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3. 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 98 and 99. Thus most of the work published in 1983 and some published at the end of 1982 will be reviewed. Chromium organometallic chemistry is not formally included in the review, but reference is made to some papers of general interest.

3.1 CHROMIUM(VI)

Chromium(VI) in acid solution (0.1 and 1.0M HCl, H_2SO_4, H_3PO_4) is extracted efficiently by trilaurylamine oxide into chloroform solution, probably in the

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form of the $[HCrO_4]^-$ ion [1]. However, at higher concentrations of hydrochloric acid there is evidence for the extraction of $HCrO_3Cl$. The oxygen exchange reaction between water and pentaamminechromatocobalt(III), $[(NH_3)_5Co\text{-}O\text{-}CrO_3]^+$ (= $[RCrO_4]^+$) has been studied in the pH range 6.0-8.0 [2]. The reaction is complicated by concurrent hydrolysis, but the results may be interpreted in terms of the reactions

$$[RHCrO_4]^{2+} + [RCrO_4]^+ \rightleftharpoons [RCr_2O_7R]^{4+} + OH^-$$

$$[RHCrO_4]^{2+} + [HCrO_4]^- \rightleftharpoons [RCr_2O_7]^+ + H_2O$$

$$[RCrO_4]^+ + [HCrO_4]^- \rightleftharpoons [RCr_2O_7]^+ + OH^-$$

$$[RCrO_4]^+ + H_2O \rightleftharpoons [R(OH)]^{2+} + [HCrO_4]^-$$

$$[HCrO_4]^- + H_2{}^{18}O \rightleftharpoons [HCrO_3{}^{18}O]^- + H_2O$$

$$[R(OH)]^{2+} + [HCrO_3{}^{18}O]^- \rightarrow [RCrO_3{}^{18}O]^+ + H_2O$$

It was concluded [2] that the bond breaking in the hydrolysis of the chromato complex occurs at the Cr-O bond.

The molecular structure of CrO_2F_2 in the gas phase has been re-investigated by electron diffraction [3]. The geometry of the molecule is described by the parameters

Cr=O	1.575(2)Å	O-Cr-O	107.8(8)°
Cr-F	1.720(2)	F-Cr-F	111.9(9)
O-O	2.543(14)	O-Cr-F	109.3(2)
O-F	2.685(4)		
F-F	2.846(15)		

As with CrO_2Cl_2, whose gas phase structure was reported in the review last year, the O-Cr-O angle is smaller than the halogen-Cr-halogen angle. This is contradictory to the predictions of VSEPR theory and there is no obvious explanation for phenomenon.

An investigation of organoimido complexes of d^0 configuration transition metals, including Cr(VI), has been reported [4]. Reaction of CrO_2Cl_2 with *tert*-butyl(trimethylsilyl)amine according to the reaction

$$CrO_2Cl_2 + 4{}^tBuNH(SiMe_3) \rightarrow (Me_3SiO)_2Cr(N^tBu)_2 + 2[{}^tBuNH_2(SiMe_3)]Cl$$

gave the imido complex which could also be prepared from CrO_3. Preliminary X-ray diffraction studies show the compound to be monomeric. Reaction with one equivalent of benzaldehyde replaced an imido group to give the mono-oxo derivative $(Me_3SiO)_2CrO(N^tBu)$ [4].

3.2 CHROMIUM(V)

The EPR and ENDOR spectra of CrO_4^{3-} in a single crystal of K_2SO_4 have been investigated [5]. The ion cannot be incorporated directly into the lattice so crystals of the host doped with CrO_4^{2-} were grown and the CrO_4^{3-} ion produced by X-ray irradiation. All spectral parameters are consistent with the d^1 CrO_4^{3-} isomorphously replacing SO_4^{2-} in the lattice. However, the EPR signal was split by a single proton which may arise from a water molecule incorporated in the lattice and subsequently decomposed by the X-ray irradiation, or alternatively by chromium entering the lattice as $[HCrO_4]^-$.

Potassium and rubidium salts of the $[CrOCl_5]^{2-}$ ion have been isolated for the first time [6]. CrO_3 and MCl (M = K,Rb) were separately dissolved in portions of acetic acid saturated with hydrogen chloride gas at as low a temperature as possible (0 to -10 ℃) and the solutions then mixed. Both compounds are orthorhombic and isomorphous with $K_2[MoCl_5]$ and show a Cr=O stretch at 950cm^{-1}. The complexes $Cr_2O_4Cl_2L_2$ (L = dipy, phen) were produced by heating $CrOCl_3L$ with water [7]. The oxidation state of chromium was checked, the magnetic moments are low (0.73 BM bipy; 0.94 BM phen) suggesting interaction between the chromium centres. The IR spectra show bands at about 850cm^{-1} assigned to a bridging oxygen mode. On reaction in the solid state with oxalate at 100-120 ℃ the complexes CrO(ox)ClL are formed. These have magnetic moments of 1.83-2.05 BM and Cr=O stretching frequencies of 900-960cm^{-1} suggesting terminal oxygen groups [7].

The stabilization of chromium(V) species by crown ethers has been investigated [8]. The complexes were made either directly using Na_3CrO_4 or by reduction of chromium(VI) by the ligand. The reactions were studied in the dark and also under irradiation and the products were characterized by EPR. Usually only one complex is formed in the dark, but other short-lived chromium(V) species are produced on irradiation. The pyridinium salt $(pyH)[CrOCl_4]$ gives a different chromium(V) species, but addition of Cl^- to solutions of Na_3CrO_4 immediately gives this same spectrum, so the species are closely related. It is speculated that the main product is square pyramidal with four oxygens of the crown ether in the equitorial positions and Cr=O axial. The chloro species is thought to be similar but with Cl^- *trans* to Cr=O.

