, and the conformational and vicinal CD contributions due to the puckered rings and the asymmetric carbon atoms, respectively, were differentiated [68].

Trans-$[CrX_2(aa)_2]X$ (X = Cl, Br; aa = en, 1,2-pn, 1,3-pn) are all photoisomerized to the *cis* isomer in methanol solution, but no *cis* → *trans* isomerism is observed. These observations are in contrast to thermal isomerization of the solids reported in previous years for which *cis* → *trans* isomerism occurs for en and 1,2-pn complexes and *trans* → *cis* isomerism for 1,3-pn compounds. The photoisomerization is thought to occur via a photo dissociation to give a square pyramidal structure which could then isomerize as follows



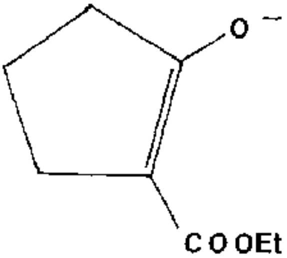
The *cis*-[CrX$_2$(aa)$_2$]X complexes all undergo a further slow photosubstitution to give products which are thought to be *fac*-[CrX$_2$(MeOH)(aa)$_2$]$^+$, containing a monodentate diamine, but these complexes could not be isolated [69]. The complexes [Cr(1,3-pn)(NCS)$_4$]$^-$ and *trans*-[Cr(1,3-pn)$_2$(NCS)$_2$]$^+$ have been isolated and characterized [70].

Using CrX$_3$(thf)$_3$ (X = Cl, Br) as starting materials, *fac* and *mer*-[CrX$_3$L] have been prepared [70] (where L = a tridentate ligand such as PPh(CH$_2$CH$_2$PPh$_2$)$_2$, CMe(CH$_2$PPh$_2$)$_3$, AsMe(CH$_2$CH$_2$CH$_2$AsMe$_2$)$_2$, S(CH$_2$CH$_2$CH$_2$SMe)$_2$ or potentially quaridentate ligands such as P(CH$_2$CH$_2$PPh$_2$)$_3$, As(CH$_2$CH$_2$CH$_2$AsMe$_2$)$_3$ which behave as tridentates). Some CrF$_3$L complexes were also prepared by reactions of CrCl$_3$(thf)$_3$ with AgF followed by addition of the ligand. Complexes of 1:2 stoichiometry CrL$_2$I$_3$ were obtained in the iodo system (L = PPh(CH$_2$CH$_2$PPh$_2$)$_2$) which are thought to have CrP$_6$ coordination, but in [CrL$_2$I$_2$]I (L = CMe(CH$_2$AsMe$_2$)$_3$) the ligand is thought to act as a bidentate. Conductivity, UV-visible and IR studies served to identify the coordination and isomeric form of the complexes. The structure of *mer*-[Cr(P{CH$_2$CH$_2$PPh$_2$}$_3$)Cl$_3$] was confirmed by an X-ray structural analysis. The Cr-P bonds are long (2.399(4) - 2.466(5)A) which is thought to be due to both steric effects and relatively weak bonding to Cr. The Cr-Cl bond lengths fall in the range 2.292(6) - 2.320(5)A [71].

A series of octahedral substitution products of K$_3$[Cr(NCS)$_6$ have been reported of the types [Cr(NCS)$_4$(L-L)]$^{n-}$ or [Cr(NCS)$_2$(L'-L')]$^{n-}$ where L-L and L'-L' are various amino acids [72]. A number of complexes of the type [Cr(AA)$_2$(H$_2$O)$_2$] have been prepared where AA = glycine, glutamic acid and glutamine. A similar complex is formed with cysteine at low pH, but at higher pH [Cr(cys)$_2$]$^-$ is formed with the ligand acting as a tridentate [73]. Although it is now believed that glucose tolerance factor (GFT) does not contain chromium, these complexes, as well as some uncharacterized mixed ligand complexes of Cr(III) containing nicotinic acid, were tested for biological activity using a yeast assay. Only $[Cr(glutamine)_2(H_2O)_2]^+$ and a mixed glycine-nicotinic acid complex showed appreciable activity. It is proposed that a *trans* arrangement of the non-coordinated nitrogen atoms in the ligands can mimic the structural feature of GTF necessary for biological activity [73].

The complexes $[Cr(L\text{-}mal)(H_2O)_4]^+$ and $[Cr(L\text{-}mal)(L\text{-}L)(H_2O)_2]^+$ (L-mal = L-malic acid, L-L = phen, bipy) have been prepared and studied using CD and ORD measurements [74]. The formation of $[Cr(glyO)(H_2O)_4]^{2+}$, which is in equilibrium with $[Cr(glyO)(H_2O)_3(OH)]^+$, from $[Cr(H_2O)_6]^{3+}$ and glycine (glyOH) has been studied at pH 3.0 - 3.8 at 40-45°C and I = 0.4moldm^{-3} ($NaClO_4$). The reaction is zero order with respect to glycine concentration [75].

Reaction of $CrCl_3$ with various amino acids has been investigated. The complexes $CrL_3.H_2O$ were isolated for LH = picolinic, nicotinic, anthranilic and *m*-aminobenzoic acids. IR studies suggested that while the picolinate anion coordinated through oxygen and nitrogen the others coordinated through both carboxylate oxygens. In contrast, tryptophan and glutamic acid gave dinuclear species $L_2Cr(OH)_2CrL_2$, which had low magnetic moments, in which the ligand is thought to coordinate through *O* and *N* [76]. The anion of ethyl-α-ketocyclopentadienylcarboxylate **(3)** chelates to Cr(III) through the anionic oxygen and



(3)

the ketone of the carboxylate group to give the CrL_3 complex [77].

The complex $Cr[Al(O^iPr)_4]_3$ is volatile. The magnetic moment of 3.90BM and the visible spectrum suggests octahedral Cr(III) thus implying that the $[Al(O^iPr)_4]^-$ ligand is acting as a bidentate [78]. The complex reacts with alcohols [79]

$$Cr[Al(O^iPr)_4]_3 + 3nROH \xrightarrow{\text{benzene}} Cr[Al(O^iPr)_{4-n}(OR)_n]_3 + 3n^iPrOH$$

(R = Me, Et, ^{n}Bu, CF_3CH_2, ^{t}Bu and Me_2PhC)

Complete exchange occurs with R = Me, Et, ^{n}Bu, and CF_3CH_2. Acac reacts similarly to give complexes formulated as $Cr[Al(O^{i}Pr)_3(acac)]_3$, $Cr[Al(O^{i}Pr)_2(acac)_2]_3$ and finally $Cr(acac)_3$ and $Al(acac)_3$ are formed [79].

The interpretation of earlier results on the formation and extraction of $Cr(acac)_3$ from aqueous solution into 4-Me-2-pentanone and 4-Me-2-pentanol involved the assumption that the rate of formation of $Cr(acac)_3$ was much faster in the organic phase than in the aqueous. However, direct measurement of the kinetics of formation now show this not to be so. As a result, a new mechanism of extraction involving $[Cr(acac)(H_2O)_4]^{2+}$ is proposed [80]. The sublimation energy of $Cr(acac)_3$ has been re-determined to be $-141.5 \pm 5.6 kJmol^{-1}$ and the corresponding enthalpy of fusion as $28.10 \pm 1.28 kJmol^{-1}$ [81].