Two papers [9,10] have reported almost identical results for the IR and EPR spectra of CrN(TTP) (TTP = 5,10,15,20-tetra-*p*-tolylporphyrinato) although the preparations are different. U.V. irradiation of $Cr(TTP)N_3$ in CH_2Cl_2 or C_6H_6 [9] is one method of preparation and the reaction

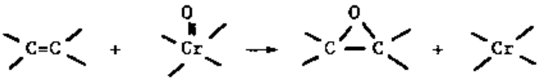
$$Cr(OH)(TTP) + NaOCl + NH_3 \longrightarrow CrN(TTP) + NaCl + 2H_2O$$

was used by the other group of workers [10] who also prepared CrN(OEP) (OEP = octaethylporphyrinato) by the same method. The EPR spectrum of CrN(TTP) shows well resolved signals at room temperature with g = 1.985. From the super-hyperfine splitting the four pyrrole N's and the axial N appear to be magnetically equivalent, and ^{53}Cr satellites were also observed. A band at $1010cm^{-1}$ in the IR spectrum was assigned to the Cr-N (nitride) stretch and this was confirmed by both groups by ^{15}N substitution which caused the emergence of a new peak at $991cm^{-1}$ (calculated $990cm^{-1}$). The mass spectrum showed the parent ion [10] and a single crystal X-ray structure [9] confirmed the compound contains square pyramidal chromium with a Cr-N (axial) distance of 1.565Å (which is very short) and equitorial Cr-N bond distances of 2.032 - 2.052(5)Å. The chromium atom is 0.42Å above the mean plane of the pyrrole nitrogens and the porphyrin ligand is saddle shaped.

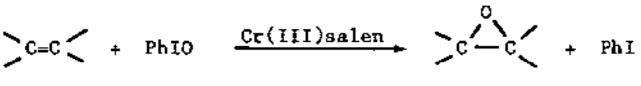
The chromium(V) species $[CrO(salen)]^+$ has been generated [11] by the reaction

$$[Cr(salen)(H_2O)_2]PF_6 + PhIO \longrightarrow [CrO(salen)]PF_6 + PhI + 2H_2O$$

An X-ray diffraction study has shown it to have a square pyramidal structure very similar to that of the porphyrin complex described above. The chromium atom is 0.52(5)Å above the mean plane of 2N's and 2O's of the salen ligand (Cr-O = 1.850(7), Cr-N = 2.006(9)Å) and the Cr=O (axial) distance is 1.56(5)Å. The geometry of the salen ligand is almost the same as in the chromium(III) starting material. An interesting feature of this complex is that it acts as an oxygen transfer catalyst to alkenes



and in fact catalytic oxidation of alkenes has been achieved by



In a related study [12] it has been shown that alkenes such as (E) and (Z)-β-methylstyrene in aprotic solvents are converted stereospecifically by

$CrO_2(NO_3)_2$ to the corresponding epoxide under mild conditions. It is believed that oxochromium(V) intermediates are again important in these reactions and EPR evidence was obtained to substantiate this belief.

3.3 CHROMIUM(IV)

The six layer polytype of $BaCrO_3$ was found to be a product from the reaction of CrO_2 and Ba_2CrO_4 at 900 °C under 60-65 kbar pressure [13]. Its structure consists of a six layer stacking sequence of close packed BaO_3 layers containing chromium(IV) in all the octahedral interstices. The Cr-O bond distance is 1.945Å.

Reaction of $CrCl_2(dmpe)_2$ with *n*-BuLi in hexane under a nitrogen atmosphere yielded yellow diamagnetic $CrH_4(dmpe)_2$, the first chromium(IV) hydride [14]. Cr-H stretches were observed at 1757, 1725 and 1701cm^{-1}. The coupled ^1H and ^{31}P NMR spectra were both quintets, thus confirming the tetrahydride formulation. The crystal structure of $CrH_4(dmpe)_2$ has been determined and confirms that it represents the first example of eight coordinate chromium(IV). The compound can be described as approximately dodecahedral with the hydrides occupying the inner sites. Alternatively, the coordination may be envisaged as octahedral with the hydrides occupying the axial sites in pairs. The H..H contacts of only 1.7Å justify this view. The Cr-P bond distances are 2.252(3)-2.258(3)Å and Cr-H bond lengths are 1.53(3)-1.60(3)Å.

Reaction of $CrCl_3(thf)_3$ with $Li[CPh{=}CMe_2]$ yields $Cr(CPh{=}CMe_2)_4$ as dark green crystals [15]. The reaction proceeds *via* an extremely unstable blue compound which is thought to be $Cr(CPh{=}CMe_2)_3$. $Cr(CPh{=}CMe_2)_4$ is paramagnetic with a magnetic moment in solution of 2.81BM. A crystal structure determination revealed tetrahedral chromium(IV) with Cr-C bond lengths in the range 2.032(13)-2.049(12)Å.

3.4 CHROMIUM(III)

This largest section of the review is generally arranged within each sub-section according to the identities of the most abundant donor atoms in the order Group(IV), Group(V) etc.

3.4.1 Complexes of simple ligands

A complete vibrational analysis of a number of hexacyano complexes, including $[Cr(CN)_6]^{3-}$, has been presented on the basis of the valence force field method, with good agreement between calculated and experimental frequencies [16]. The photosubstitution of $[Cr(CN)_6]^{3-}$ and $[Cr(CN)_5OH]^{3-}$ in alkali solution has been studied [17]. It was concluded that photosubstitution with OH^- competes effectively with the alternative pathway of aquation followed by de-protonation.

Previous electrochemical studies on $Cr(CNR)_6$ complexes [R = Ph; 2,6-dimethylphenyl (2,6-dmp)] have demonstrated the existence of $[Cr(CNR)_6]^{3+}$ and these complexes have now been isolated using $NOBF_4$ or $SbCl_5$ as oxidants [18]. Each compound gives a single C-N stretch and their magnetic moments confirmed they are complexes of chromium(III). Although they are stable in a dry atmosphere, the CN2,6-dmp compounds are reduced in air to chromium(II) and all the complexes are extremely labile with instantaneous displacement of isocyanide by acetone and acetonitrile [18].

The electrochemical reduction in acetonitrile of a number of chromium(III) dialkylamido and bis(trimethylsilyl)amido complexes was examined [19]. Only $Cr(N\{SiMe_3\}_2)_3$ and $Cr(N^iPr_2)_3$ showed behaviour which was close to reversible. Coulometric results indicated reduction to chromium(II).

The outer sphere association constants between several chromium(III) cations and the sulphate ion have been determined at ionic strength 0.2 at 25 °C using a modified version of the potentiostatic method [20]. The values obtained were $[Cr(NH_3)_6]^{3+}$ 18±2; $[Cr(en)_3]^{3+}$ 21±2; $[Cr(NH_3)_5H_2O]^{3+}$ 19±2 and $[Cr(urea)_6]^{3+}$ 13±2. A number of $[Cr(am)_6]^{3+}$ cations (am = amine) with the $B_{10}H_{10}{}^{2-}$ ion in the outer sphere have been prepared [21] by the reaction

$$[Cr(am)_6]X_3 \ + \ (NH_4)_2B_{10}H_{10} \xrightarrow{H_2O} [Cr(am)_6]X.B_{10}H_{10}.\ H_2O \ + \ 2NH_4X$$

$$(X = Cl, Br)$$

The effect of heating the complexes was studied and the most interesting results were observed for am = NH_2CH_3

$$\begin{tikzcd}
{[Cr(am)_6]Br.B_{10}H_{10}.2H_2O} \arrow[r, "70\text{-}80^\circ"] & {[Cr(am)_6]Br.B_{10}H_{10}} \arrow[d, "100^\circ"] \\
{trans\text{-}[Cr(am)_4Br(B_{10}H_{10})]} & {[Cr(am)_5Br]B_{10}H_{10}} \arrow[l, "120\text{-}150^\circ"']
\end{tikzcd}$$

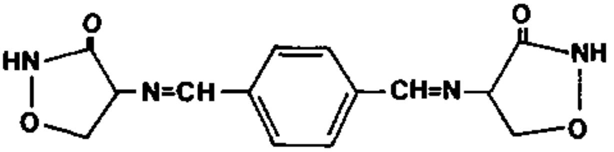
It is thought that the $B_{10}H_{10}$ligand coordinates *via* a 3-centre bond involving chromium and two borons which occupy one stereochemical position.

The base hydrolysis of isothiocyanatopentaamminechromium(III), $[Cr(NH_3)_5NCS]^{2+}$, has been studied in water/ethanol and water/acetone mixtures [22]. No release of NH_3 was detected in any reaction so the product was entirely $[Cr(NH_3)_5OH]^{2+}$. The observed rate law is given by the expression

$$[OH^-]/k_{obs} = [OH^-]/k + 1/kK$$

suggesting the formation of an intermediate in a pre-equilibrium (equilibrium constant K) followed by its transformation into the product in a rate determining step (rate constant k). Values of k and K were determined at various temperatures and at various aqueous/organic solvent ratios. The rate constants are strongly influenced by the solvent composition and plots of k against 1/D (D = dielectric constant) were linear with large positive slopes. The dissociation of the Cr-NCS bond is probably solvent assisted due to solvation of the departing ligand.

A number of complexes of chromium(III) with 4,4'-[1,4-phenylenebis(methylidynenitrilo)]bis(isoazolidin-3-one) (trz) (1)



(1)

have been prepared [23]. The complexes $[Cr(trz)_6]^{3+}$, $[Cr(trz)_3X_3]$ and $[Cr(trz)_2(H_2O)X_3]$ (X = Cl, Br) appear to be bonded to chromium *via* one N of the ligand as judged by the IR spectra since the N-H stretch is split, but only one C=O stretch was observed. The IR spectra also showed $[Cr(trz)_3X_3]$ to be the *mer* isomer. A further complex $[Cr(trz)(H_2O)_2X_3]$ is somewhat different; it shows only one N-H stretch and two C=O stretches suggesting that in this complex the ligand is bonded through one carbonyl group.

A study has been made [24] of the kinetics of anation of $[Cr(NH_3)_5H_2O]^{3+}$ by $H_3PO_2/H_2PO_2^-$ in aqueous solution at 40, 50 and 60 °C. Both the acid and its anion give the same product, $[Cr(NH_3)_5(H_2PO_2)]^{2+}$. From an analysis of the kinetic data it appears that both reagents first form outer sphere complexes which have identical interchange constants. The mechanism is thought to be on the borderline between I_d and I_a. As part of a wider study involving several other metal ions, the partial molar volume $\overline{V}°$ for $[Cr(NH_3)_5H_2O]^{3+}$ and $[Cr(H_2O)_6]^{3+}$ have been determined by extrapolation from density measurements at 298.15 K [25]. The values for a series of high spin aqua ions can be represented for ionic charges z = 1-4 by

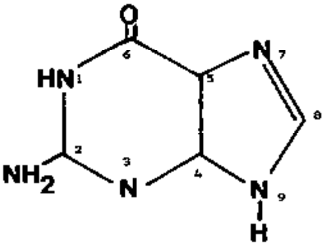
$$\bar{V}^{\circ}_{obs} = 2.523 \times 10^{6}(r + 238.7)^{3} - 18.07n - 417.5z^{2}/(r + 238.7)$$

where $\bar{V}^{\circ}_{obs}$ is the absolute partial molar volume in $cm^{3}mol^{-1}$ of M^{z+} relative to $\bar{V}^{\circ}_{obs} = -5.4\ cm^{3}mol^{-1}$ for $H^{+}(aq)$ and r is the radius in pm of M^{z+} with coordination number n.

The complexes $[Cr(NH_3)_5L]^{3+}$ (L = formamide, urea, dimethylurea) were prepared as the *O*-bonded isomers by treatment of $[Cr(NH_3)_5(OSO_2CF_3)]^{2+}$ with the ligand [26]. The mode of coordination was determined by observation of characteristic IR bands very similar to those of the analogous cobalt(III) complexes. In aqueous base solution the compounds isomerize to the de-protonated *N*-bonded isomer without competitive hydrolysis and the isomerization is completely reversible on re-acidification.

A number of nicotinates of chromium(III) have been prepared by the interaction of nicotinic anhydride and a chromium(III) hydroxy complex in dmf as solvent [27]. Some of the complexes isolated were $[Cr(NH_3)_5(NA)](ClO_4)_2$, *cis* and *trans*-$[Cr(NH_3)_4(NA)_2]ClO_4$, *cis*-$[Cr(NH_3)_4(NA)_2]Br$ and *cis*-$[Cr(en)_2(NA)_2]Br$ (NA = nicotinic acid, 3-carboxypyridine). Although the ligand could coordinate *via* O or N, all spectroscopic evidence in the solid state and in solution suggest an *O*-bonded (monodentate) ligand. This was confirmed by an X-ray structural determination on the protonated form of *trans*-$[Cr(NH_3)_4(NAH)_2](ClO_4)_3.2H_2O$. The Cr-O distances are 1.947(6) and 1.958(6)Å and Cr-N bond lengths are in the range 2.059(7) - 2.072(8)Å. The Cr-O-C-O portions of the molecule are planar, but the pyridinium ring is about 20° out of this plane.

Complexes of 2-amino-6-oxo-purine, (LH), (2) with several metals including chromium(III) have been isolated by reaction of a soluble metal salt and the ligand in an ethanol/triethylformate solvent mixture [28]. Based on IR, magnetic, spectral and conductivity data the chromium complex was thought to be $[Cr(LH)_2(EtOH)_2(OClO_3)_2]ClO_4$. The portion of the IR spectrum due to the perchlorate groups showed ν_3 and ν_4 triply split and ν_1 and ν_2 IR active suggesting both ionic and monodentate perchlorate. It is thought the ligand is



(2)

coordinated through N9.