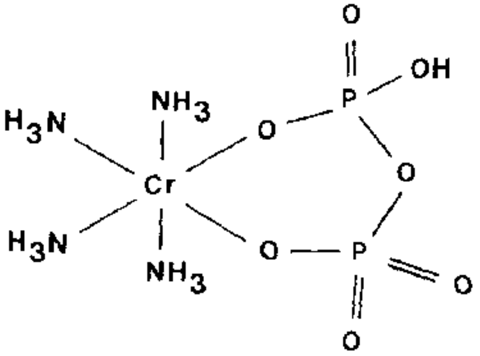
An electrochemical study of a series of $M(acac)_3$ complexes, including $Cr(acac)_3$, has found that in general the reversibility of the electrochemical reduction is inversely proportional to the Ziegler-Natta catalytic activity of the metal acac species [82].

Bromination of $Cr(acac)_3$ with excess N-bromosuccinimide is well known to yield the complex with all three ligands brominated at the 3-position. However, a deficiency of the brominating agent gives mixed ligand complexes with partial bromination. It has been shown that HPLC is a very efficient means of separating the components of the mixture of $Cr(acac)_3$, $Cr(acac)_2(acacBr)$, $Cr(acac)(acacBr)_2$ and $Cr(acacBr)_3$. Carbon-13 NMR spectra of the complexes show interesting effects and are useful for identifying the products [83].

The rates of metal catalyzed oxalate dissociation of $[Cr(ox)_3]^{3-}$ (to give $[Cr(ox)_2(H_2O)_2]^-$ and $[Cr(ox)(H_2O)_4]^+$) has been investigated spectrophotometrically. The order of catalytic activity, as measured by the second order rate constant K_M, follows the sequence $Fe^{2+} >> Cr^{2+} > Ni^{2+} > Zn^{2+} > Co^{3+} > Mn^{2+}$ which is also the order of the formation constant of the monooxalate complex of the catalyzing metal. A mechanism similar to that described in the review for 1983 for the corresponding malonate complexes is thought to be operative [84].

The lanthanide catalyzed isomerization of *trans*-$[Cr(ox)_2(H_2O)_2]^-$ and *trans*-$[Cr(mal)_2(H_2O)_2]^-$ has been systematically studied using most of the lanthanide ions. For the lighter lanthanides (La-Gd) there is evidence of formation of monodentate carboxylate groups prior to isomerization [85].

Complexes of Cr(III) and other first row transition metals have been prepared using 2,2,3,4,4-pentaphosphetamic acid, RPO_2^-, (L). This ligand is thought to be analogous to acetate in its coordination mode and the complex CrL_3 is monomeric [86]. The crystal structure of $[Cr(NH_3)_4(HP_2O_7)].2H_2O$ has been determined and is as shown in **(4)**. Bond distances are Cr-N = 2.07(1) (av) and Cr-O = 1.968(5)A (av) [87].

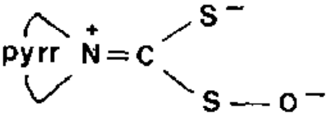


(4)

α,β-bidentate $[Cr(H_2O)_4(adp\alpha s)]$ (adpαs = adenosine-5'-(1-thiodiphosphate) were prepared by interaction of the ligand and $[Cr(H_2O)_4Cl_2]Cl$ at pH 3 at 80°C, followed by chromatography. Similarly, α,β-bidentate $[Cr(NH_3)_4(adp\alpha s)]$ was prepared from the neucleotide and $[Cr(NH_3)_4Cl_2]Cl$. The complexes were shown to contain Cr-O rather than Cr-S coordination by isolation of the appropriate isomers [88]. The synthesis and stereochemical assignment of the enantiomers of $[Cr(H_2O)_4(pps)]$ (pps = thiopyrophosphate) from the pure enantiomers of $[Cr(H_2O)_4(adp\alpha s)]$ has been reported. It is hoped these will be useful probes to study the specificity of enzymes [89].

Reaction of $[Cr(NCS)_6]^{3-}$ with a β-diketone (O-O) and a nitrogen donor ligand produces mixed ligand complexes of the types $[Cr(O\text{-}O)(\gamma\text{-pic})_2(NCS)_2]$ and $[Cr(O\text{-}O)(L\text{-}L)(NCS)_2]$ (where L-L = bipy, phen) [90].

Electrochemical studies on $Cr(pdtc)_3$ (pdtc = pyrrolidinedithiocarbamate) and $Co(opdtc)(pdtc)_2$ (where opdtc is the oxygen expanded ligand (5)) show that



(5)

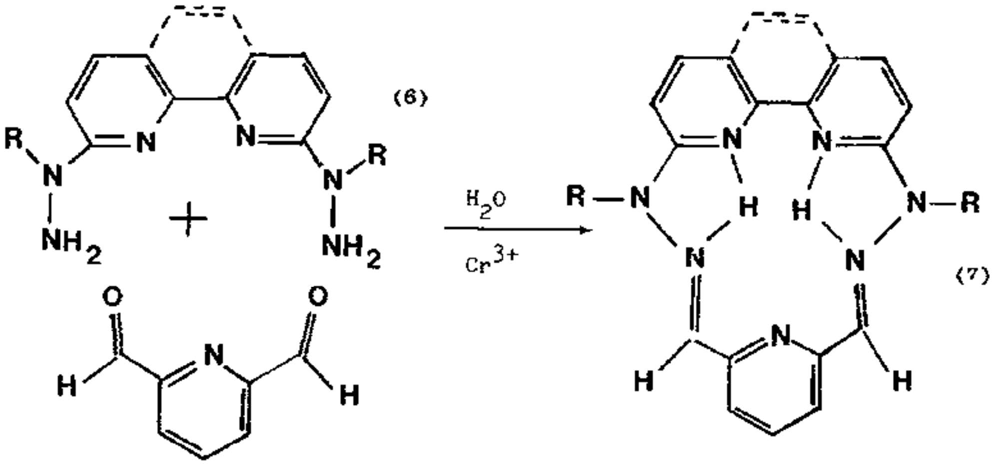
the formally Cr(IV) complex formed on electrochemical oxidation is more stable for the opdtc compound. In the case of $Cr(pdtc)_3$, electrochemical reduction leads to the formation of Cr(II) with loss of a pdtc ligand, whilst for the mixed ligand compound reduction proceeds entirely by loss of $pdtc^-$ to give Cr(opdtc)(pdtc) [91].

Different *O,O*-dialkyldithiophosphate complexes of the type $Cr(S_2P(OR)_2)_3$ undergo ligand exchange on refluxing to give rise to new mixed ligand complexes which were identified by HPLC [92]. The attempted preparation of $Cr(dtc)_3$ from Cr(VI) always gives both $Cr(dtc)_3$ and another product which can be separated by chromatography. Although its molecular weight corresponds to $Cr_2O(dtc)_4$, it is formulated as a thiuram disulphide complex $Cr_2O(dtc)_2(tds)$. It readily breaks down to give $Cr(dtc)_3$ [93].