A survey [29] has been made of a number of chromium(III) complexes, with and without another paramagnetic counter ion, in an attempt to find examples of super-exchange, but without success. Thus $[Cr(urea)_6][Cr(NCS)_6].2H_2O$ remains paramagnetic to as low as 40 mK although $[Cr(NH_3)_5H_2O][CuCl_5]$ appears to undergo magnetic ordering at 298 mK.

The thermal aquation of $[Cr(NH_3)_5F]^{2+}$ in the dark has been examined to determine whether fluoride has a *cis* labilizing effect [30]. Thus it was necessary to determine the stereochemistry of the aquated product and it was found to be 25% *trans* and 75% *cis*-$[Cr(NH_3)_4(H_2O)F]^{2+}$. However, after taking into account the statistical factor (4) the *trans* isomer is slightly favoured and so it was concluded that fluoride has no *cis* labilizing effect.

The formation of α-Cr_2O_3 from hydrated chromium oxides in a hydrogen atmosphere has been examined by a number of techniques including extended X-ray absorption fine structure, magnetic susceptibility, IR and differential scanning calorimetry. All the methods showed the absence of any CrO(OH) phase as an intermediate [31]. The ^{151}Eu and ^{57}Fe Moessbauer spectra of the orthorhombic perovskite $EuFe_{1-x}Cr_xO_3$ $(0<x<1)$ were examined and it was shown that the supertransferred hyperfine field at ^{57}Fe due to Cr^{3+} nearest neighbour cations has the same spin as that due to Fe^{3+} [32]. The compound Cr_2WO_6 has the inverse rutile structure containing chains of MO_6 octahedra (M = Cr and W) parallel to the *c* axis. It is non-conducting in contrast to Rh_2WO_6, which has the random rutile structure, and which is conducting [33].

It has been shown previously that the oxidation of $[Cr(H_2O)_6]^{3+}$ with periodate involves an unusual second order dependence on the concentration of Cr(III). A mechanism involving an activated species containing two Cr(III) groups and one periodate, with subsequent oxidation to Cr(IV), was suggested. An alternative mechanism involving Cr(V) has now been suggested which could also fit the observed second order dependence, but it also predicts a retardation of reaction rate with excess periodate. Experimentally, no such retardation is observed [34], thereby eliminating this newly proposed mechanism. The kinetics of substitution of aqua ligands in $[Cr(H_2O)_6]^{3+}$ by quinolinic acid in H_2O/EtOH media has been studied [35]. The rate law is

$$\frac{d[Cr(QuinH)_3]}{dt} = \frac{kK_E[Cr(H_2O)^{3+}]_{total}[QuinH^-]}{1 + K_E[QuinH^-]}$$

where K_E = ion pair equilibrium constant

k = rate constant for conversion of outer sphere complex to inner sphere complex

The cyclopentyl complex $[(H_2O)_5Cr\text{-}c\text{-}C_5H_9]^{2+}$ is formed by the reaction of Cr(II) with H_2O_2 in aqueous solution saturated with cyclopentane according to the reactions

$$[Cr(H_2O)_6]^{2+} + H_2O_2 \longrightarrow [(H_2O)_5Cr(OH)]^{2+} + HO\bullet + H_2O$$

$$HO\bullet + c\text{-}C_5H_{10} \longrightarrow \bullet C_5H_9 + H_2O$$

$$\bullet C_5H_9 + [Cr(H_2O)_6]^{2+} \longrightarrow [(H_2O)_5Cr\text{-}c\text{-}C_5H_9]^{2+} + H_2O$$

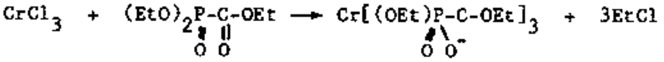
$$[(H_2O)_5Cr(OH)]^{2+} + H^+ \longrightarrow [Cr(H_2O)_6]^{3+}$$

overall

$$2[Cr(H_2O)_6]^{2+} + H_2O_2 + c\text{-}C_5H_{10} + H^+ \longrightarrow [Cr(H_2O)_6]^{3+} + [(H_2O)_5Cr\text{-}c\text{-}C_5H_9]^{2+} + 3H_2O$$

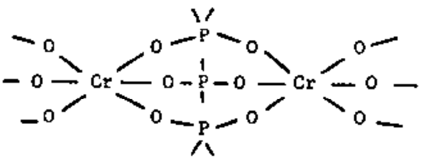
The complex $[(H_2O)_5Cr\text{-}c\text{-}C_5H_9]^{2+}$ is relatively stable in solution but sensitive to oxygen. It decomposes by parallel unimolecular pathways of acidolysis (to give $[(H_2O)_5Cr(OH)]^{2+}$ and $c\text{-}C_5H_{10}$) and by homolysis (to give $[Cr(H_2O)_6]^{3+}$ and $\bullet C_5H_9$). The latter pathway is reversible and not thermodynamically favoured and only occurs in the presence of oxidizing agents [36].

Complexes of several metals, including chromium(III), have been made [37] with the diethylphosphonoformato ligand by heating the metal chloride with triethylphosphonoformate



$$CrCl_3 + (EtO)_2\underset{O}{\underset{\|}{P}}\text{-}\underset{O}{\underset{\|}{C}}\text{-}OEt \longrightarrow Cr[(OEt)\underset{O\ \ O^-}{\underset{/\ \backslash}{P}}\text{-}C\text{-}OEt]_3 + 3EtCl$$

IR studies show that the carboxylate is not coordinated and it is thought that because of their insolubility the complexes have the same type of structure as those adopted by complexes of similar ligands, that is, both oxygens on phosphorus are coordinated to adjacent metal atoms to form chains (3)

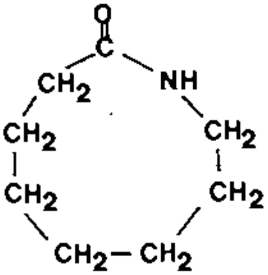


(3)

The magnetic moment is low (2.99 BM) perhaps supporting this suggestion. Complexes of chromium(III) with 2'AMP and 3'AMP (adenosine 2' or 3'-monophosphoric acid respectively) have been isolated and characterized [38]. On the basis of IR studies it appears that chromium is coordinated to the phosphate group in both complexes and that in addition some interaction with the adenine ring may occur with 2'AMP.

Chromium metal can be dissolved in SO_2/dmso solvent mixture by using it as a sacrificial electrode [39]. The compound initially isolated is formulated as $[Cr_2(dmso)_{20}](S_2O_7)_3$ in which the dispositions of the dmso molecules are unknown. On heating to 400 ℃ $Cr_2(S_2O_7)_3$ is obtained.

The crystal structure of $CrCl_3L_3$ (L = 1-aza-2-cyclononanone) (4) has been



(4)

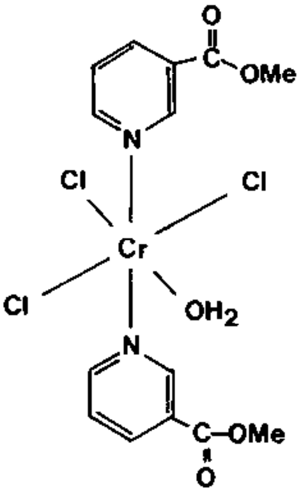
determined [40] . The compound is *facial* ; the ligands adopt a *cis* configuration and are coordinated through oxygen. The Cr-O bond lengths are in the range 2.000(5) - 2.083(5)Å and Cr-Cl 2.324(2) - 2.436(2)Å.

The standard enthalpy of formation at 25 ℃ of K_3CrF_6 has been determined by solution calorimetry as -2,977 $KJmol^{-1}$ [41]. CrO_3 undergoes facile reduction with formic acid in the presence of 40% aqueous HF and a fluoride salt AF (A = NH_4, Na, K, Rb) to give $A_2[CrF_5(H_2O)]$ [42].

The IR and Raman spectra of solid anhydrous $CrCl_3$ have been examined, but although a number of well defined absorptions were observed no detailed assignments were made [43]. The conductivity of a mixture of $CrCl_3$ and α-picolinium chloride was examined and compared with the $FeCl_3$/α-picolinium chloride mixture [44]. These superficially similar binary molten salt systems have very different characteristics. The addition of $FeCl_3$ to the organic salt causes the fluidity and conductivity to increase while addition of $CrCl_3$ to the organic salt causes a rapid decrease in these properties. The differences are attributable to the different coordination numbers of the two metal ions. The single crystal susceptibilities of $Cs_2CrCl_5.4H_2O$ have been measured over the temperature range 40 mK to 4.2 K [45]. Long range magnetic ordering occurs at 0.185±0.005 K. Successful data analysis was carried out in terms of S = 3/2 Heisenberg linear chain antiferromagnets with CF and exchange energies of comparable magnitude. The heat capacity of the S = 2 layer antiferromagnet

$(CH_3NH_3)_2CrCl_4$ has been measured over a wide temperature range (10 - 302 K). There is a broad anomaly in the heat capacity between 100 and 200 K which is thought to arise from the development of magnetic disordering [46].

$[Cr(Me\text{-}nic)_2(H_2O)Cl_3]$ (Me-nic = methylnicotinate) was prepared by reacting $CrCl_3.6H_2O$ and the ligand in ethanol [47]. The structure (5) contains the nicotinate ligands almost in the same plane bonded through N in *trans* positions with the carboxylate groups non-bonding and both on the same side of the molecule. There are two independent, but very similar, molecules in the unit cell and bond lengths are

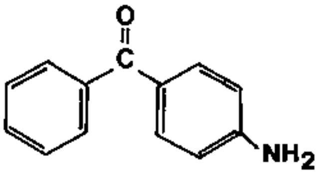


(5)

Cr-N	2.071(9) - 2.119(9)Å
Cr-Cl	2.303(4) - 2.328(4)
Cr-O	2.016(9)

The compound may be a model for glucose tolerance factor which is thought to contain chromium bound to nicotinic acid *via* N.

A series of rather poorly defined insoluble complexes CrX_3L_n (X = Cl,Br n = 1,2,3,6 and 7,8 for X = Br only) have been reported [48] where L = 4-aminobenzophenone (6)



(6)

which has previously been shown to coordinate to non-transition metals by either N or O. However, in the present case, both modes of coordination were ruled out since $\nu_{C=O}$ and ν_{N-H} vibrations are very similar to those of the free ligand. On the basis of these results it was proposed that these are "molecular complexes" in which the π-electron system interacts with the metal.

Although $CrCl_3(thf)_3$ is well known, the corresponding bromo and iodo compounds are not. They have now been prepared by reacting thf with pure CrX_3 and further reaction of $CrX_3(thf)_3$ with *n*-Bu_4NX gave (*n*-$Bu_4N)[Cr(thf)_2X_4]$. The corresponding thiocyanate was also prepared from $CrCl_3.6H_2O$, thf and KCNS [49].

3.4.2 Complexes of bidentate ligands

A much improved preparation of *cis*-$[Cr(en)_2F(NH_3)]Cl$ has been reported by the sealed tube reaction of (±)*cis*-$[Cr(en)_2FCl]I$ and dry liquid NH_3 at room temperature [50]. The product is a mixture of *cis*/*trans*-$[Cr(en)_2F(NH_3)]Cl$ with >70% *cis*. The *cis* isomer was separated as the iodide and resolved using silver bromocamphor-π-sulphonate (thus confirming the *cis* configuration of the original cation) and assigned an absolute configuration of Δ by comparison with other complexes.

The complexes *trans*-$K[Cr(aa)_2F(H_2O)][Co(CN)_6].H_2O$ (aa = en, 1,3-pn) each show a single cyano stretch at 2125 cm^{-1}. On heating, water is lost (1 mole at 320 K, a second at 425 K) and bridge formation together with isomerization (*trans* to *cis*) occurs to give *cis*-$K[(aa)_2FCr\text{-}NC\text{-}Co(CN)_5]$. The IR spectra now show two C-N stretches indicating terminal and bridging cyano groups and the visible spectra reveal the change in stereochemistry about chromium [51]. Very similar results were obtained [52] from the action of heat on *trans*-$[Cr(1,2\text{-}pn)_2F(H_2O)][M(CN)_4]$ (M = Ni, Pd, Pt) to give *cis*-$[(1,2\text{-}pn)_2FCr\text{-}NC\text{-}M(CN)_3]$.

Some simple adducts of chromium(III) methylsulphate of the types $Cr(CH_3SO_3)_3bipy$, $Cr(CH_3SO_3)_3phen$ and $Cr(CH_3SO_3)_3py$ have been reported but little structural information is available [53].