New complexes of Cr(III), Fe(III) and Co(III) with *o*, *m*, and *p*-hydroxydithiobenzoate have been prepared and the bonding in the complexes has been discussed in MO terms [94].

1.4.3 Complexes of polydentate ligands

Reaction of the bis(hydrazine) compound, L, **(6)**, (2,2'-bipyridine or 1,10-phenanthroline; R = H, Me, CH_2CH_2OH) with 2,6-pyridine dialdehyde in the presence of aqueous $CrCl_3$ rapidly gave good yields of the macrocyclic N_5 **(7)**.

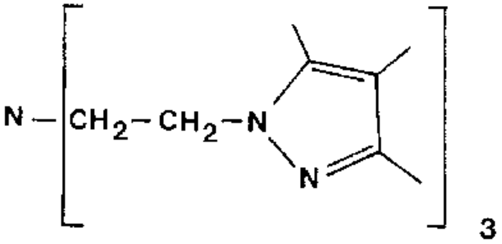


Similar results were obtained in the presence of hydrochloric acid in the absence of chromium, showing that the transient template is in fact the proton. However, Cr(III) reacts slowly with L to give $[CrLCl_2]Cl$, which then slowly reacts with 2,6-pyridine dialdehyde to give a chromium complex of the N_5

macrocycle, $[Cr(N_5)(H_2O)_2]^{3+}$ [95]. A crystal structure determination for the compound with R = CH_2CH_2OH revealed an example of the very rare (for Cr(III)) pentagonal bipyramidal structure with the water ligands axial and the macrocyclic ligand strictly planar. Bond distances are

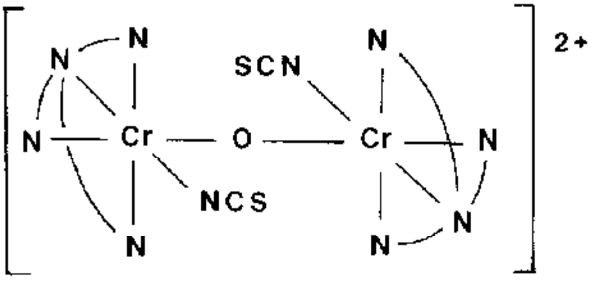
Cr-N(bipy) = 2.027(5), 2.059(4)   Cr-N(py) = 2.206(5)A
Cr-N(N=C) = 2.196(4), 2.259(5)   Cr-O = 2.009(4), 2.036(4)

The ligand tris(2-pyrazol-1-ylethyl)amine (L) **(8)** reacts with $Cr(NCS)_2$ in



(8)

ethanol to give air sensitive $[Cr(NCS)L]^+$ which was isolated as the $[BPh_4]$ salt [96]. This complex reacts immediately with oxygen to give $[\{Cr(NCS)L\}_2O](BPh_4)_2$ and a crystal structure determination for this binuclear complex **(9)** revealed an almost linear oxygen bridge.



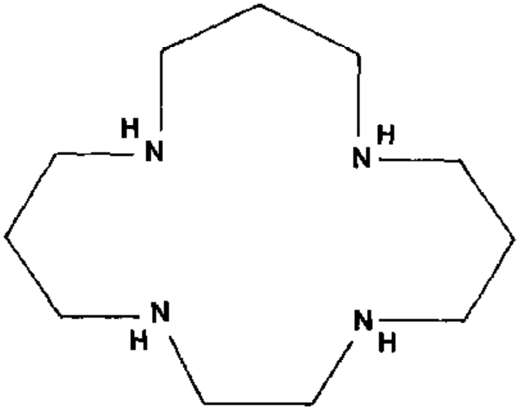
(9)

Bond distances are

Cr-N (*trans* O) = 1.82(1)   Cr-N (*cis* O) = 2.07(1) - 2.10(1)A
Cr-N (amine) = 2.13(1)   Cr-N (NCS) = 2.01(1)
Cr-O = 1.82(1)

The complex is feebly paramagnetic (μ/Cr atom = 1.63BM at 300 K; 0.98BM at 86 K) consistent with strong antiferromagnetic coupling through the oxygen bridge. The UV-visible spectrum is unlike those of most Cr(III) compounds, but is similar to those of the basic rhodo salts which also contain linear oxo bridges. The antisymmetric Cr-O-Cr stretch occurs at 830cm^{-1} (790cm^{-1} for the ^{18}O labelled complex) [96].

Air oxidation of $CrCl_2.4H_2O$ in an aqueous solution of the 15 membered macrocyclic ligand 1,4,8,12-tetraazacyclopentadecane (N_4, **(10)**) gives



(10)

$[Cr(N_4)(H_2O)_2]^{3+}$. Deprotonation and substitution by thiocyanate ion were studied and the results interpreted according to the scheme

$$\begin{tikzcd}
{[Cr(N_4)(H_2O)_2]^{3+}} \arrow[r, "NCS^-"] \arrow[d, shift left, "-H^+"] & {[Cr(N_4)(H_2O)(NCS)]^{2+}} \arrow[d, shift left, "-H^+"] \\
{[Cr(N_4)(OH)(H_2O)]^{2+}} \arrow[r, "NCS^-"] \arrow[u, shift left, "+H^+"] \arrow[d, shift left, "-H^+"] & {[Cr(N_4)(OH)(NCS)]^{+}} \arrow[u, shift left, "+H^+"] \\
{[Cr(N_4)(OH)_2]^{+}} \arrow[u, shift left, "+H^+"] &
\end{tikzcd}$$

All the relevant rate constants were determined, but the kinetic plots did not give good linearity and there was also a mismatch of dependence of k_{obsd} and absorbance of $[Cr(N_4)(H_2O)_2]^{3+}$ with pH. These effects are attributed to the existence of configurational (NH) or *cis* isomers of the *trans*-[15]ane N_4 macrocyclic complex [97].

The crystal structures of *cis*-$[Cr(N_4)(OH)_2]ClO_4.2H_2O$ and *cis*-$[Cr(N_4)(O_2CO)]_2(S_2O_6).4H_2O$ have been determined (where N_4 = *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane). Both structures contain equal numbers of optical isomers. In both cases the ligand is folded to give N4 and N11 *trans* to each other and in the carbonate complex the $[CO_3]^{2-}$ ligand is bidentate [98]. Bond distances are

	cis-$[Cr(N_4)(OH)_2]^+$	*cis*-$[Cr(N_4)(O_2CO)]^{2+}$
Cr-N1, N8	2.142	2.091, 2.106A
Cr-N4, N11	2.140	2.108, 2.111
Cr-O	1.918	1.945, 1.959

Electrochemical studies on $(TPP)CrClO_4$ reveal two reversible oxidations and two reductions, one reversible and one not. The first reduction corresponds to the formation of (TPP)Cr (irreversible) and the second to the formation of $[(TPP)Cr]^-$. The oxidations show a counter ion dependence and are probably metal based. Spectrophotometric and electrochemical studies in mixed solvent systems indicate formation of $[(TPP)CrL_2]^+$ (L = dmf, dmso, py). (TPP)Cr(NO) shows two reversible reductions corresponding to the formation of $[(TPP)Cr(NO)]^-$ and $[(TPP)Cr(NO)]^{2-}$, whilst on oxidation an irreversible process is observed due to the EC mechanism

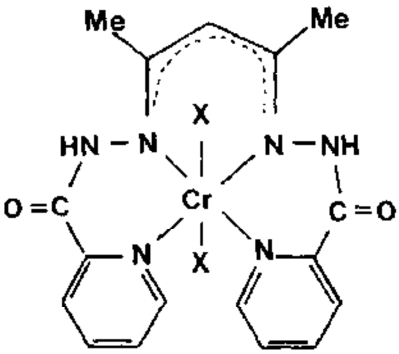
$$(TPP)Cr(NO) \xrightarrow{-e^-} [(TPP)Cr(NO)]^+ \longrightarrow [(TPP)Cr]^+ + NO$$

which is followed by a second oxidation similar to that observed for $(TPP)CrClO_4$ [99].

Picolinic acid hydrazide and *iso*-nicotinic acid hydrazide react with acacH in the presence of Cr(III) to give complexes of open chain tetradentate ligands directly. Spectroscopic evidence suggests the products are **(11)** and **(12)** respectively. The picolinic acid derivative coordinates through the azomethine and pyridinium nitrogens whilst the *iso*-nicotinic acid derivative coordinates through the azomethine nitrogen and the amide oxygen atoms [100].

The magnetic properties of two monomeric stereoisomers of $[Cr(L\text{-hist})_2]^+$ and the dimeric $[Cr(L\text{-hist})_2(OH)]_2$ have been measured. The monomeric complexes exhibit Curie-Weiss behaviour while the dinuclear complex showed ferromagnetic behaviour at low temperature lending strong support to the proposed dihydroxo bridged structure [101].

A review has been published on the optically active Cr(III), Co(III) and Rh(III) complexes of edta and related type ligands [102]. In a continuation of the use of ^{2}D NMR to investigate paramagnetic Cr(III) complexes, the ^{2}D NMR spectrum of $[Cr(edta)]^-$ and other complexes with similar ligands have been



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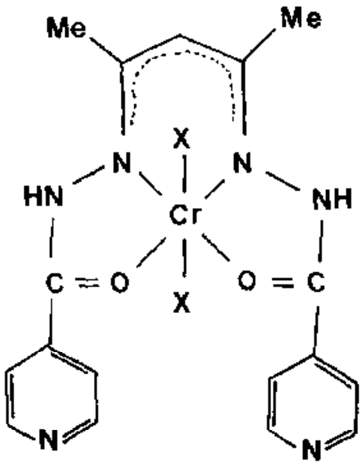


(12)

studied. It was shown that at most pH's edta forms a sexidentate complex, rather than the pentadentate [Cr(edta)(H_2O)]$^-$ previously assumed, although at both very high and very low pH's, pentadentate coordination is indicated [103].

The crystal structure of Na[Cr(pdta)].3H_2O (pdta = 1.3-propanediaminetetraacetate) has been determined. The ligand coordinates in a sexidentate manner and bond distances are Cr-O = 1.941(5) - 1.973(5) and Cr-N = 2.065(6)A [104].

The acid catalyzed aquation of [Cr(atda)(acac)]$^-$ to give [Cr(atda)(H_2O)$_2$] (atda = N-(*o*-carboxylphenyl)iminodiacetate) has been followed spectrphotometrically over the temperature range 50 - 80°C. The rate law is given by

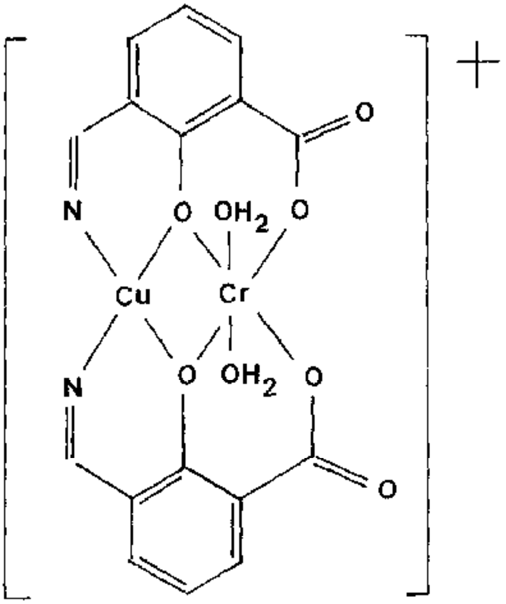
$$\text{rate} = k_1[\text{complex}] + k_2[\text{complex}][H^+]$$

with $k_1 < k_2$. Both pathways are thought to involve a rate determing step of opening the acac (or acacH) chelate ring followed by rapid replacement of the monodentate acac by water. The rate constants k_1 and k_2 are similar in magnitude to those observed for Cr(acac)$_3$ and much less than those involving replacement of acac at Cr(III) when an additional pendant ligand is present. This supports the concept that the pendant group in, say, [Cr(edtaH)(acac)]$^-$ promotes dissociation of the acac ligand [105].

Reaction of [CrO_4]$^-$ with [NH_3OH]Cl in the presence of pyridine-2,6-

dicarboxylic acid (dipicH$_2$) gives three products: [Cr(dipic)(NO)(H$_2$O)$_2$] (I), [Cr(dipic)(NO)(H$_2$NOH)$_2$] (II) and [Cr(dipic)(H$_2$NO)(H$_2$NOH)] (III). Compounds I and II have a single unpaired electron whilst III has three as expected for Cr(III). The coordination of the neutral hydroxylamine ligands in II and III is unknown, but the hydroxylamido(1-) ligand in III iis probably *O,N* coordinated. A crystal structure of I showed the dipic ligand to be tridentate with the NO ligand *trans* to the pyridine nitrogen. The bond distances are Cr-NO = 1.699(4), Cr-H$_2$O = 2.009(3), Cr-O = 2.027(2) and Cr-N = 2.012(3)A [106].

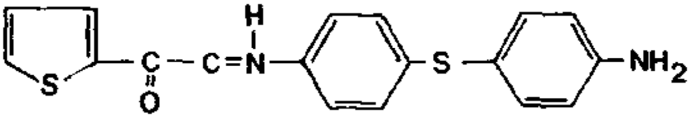
The structure of [CuCr{(fsa)$_2$en}(H$_2$O)$_2$]Cl.3H$_2$O is thought to be **(13)** on the



(13)

basis of magnetic studies. The magnetic ground state is a quintet (s = 2) arising from a ferromagnetic interaction due to the strict orthogonality of the b_1 magnetic orbital around Cu and the a_1, a_2 and b_2 magnetic orbitals around Cr [107].