The crystal structure of *trans*-$[Cr(en)F_2(H_2O)_2]Cl$ has been determined [54]. Bond lengths are Cr-F = 1.885(1), Cr-N = 2.044(2) and Cr-O = 1,997(2)Å. There is an ill-defined shoulder in the visible spectrum typical of *trans* dihalo chromium(III) complexes.

A series of chromium(III) complexes with a number of ditertiary phosphines and ditertiary arsines (L-L) have been prepared [55]. Reaction of $CrX_3(thf)_3$, $(NR_4)X$ and the ligand usually gives $(NR_4)[Cr(L\text{-}L)X_4]$. Most show four Cr-X stretches in their IR spectra and confirmation of the structure of $(N^nPr_4)[Cr($*cis*-$Ph_2PCHCHPPh_2)Cl_4]$ was obtained by a crystal structure determination. The Cr-Cl bond lengths do not vary significantly (2.316(4) -

2.331(4)Å), suggesting that phosphorus has no *trans* effect on chromium, and the Cr-P bond lengths are rather long (2.485(4) and 2.511(4)Å). Confirmation of weak Cr-P bonding is obtained from the visible spectral parameters. The complexes of empirical formula $Cr(L\text{-}L)_{2.5}X_3$ are formulated as *trans*-$[Cr(L\text{-}L)_2X_2][Cr(L\text{-}L)X_4]$ as described for one of the ligands in the review last year. Simple salts of a few *trans*-$[Cr(L\text{-}L)_2X_2]^+$ cations were isolated by reacting $CrX_3(thf)_3$ with the ligand in 1:2 proportions [55]. A series of complexes containing the elusive CrP_6 and $CrAs_6$ cores have been prepared [56]. They are of the form $[Cr(L\text{-}L)_3]^{3+}$ and $[Cr(L\text{-}L\text{-}L)_2]^{3+}$ where L-L and L-L-L are ditertiary and tritertiary phosphines or arsines respectively. The complexes were prepared by interaction of the ligands with $[Cr(thf)_6]^{3+}$; in general, they are reactive and fairly unstable, possibly as a result of steric crowding about chromium.

The complex $Cr(eta)_3$ (etaH = 2-aminoethanol) has been prepared in which the ligand is bidentate [57]. Addition of strong acid causes hydrolysis in three distinct steps

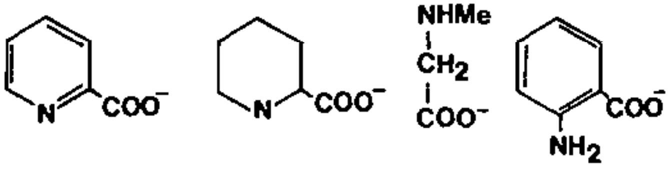
a) instantaneous protonation to give $[Cr(etaH)_3]^{3+}$ in which the ligand is still bidentate

b) rapid (complete in about 10 mins at 20 °C) conversion to $[Cr(etaH)_3(H_2O)_3]^{3+}$ in which the ligand is monodentate through N

c) slow aquation to give $[Cr(H_2O)_6]^{3+}$.

A number of transition metal complexes of formylhydrazide, HC(OH)=NNH$_2$, have been prepared [58] and the chromium(III) complexes are of the type $[Cr(L\text{-}L)_3]^{3+}$. Chromium(III) chloro complexes with L(+) cysteine (L-L) have been reported [59] of the types $[CrCl_2(L\text{-}L)_2]^-$ in which the ligand is bidentate coordinating through the amino and carboxylate groups and $[CrCl_2(L\text{-}L)_4]^{3-}$ in which cysteine is thought to be monodentate through the carboxylate group. Less well-defined complexes were also prepared using DL-penicillamine and L(-) cystine [59].

A series of complexes $Cr(L\text{-}L')_3$ have been prepared [60] (where L-L' is the anion of an aminocarboxylate as shown below (7))

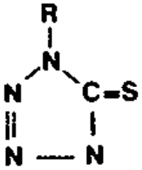


(7)

pic pip sar aba

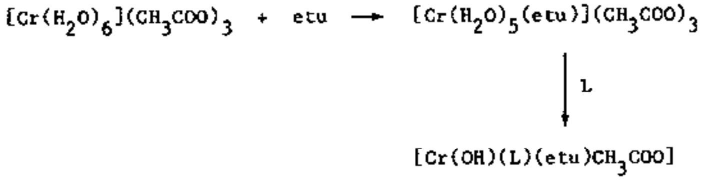
in order to arrange the nitrogen containing groups in a spectrochemical sequence. The compounds $Cr(L\text{-}L')_3$ were assumed to be *facial*, but this is not certain. Visible absorption and luminescence spectra were recorded and spectral parameters determined; the splitting parameters decreased from left to right in the sequence above with those for pic being similar to those for NH_3.

Some mixed ligand complexes of chromium(III) containing acetate, ethylenethiourea (etu) and 1-substituted tetrazoline-5-thiones (8) have been



(8)

prepared [61] according to the reaction



$$\begin{array}{ccc}[Cr(H_2O)_6](CH_3COO)_3 + etu & \longrightarrow & [Cr(H_2O)_5(etu)](CH_3COO)_3 \\ & & \Big\downarrow L \\ & & [Cr(OH)(L)(etu)CH_3COO]\end{array}$$

The electronic spectrum of Cr^{3+} ions in molten NH_4HSO_4 (160-350 ℃) and $NaPO_3$ (600-700 ℃) indicate formation of $[Cr(HSO_4)_3]$ and $[Cr(PO_3)_3]$ respectively with a CrO_6 environment [62]. Crystal field parameters fix HSO_4^- and PO_3^- in the spectrochemical series as

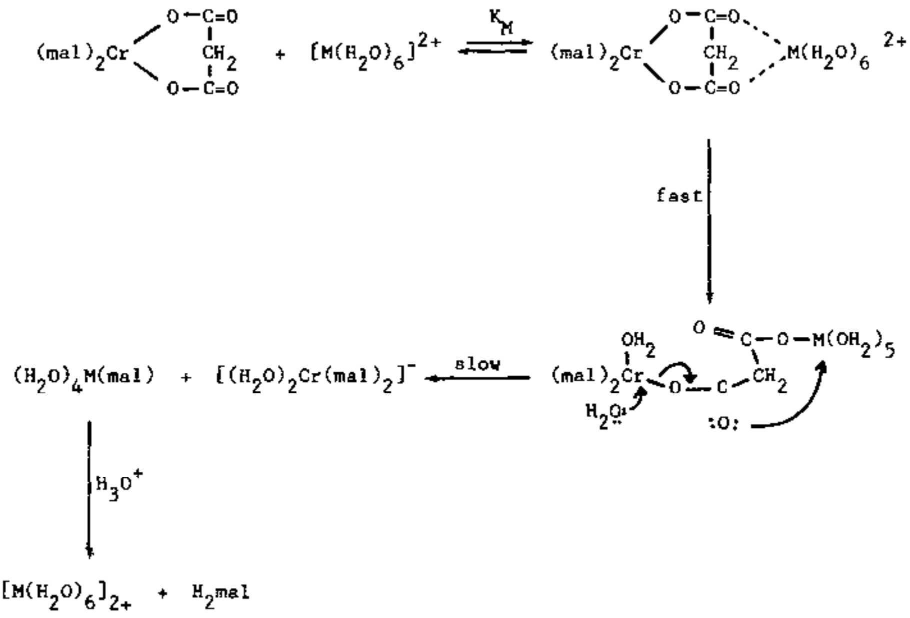
$$SO_4^{2-} < PO_3^- < HSO_4^- < Cl^- < SCN^-$$