A new tridentate ligand *γ*-(*p*'-aminophenyl)thiophenylimino)methyl-2-thienyl ketone **(14)** has been prepared and reacted with a number of first row transition metals, including Cr(III). Reaction with CrCl$_3$ gave CrLCl$_3$ which on the basis of spectroscopic measurements is octahedral with the ligand coordinated through the *S,O* and *N* at the thienyl ketone end of the ligand [108].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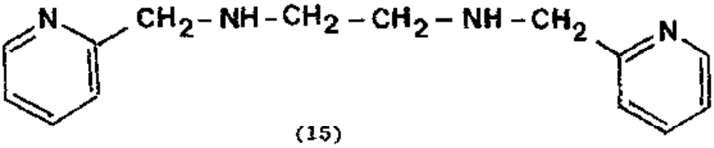
1.4.4 Dinuclear complexes

A new blue-violet isomer of the dimeric cation $[(\text{bispicen})\text{Cr(OH)}]_2$ (bispicen = (15)) has been characterized by X-ray crystallography and its magnetic properties studied. The complex is not optically active and the perchlorate crystallizes as a racemate of (16) with non-equivalent chromium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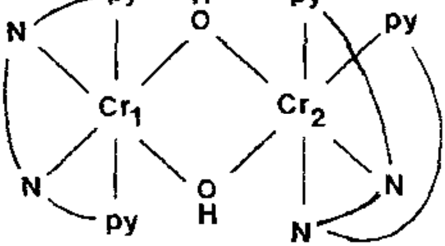
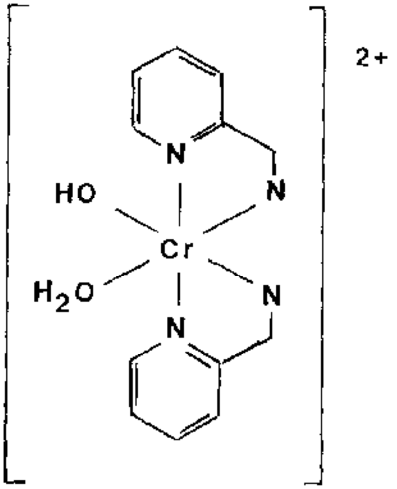


(16)

atoms. The $Cr_2(OH)_2$ unit is almost planar with Cr-Cr = 3.046(2)A. The magnetic properties were found to fit the previously reported model which emphasizes the importance of the geometry of the bridging groups [109].

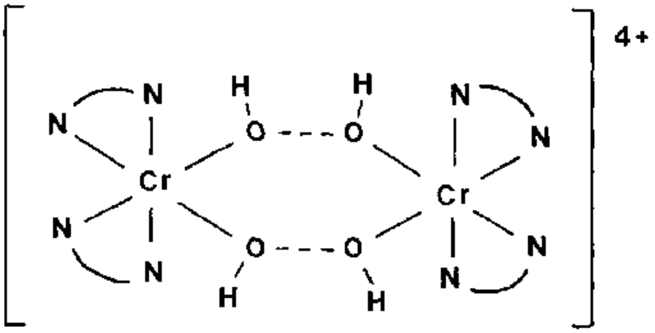
Two crystal structures have been determined which both present evidence that the $[H_3O_2]^-$ group, formed by interaction of a hydroxo ligand and a water molecule on an adjacent metal atom, is a bridging group between metals. The structure of the cation in *cis*-$[CrL_2(OH)(H_2O)](S_2O_6)$ (L = 2-pyridylmethylamine) is shown in **(17)**.



(17)

Both types of Cr-N bonds are essentially the same length, 2.054(5) - 2.089(5)A, but the Cr-O distances are markedly different, 1.926(4) and 1.998(5)A with the shorter distance assigned to Cr-OH. However, the packing in the lattice is such that two cations make close contact with the hydroxo group of one close to the water ligand of the other, so it seems this may be interpreted as an example of $[H_3O_2]^-$ bridging. Unfortunately the position of the bridging hydrogen was not resolved in the structure determination [110]. It has generally been accepted that deprotonation of *cis*-$[Cr(dipy)_2(H_2O)_2]^{3+}$ gave the corresponding monohydroxo ion, but a structural determination on the iodide shows it to be dimeric in the solid state and bridged by two $[H_3O_2]^-$ groups, very similar to the previous example. Once again, the bridging hydrogens were not observed although the terminal ones were. The structure is shown in **(18)** and it is suggested that such bridged complexes may be common intermediates in olation reactions [111].

The complex *trans*-aquohydroxo-di-μ-hydroxobis(*fac*-triammine chromium(III)) ion, *trans*-$[(H_2O)(NH_3)_3Cr(OH)_2Cr(NH_3)_3(OH)]^{3+}$ (I) was prepared by the condensation of *fac*-$[Cr(NH_3)_3(H_2O)_3](ClO_4)_3$ in aqueous solution by addition of



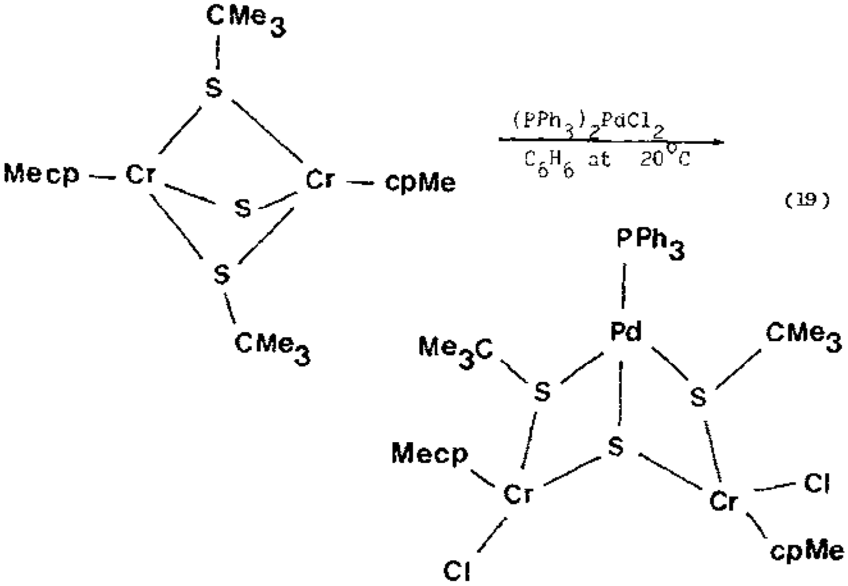
(18)

LiOH. The iodides of the protonated and deprotonated diol cations of I were also isolated and the two successive acid dissociation constants of the 4+ cation were determined to be $10^{-6.0}$ and $10^{-7.5}$M at 25°C, 1M $HClO_4$. A crystal structure determination of the tribromide of I showed that in the solid state the compound exists as infinite chains of alternating *trans*-diaquo and *trans*-dihydroxo diol cations linked by very short (2.45A) O..H-O bonds. However, considering the uncertainty in the position of the bridging hydrogen it is doubtful if it should be regarded as "belonging" to only one of the cations [112]. Bond distances are Cr-N = 2.058(4) - 2.093(5), Cr-μOH = 1.950(3) - 1.975(3), $Cr-H_2O$ = 1.979(4)A (av).

In the review last year the structure and magnetic properties of a monoclinic form of $[(NH_3)_4Cr(OH)_2Cr(NH_3)_4]Cl_4$ were described. A new triclinic form of this complex has now been isolated which is isostructural with the corresponding Co(III) complex. The structure is similar to the form previously described except that the dihedral angle θ is 50(3)° compared with 41° in the monoclinic form. It has emerged over recent years that it is this angle which has a critical effect on magnetic properties, but unfortunately the structure determination is not really accurate enough with regard to the hydrogen position to completely test the model for magnetic behaviour [113].

A complex of Cr(III) with thiosuccinic acid (L), $[Cr_2L(OH)_2].2H_2O$, has been prepared. IR evidence suggests no coordination through sulphur, although the complex appears to contain octahedral Cr(III) with a low magnetic moment of 3.27 BM [114].

The interaction of violet $[\{(RC_5H_4)CrSCMe_3\}_2S]$ (R = H, Me) with $(PPh_3)_2PdCl_2$ gave an almost instant colour change to deep green and a structural determination on crystals of the complex R = Me showed that a trinuclear complex had been formed with transfer of chlorine to chromium as shown in (19).



(19)

The Cr-Cr distance is 4.079(1)A but magnetic interaction still occurs between the chromium centres (presumably through the μ_3-S) in a ferromagnetic manner ($2J = 11cm^{-1}$) in contrast to the starting material which displays antiferromagnetic coupling [115].

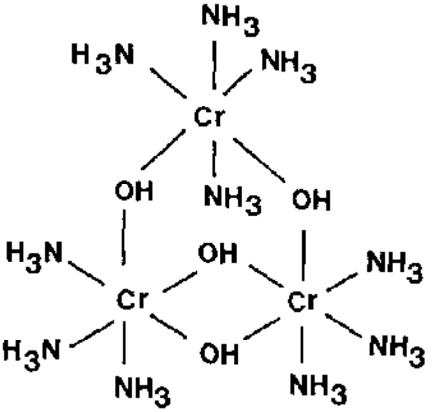
1.4.5 Polynuclear complexes

The magnetic susceptibility of the complex cation $[(en)_2Cr(OH)_2Cr(en)(OH)_2Cr(en)(OH)_2Cr(en)_2]^{6+}$, whose structure is known to be a linear chain, has been measured. The data have been interpreted using several different theoretical models based on Heisenberg-Dirac-Van Vleck Hamiltonians. The simplest description envisages two antiferromagnetic couplings $J_{12} = J_{34} = 19cm^{-1}$ and $J_{23} = 14cm^{-1}$ where chromiums 1 and 4 are terminal. These parameters are combined with the structural data using the model recently developed for dinuclear chromium complexes [116].

There has been a re-determination of the crystal structure of

$[Cr_4(NH_3)_{12}(OH)_6]Cl_6.4H_2O$ to determine the positions of the hydrogens of the bridging hydroxo groups, so that correlations between structure and magnetic properties can be made. The main features of the earlier determination were confirmed [117]. Bond distances are Cr-N = 2.070(2) - 2.095(2), Cr-OH = 1.962(2) - 1.973(1), O-H = 0.66 - 0.73A.

The complex $[Cr_3(NH_3)_{10}(OH)_4]Br_5.3H_2O$ has been isolated and X-ray diffraction showed the cation to have the structure (20) with the bridging octahedral group tilted by 21°.



(20)

Bond distances are

Cr_1,Cr_2-OH = 1.963(9) - 1.989(9)A
Cr_3-OH = 1.963(11) - 1.960(7)
Cr-N = 2.085(12) - 2.116(9)

The magnetic susceptibility and EPR spectrum were investigated and all interactions were found to be antiferromagnetic. The complexes $[Cr\{(OH)_2Cr(NH_3)_4\}_3]Br_6$ and $[Cr_4(NH_3)_{12}(OH)_6]Cl_6$ were also isolated and characterized [118].

Further work has been carried out on the reversible conversion of $[Cr_4(OH)_6]^{6+}$ to $[Cr_4O(OH)_5]^{5+}$ which was discussed in detail in the review last year. It has now been shown that the reaction is not a single proton transfer but involves the scheme (21).

$$\begin{tikzcd}[Cr_4(OH)_6]^{6+} \arrow[r, shift left, "H^+"] \arrow[d, shift left] \arrow[d, phantom, "\text{isomerization}"', shift right=8] & {[Cr_4(OH)_7]^{5+}} \arrow[l, shift left] \arrow[d, shift left, "\text{slow}"] \\ {[Cr_4(OH)_6]^{6+}} \arrow[r, shift left, "H^+"] \arrow[u, shift left] & {[Cr_4O(OH)_5]^{5+}} \arrow[l, shift left] \arrow[u, shift left]\end{tikzcd} \qquad (21)$$

Rate constants for all steps were measured and lend support to the structures previously proposed for the compounds [119].

The mixed metal cation $[FeCr_2(\mu_3\text{-}O)(CH_3COO)_6(H_2O)_3]^+$ has been prepared and isolated as the $[FeCl_4]^-$ salt. A crystal structure determination showed the metal atoms to be statistically disordered within the usual $[Cr_3O(RCOO)_6(H_2O)_3]^+$ structure which was described in the review for 1982. Average bond distances are $M\text{-}\mu_3O$ = 1.891, M-O = 1.966A [120].

1.4.6 Photochemistry

The effects that molecular structure have upon radiationless transitions have been examined for a series of Cr(III) complexes. High frequency vibrations (C-H, O-H) are mainly responsible for non-radiative relaxation, so progressive deuteration decreases the non-radiative rate. ^2E relaxation rates in glassy solutions at 77 K have been determined for $[Cr(NH_3)_{6-x}(H_2O)_x]^{3+}$, $[Cr(NH_3)_{6-x}(D_2O)_x]^{3+}$, $[Cr(ND_3)_{6-x}(H_2O)_x]^{3+}$, $[Cr(ND_3)_{6-x}(D_2O)_x]^{3+}$ and $[Cr(NH_3)_{6-x}(NCS)_x]^{(3-x)+}$. In most cases the non-radiative rate for a mixed ligand complex lies between the values for a homoligated compound [121].

The emission lifetime, τ, and its temperature dependence have been measured for aqueous solutions of $[Cr(NH_3)_5CN]^{2+}$ and *trans*-$[Cr(NH_3)_4(CN)_2]^+$. The lifetimes are relatively long at 20°C and pH 3 (22 and 65µs respectively) and conform with previously suggested rules for Cr(III) photochemistry. In the case of $[Cr(NH_3)_5CN]^{2+}$ the photoreaction (NH_3 aquation) gives both *cis* and *trans*-$[Cr(NH_3)_4(H_2O)(CN)]^{2+}$ [122].

The spectra and rise times for the doublet excited state absorption of *trans*-$[Cr(NH_3)_2(NCS)_4]^-$, $[Cr(NCS)_6]^{3-}$ and *trans*-$[Cr(en)_2(NCS)_2]^+$ have been measured. After approximately half the rise time, the spectra remained constant with time, which is consistent with vibrational relaxation times being comparable with or shorter than the rise times [123].

The photochemistry and photophysics of a number of Cr(III) complexes have been studied with pulsed laser excitation coupled with conductivity and emission detection methods. The compounds examined were $[Cr(1,3\text{-}pn)_3]^{3+}$, $[Cr(en)_3]^{3+}$, $[Cr(NH_3)_6]^{3+}$, *trans*-$[Cr(en)_2F_2]^+$, $[Cr(NH_3)_5CN]^{2+}$ and $[Cr(NH_3)_5(NCS)]^{2+}$ and most were studied in both acidic and basic media. The major photochemical process is photoaquation resulting in either the release of ammonia or the formation of a monodentate en or 1,3-pn ligand. In acidic media, the conductivity detection method depends upon protonation of these products. There are two components to the decrease in conductivity with the (minor) short-lived stage probably arising from the very short-lived quartet states. The major slower stage has the same life time as emission and is probably associated with thermal back intersystem crossing to the lowest quartet state, followed by aquation [124].