The crystal structure of $Na_3[Cr(ox)_3].5H_2O$ has been determined [63]. The average Cr-O bond distance is 1.972(9)Å. Above 303 K solid state exchange of ^{51}Cr was found to occur in cationically labelled $[Cr(H_2O)_6][Cr(ox)_3]$, probably by ligand exchange. However the situation was complicated by some isomerization to $[Cr(ox)(H_2O)_4][Cr(ox)_2(H_2O)_2]$ and a definite mechanism could not be established [64].

The metal catalysed aquation of $[Cr(mal)_3]^{3-}$ to give $[Cr(mal)_2(H_2O)_2]^-$ has been investigated in perchloric acid solution (0.05M) using Cu(II), Ni(II), Co(II), Zn(II) and Mn(II) as the catalyst ions [65]. The aquation follows a two term rate law

$$k_{obs} = K[H^+] + k_2[M^{2+}]$$

with a substantial contribution from the metal catalysed pathway. The values of k_2 follow the sequence of the metal ions given above which is also the order of stability of the metal monomalonate complexes. The proposed mechanism involves a bridged intermediate as shown below



A large scale optical resolution of $Cr(acac)_3$ and other tris(acac) complexes through enantioselective complex formation with (2R,3R)-(-)-dibenzyltartaric acid ((-)-dbt) has been described [66]. In each case it is the Δ isomer which forms a crystalline complex with (-)-dbt. In a typical reaction, racemic $Cr(acac)_3$ and (-)-dbt are stirred in cyclohexane for 2 days. During this time a solid forms which is filtered off, washed and dissolved in chloroform. The (-)-dbt is extracted with aqueous Na_2CO_3 and the complex recovered from the chloroform solution as the optically pure -(+) isomer. The original filtrate is washed with aqueous Na_2CO_3 and removal of the solvent gives the Λ isomer in ≈90% optical purity. The axial circular dichroism of the lowest energy electronic transition has been measured for Λ $Cr(acac)_3$ doped in a single crystal of $Rh(acac)_3$ and the rotational strength compared with those of the corresponding oxalato and 1,2-pn complexes [67].

The complex $[Cr(acac)(bpdo)_2]$ (bpdo = 2,2'-bipyridyl-NN'-dioxide) was prepared by heating a mixture of $Cr(acac)_3$ and bpdo (1:2) in 90% ethanol adjusted to pH 2 with hydrochloric acid [68]. The complex was resolved using potassium *d*-tartratoantimonate and the less soluble complex was converted to perchlorate to give $(-)_{546}$-$[Cr(acac)(bpdo)_2](ClO_4)_2.2H_2O$ identified as the lel_2 $(\Delta(\lambda\lambda),\Lambda(\delta\delta))$ isomer by comparison with the corresponding 3,3'-dimethyl-2,2'-bipyridyl-NN'-dioxide (mbdo) complex. Solutions in water show a rapid absorption spectral change with an isobestic point at 427 nm. The solution loses optical activity in two steps at different rates, but spectral changes only accompany the initial fast rate. This suggests the first step involves only conformational inversion of the flexible bpdo rings $(\delta \rightleftharpoons \lambda)$ and the second step involves both $\delta \rightleftharpoons \lambda$ and racemization $\Delta \rightleftharpoons \Lambda$. The product was identified as the lel.ob $(\Delta(\lambda\delta),\Lambda(\delta\lambda))$ isomer. The rate constant for the isomerization is $3.31 \times 10^{-3}\ S^{-1}$ at 295.2 K and the rate constant for racemization is $1.08 \times 10^{-4} S^{-1}$ at 295.2 K [68].

The unsymmetrical β-diketone 111-trichloro-2,4-pentanedione was synthesized and several metal complexes, including $Cr(L\text{-}L')_3$, were prepared and their mass spectra studied [69]. The fragmentation patterns are not typical of the usual β-diketone breakdown, but rather they are dominated by chlorine transfer to the metal and elimination of CO from the ligand. The liquid-liquid partition coefficients of *cis/trans* $Cr(tfa)_3$ (tfa = 111-trifluoro-2,4-pentanedione) between dodecane and 12 immiscible polar solvents were investigated. In all cases the partition coefficient is slightly larger for the *trans* isomer [70].

The rate constants for quenching of the triplet states of a number of organic molecules by $Cr(hfacac)_3$ have been determined in bezene solution [71]. It is believed quenching occurs through a combination of energy and electron transfer, the latter giving rise to $[Cr(hfacac)_3]^-$ which is likely to be high spin chromium(II).

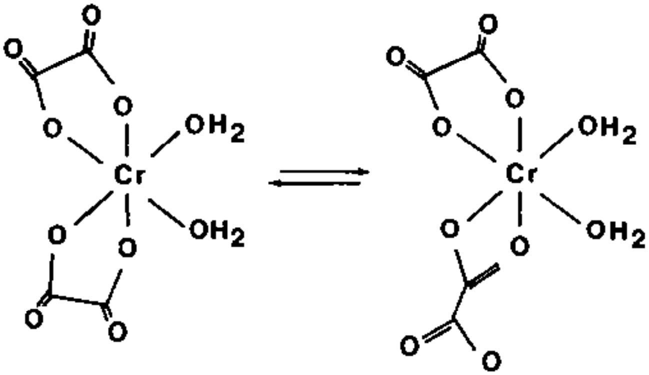
The kinetics of anation of *cis*-$[Cr(ox)_2(H_2O)_2]^-$ by oxalate in aqueous solution over the temperature range 40 - 60 °C, pH range 3 - 5 and varying oxalate concentrations at various ionic strengths have been investigated [72]. Since NO_3^- catalyses the reaction, the kinetics were also studied in NO_3^-, Cl^- and mixed NO_3^-/Cl^- media. The reaction is extremely complicated but the overall reaction equation at pH 3 (81.8% $HC_2O_4^-$) is given by

$$cis\text{-}[Cr(ox)_2(H_2O)_2]^- + HC_2O_4^- \longrightarrow [Cr(ox)_3]^- + H_2O + H_3O^+$$

and at pH 5 (95.4% $C_2O_4^{2-}$)

$$cis\text{-}[Cr(ox)_2(H_2O)_2]^- + C_2O_4^{2-} \longrightarrow [Cr(ox)_3]^{3-} + 2H_2O$$

The reaction mechanism is believed to involve an isomerization of a coordinated oxalato group



Substitution by a third monodentate oxalato group then competes with the back isomerization process.