It has been found that, contrary to earlier reports, the lifetime of the $^4T_2$ excited states of $[Cr(bipy)_3]^{3+}$ and $[Cr(4,7\text{-}Me_2phen)_3]^{3+}$ are of the order of 10-20ns [125].

Luminescence and photoselection spectra have been measured at 80 K for a number of Cr(III) complexes of D_3 and C_{2v} symmetry, including $[Cr(bipy)_3]^{3+}$, $[Cr(en)_3]^{3+}$ and $[Cr(L\text{-}hist)_2]^+$. The photoselection data indicate that the intensity mechanism for emission involes a second order spin-orbit coupling mechanism for $[Cr(en)_3]^{3+}$ and $[Cr(L\text{-}hist)_2]^+$, but for $[Cr(bipy)_3]^{3+}$ the predominant intensity mechanism involves charge transfer bands overlapping the *d-d* transition [126]. The molar absorption coefficients of the ^2E states of $[Cr(bipy)_3]^{3+}$ and $[Cr(4,7\text{-}Ph_2phen)_3]^{3+}$ have been determined and the reduction of the ^2E states to Cr(II) by Fe(II) and aromatic amines was studied [127].

The quantum yield for the photoaquation of $[Cr(bipy)_3]^{3+}$ has been measured in basic media as a function of pressure to give an apparent volume of activation of 3.8 ± 1.0 mlM^{-1}. From the phosphoresence lifetimes the volume of activation for aquation is $+2.9$ mlM^{-1}. This value, unfortunately, does not differentiate between associative and dissociative mechanisms [128].

The lifetimes of emission for a number of Cr(III) complexes of the types *cis* and *trans*-$[Cr(diamine)_2XY]$ (X,Y = monodentate ligand) have been measured in aqueous solution by time-correlated single photon detection. The data are interpreted using a model which assumes back intersystem crossing is the dominant mode of decay of the excited states of Cr(III) amine complexes and estimates the rates of these processes [129].

The absorption and fluorescence spectra of *trans*-$[Cr(en)_2(NCS)_2]^+$ have been investigated in a range of solvents with widely varying donor number and it was found that in most cases the two spectra shift in the same direction with change of solvent (in most other systems opposite shifts are observed). This correlation is discussed in terms of a vibronic intersystem crossing mechanism. The activation parameters of phosphoresence in the various solvents are consistent with a possible single mechanism, but they do not correlate with the solvent donor numbers [130].

Single crystals of $Al(acac)_3$ containing 1% $Cr(acac)_3$ show three principal phosphorescent bands due to Cr(III) at 1.8 K (in contrast to ruby which shows only one) and these have been examined in magnetic fields (0-5.7 T) for various orientations of the crystals. The principal g values of the corresponding doublet states lie in the ranges $g_{\parallel}$ 1.4-1.7 and $g_{\perp}$ 1.8-2.0 in contrast to ruby. It is suggested that the most likely explanation for the differences is a reversal of the usual ^2E, ^2T ordering [131].

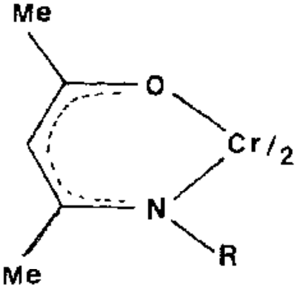
1.5 CHROMIUM(II)

1.5.1 Simple complexes of chromium(II)

The crystal structure of the previously reported $(NEt_4)[Cr(SnPh_3)_3(CO)_4]$ has been determined and the anion has the C_{3v} (capped octahedral) stereochemistry, similar to that found for Mo(II) and W(II) carbonyl halide derivatives [132]. However, the capping carbonyl in $[Cr(SnPh_3)_3(CO)_4]^-$ spans a triangular face of three tin atoms, but in $[W(CO)_4Cl_3]^-$ the capped face has the three carbonyl groups.

The electronic structures of a number of one-dimensional metal phthalocyanines, including CrPc, and their partially oxidized forms have been studied by the tight binding (LCAO) method. It is shown that the increase in conductivity on oxidation is due to both the existence of a partially filled band and the simultaneous increase in the inter-ring overlap associated with the decreased Cr-Cr distance [133].

Chromium(II) complexes of the two β-ketoamines (22) and (23) have been



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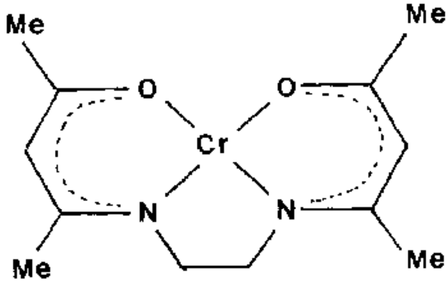


(23)

prepared and characterized by X-ray crystallography. Both complexes are planar and show unusual magnetic properties with rather low and temperature dependent magnetic moments [134].

The Cr(II) complex of saccharine, $[Cr(H_2O)_4(C_7H_4NO_3S)_2].2H_2O$ has been shown to have the *trans* structure with the ligand coordinated in a monodentate fashion through nitrogen. Bond distances are Cr-N = 2.196(3) and Cr-H_2O = 2.048(3) and 2.396(4)A. The distortions in the Cr-H_2O distances are clearly assigned to Jahn-Teller effects when the structure is compared with those of other first row transition metals since similar distortions occur for the Cu(II) derivative but for none of the others [135].

$Cr(SO_3Cl)_2$ and a number of its derivatives of the types $Cr(py)_4(SO_3Cl)_2$, $Cr(MeCN)_4(SO_3Cl)_2$ and $Cr(bipy)_2(SO_3Cl)_2$ have been prepared and characterized. IR studies indicate the chlorosulphate ligands are coordinated through oxygen [136].

Self-consistent charge and configuration calculations (SCCC) have been reported for all the first row transition metal ions $[M(H_2O)_6]^{2+}$. The trends in the computed energy levels are in agreement with the experimental data, For example, the stability increases from $[Ti(H_2O)_6]^{2+}$ to $[Cu(H_2O)_6]^{2+}$ [137].

The Cr(II) reduction of $Co(acac)_3$ was studied in various H_2O/dmf mixtures over the temperature range 25-45°C at μ = 1.00M. Three concurrent mechanisms of reaction were identified; outer sphere, monobridged inner sphere and dibridged outer sphere [138].

The alkali metal salts $M_2[CrX_4(H_2O)_2]$ (X = Cl,Br) are isomorphous, and presumably isostructural with, the octahedral *trans*-$[CuX_4(H_2O)_2]$ salts. However, the salt $(pyH)_2[CrBr_4(H_2O)_2]$ is not isomorphous and a crystal structure determination revealed that the compound contains the unusual neutral square planar *trans*-$[Cr(Br_2(H_2O)_2]$ unit with the other ionic bromides remote from the chromium atom. Bond distances are Cr-O = 2.038(2) and Cr-Br = 2.579(1)A [139].

The heat capacities of $Cs[CrCl_3]$ and $Rb[CrCl_3]$ have been measured from 6-350 K by adibatic calorimetry and from 300-500 K by differential scanning calorimetry [140].

1.5.2 Metal-metal bonded species

A series of INDO calculations on $[Cr_2Me_8]^{4-}$ and the unknown $[Cr_2Cl_8]^{4-}$ complex suggest that the dominant description of the bonding involves ferromagnetic coupling between the two chromium atoms, although this approach gives an estimate of the Cr-Cr distance which is too long. However, it is suggested that although the role of the multiply bonded structures may be small, they have importance in shifting the very flat potential energy surface to shorter Cr-Cr distances [141]. The mass spectra of $[Cr_2(O_2CR)_4]$ (R = Me, Et, ^{i}Pr, ^{t}Bu) have been examined. All gave the parent ion as the base peak but, surprisingly, all gave peaks due to fragments containing only one chromium atom. A study of the metastable peaks showed that these species arose from direct cleavage of $[Cr_2(O_2CR)_4]^+$ units [142]. The molar enthalpy of sublimation of $[Cr_2(O_2CMe_3)_4]$ has been determined [143] to be 299.6±10.2 $kJmol^{-1}$, which is considerably higher than for the corresponding molybdenum complex (170.5±6.5 $kJmol^{-1}$). This result is probably due to the tight packing in the lattice of the chromium compound which gives rise to quite short Cr...O contacts between dimer units. The molar enthalpy of dehydration for the reaction

$$[Cr_2(O_2CMe_3)_4].2H_2O\ (cr) \qquad [Cr_2(O_2CMe_3)_4]\ (cr) + 2H_2O\ (g)$$

is 96.3±8.2 $kJmol^{-1}$ [143].

An X-ray structure determination on $(NEt_4)_2[Cr_2(O_2CEt)_4(NCS)_2]$ showed it to have the usual eclipsed configuration for the anion with axial *N*-bonded thiocyanate groups. The Cr-Cr separation is 2.249(3)A, one of the longest known, Cr-O = 2.019(4) and Cr-N = 2.249(3)A. The complex exhibits a weak temperature independent paramagnetism [144]. The complexes $[Cr_2(O_2CCH_2NH_3)_4]X_4.nH_2O$ (X = Cl, n = 3; X = Br, n = 4) contain glycine coordinated in the zwitterion form $^{-}O_2CCH_2NH_3^{+}$ to give the usual carboxylate bridged dimeric structure with the two halides coordinated in tha axial positions. Bond distances are

	X = Cl	X = Br
Cr-Cr	2.524(1)	2.513(1)A
Cr-O	2.011(5)-2.032(5)	2.022(4)-2.041(4)
Cr-N	2.581(1)	2.736(1)

The complexes are especially stable in the solid state, which is attributed to an extensive network of hydrogen bonding [145].

Ab initio restricted Hartree-Fock calculations have been made on the ground state of $[CrMo(O_2CH)_4]$. Complete CI expansions were carried out and the resulting natural orbital analysis is similar to the correlated wavefunctions obtained for the homo bimetallic parent systems [146].

1.6 CHROMIUM(I)

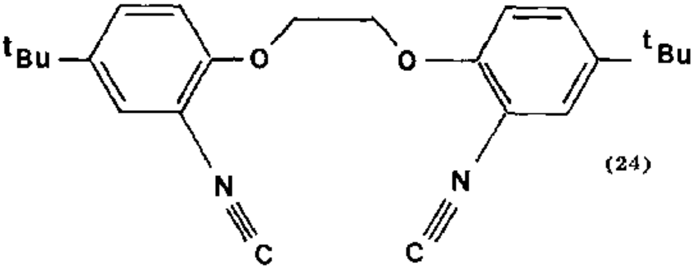
Cr^+ in its ground state does not react with hydrocarbons, but activated states of Cr^+ (produced in a spark plasma) do react with propane and propene to give substantial amounts of $[CrCH_3]^+$ as detected by mass spectrometry [147].

Reduction of chromate by hydroxylamine hydrochloride, azide ion and hydroxyl ion leads in a single step to $[Cr(NO)(N_3)_5]^{3-}$. If the reduction is done in the presence of L-L (= bipy, phen) then complexes formulated as $[Cr(NO)(N_3)_2(L\text{-}L)]$ are readily isolated. All the complexes are low spin [148].

Trans-$[Cr(CO)_4(PPh_3)_2]$ shows reversible electrochemical oxidation in CH_2Cl_2 solution. Either chemical or electrochemical oxidation (at Hg, Pt or Ag electrodes) leads to the isolation of paramagnetic *trans*-$[Cr(CO)_4(PPh_3)_2]^+$ which is sensitive to light and moisture. *Trans*-$[Cr(CO)_4(PPh_3)_2]^+$ reacts with I^-, Br^-, MeCN etc and all reactions give *trans*-$[Cr(CO)_4(PPh_3)_2]$, either by redox processes (I^-, Br^-) or by disproportionation reactions (H_2O, MeCN) [149]. The complexes *fac/mer*-$[Cr(CO)_3(P_3]$ (P = monodentate phosphorus ligand) may be reversibly oxidized electrochemically to *fac/mer*-$[Cr(CO)_3P_3]^+$ on the short time scale of cyclic voltammetry, although on the longer preparative time scale the isolated products are always the *mer*$^+$ species. Rapid electron transfer between *mer*^{o} and *mer*$^+$ isomeric pairs was observed by EPR and NMR techniques [150].

1.7 CHROMIUM(0)

The first bond dissociation energies in the gas phase of a number of binary carbonyls have been determined using a pulsed laser pyrolysis technique. The values for the Group VI carbonyls are 37, 40 and 46 kcal/mol for $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$ respectively [151]. Using the ligand ^{t}BudiNC (24) the

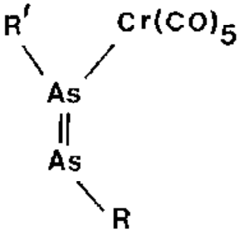


(24)

18-electron complex $Cr(^tBudiNC)_3$ was prepared from $CrCl_3(thf)_3$ by Na/Hg reduction. Oxidation with 1 or 2 moles of $Ag[PF_6]$ gave the corresponding 17 and 16-electron homoleptic complexes [152].

$Cr(CO)_5(N_2)$ has been identified by fast IR detection methods in cyclohexane solution at room temperature. It was generated by photolytic decomposition of $Cr(CO)_6$ in cyclohexane under N_2 through the intermediate $Cr(CO)_5(C_6H_{12})$ [153].

All previous examples of complexes of diarsenes (RAs=AsR) have both arsenics bound to the metal and an As-As bond oredr of about 1.5. However, the reaction between $Cr(CO)_5(thf)$ and RAs=AsR' (R = $2,4,6-(\ Bu)_3C_6H_2$, R' = $CH(SiMe_3)_2$) gave $Cr(CO)_5(RAs=AsR')$ which a crystal structure determination showed to have only one arsenic bound to chromium as shown in (25).



(25)

The As-As distance of 2.246(1)A is significantly shorter than in η^2 diarsene complexes [154].

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