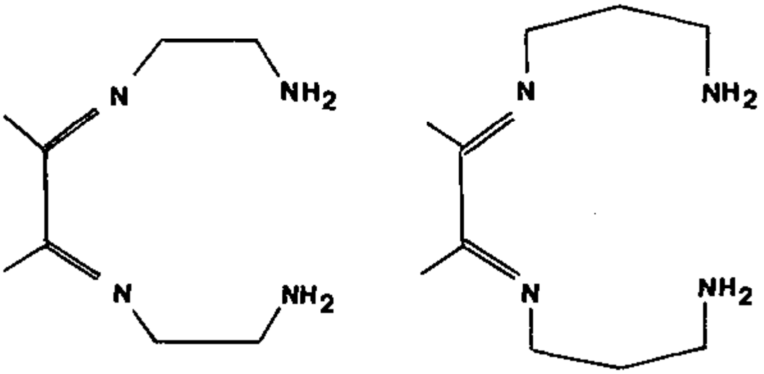
The complexes [Cr(*o*-quinone)$_2$bipy] (*o*-quinone = 3,5-di-*tert*-butyl-1,2-benzoquinone, tetrachloro-1,2-benzoquinone and 9,10-phenanthrenequinone) were prepared by refluxing the quinone with Cr(CO)$_4$bipy in toluene [73]. The major problem with these compounds is to determine the oxidation state of the ligand and the metal (the ligand can exist in three forms: quinone, semiquinone (SQ) and catecolate (cat)). All the complexes have two unpaired electrons which does not distinguish between the different possibilities. All show one electrochemically reversible oxidation and one reversible reduction and these products can also be made using chemical oxidants and reductants. The resultant cation (which has one unpaired electron) shows strong coupling to ^{53}Cr in its EPR spectrum suggesting a metal based ground state and there is further coupling to the nitrogens of bipy. It is concluded that all three compounds are complexes of chromium(III) and should be formulated as $[Cr(SQ)_2bipy]^+$, [Cr(SQ)(cat)bipy] and $[Cr(cat)_2bipy]^-$.

The crystal structure of *d*-quinidinium (-)$_{546}$-[Cr(ox)$_2$phen].H_2O has been determined [74] and it reveals that the anion has the Δ configuration. Bond lengths are Cr-N = 2.065(8)Å (av), which corresponds well with other phen complexes of chromium, and Cr-O = 1.939(7)Å (av) which is a little shorter than usual. It has previously been found that addition of *d* or *l* quinidinium chloride to racemic $[Cr(ox)_2phen]^+$ shifts the chiral equilibrium. This may now be rationalized in terms of the crystal structure which shows strong H-bonding between the free carbonyl of an oxalate group and the $N\text{-}H^+$ proton and between another carbonyl group, coordinated to chromium, and the OH group on the C9 atom of the cation. However it is not, of course, certain that these interactions persist in solution [74].

The crystal structure of $Cr(S_2CNEt_2)_2(OS_2CNEt_2)$, prepared by interaction of K_2CrO_7 and NaS_2CNEt_2, has been re-determined [75]. The dithioperoxycarbamato ligand is disordered over three sites and recognition of this phenomenon leads to more satisfactory bond lengths. The X-UV excitation spectrum of $Cr(S_2P\{OEt\}_2)_3$ in the region of the P L_{23} , S L_{23} and CrL_{23} edges has been investigated. By comparison with the corresponding cobalt(III) complex, the spectrum of the chromium compound shows additional fine structure which is related to the differing *d* orbital electron populations [76].

3.4.3 Complexes of polydentate ligands

Few template reactions have been carried out on tervalent metal centres and a successful attempt has now been made [77] to condense diacetyl with en and 1,3-pn on chromium(III). The complexes *cis*-$[Cr(L\text{-}L\text{-}L'\text{-}L')(H_2O)\ ]$, where L-L-L'-L' is one of the ligands (9), were isolated and their stereochemistry determined by UV-visible spectra; they showed no $\nu_{C=O}$ vibrations. Reaction with CNS^- gave *cis*-$[Cr(L\text{-}L\text{-}L'\text{-}L')(H_2O)(NCS)]^{2+}$, but the bis(NCS) complex could not be prepared.



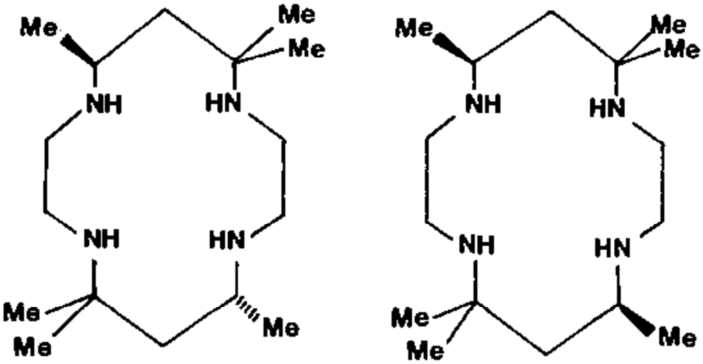
(9)

A number of *trans*-$[CrBr_2(N_4)]^+$ complexes (N_4 = 2,3,2-tet, 3,2,3-tet, cyclam, teta (5,7,7,12,14,14-hexamethylcyclam)) have been prepared and the first stage of their acid hydrolysis followed spectrophotometrically [78,79]. It has been noted that, based on just a few measurements for chromium(III), the ratio of the bromo/chloro aquation rates for analogous compounds is 4 for cobalt(III) but about 15 for chromium(III) complexes. Thus the aim of this work was to investigate whether this effect is real. Apparently it is; although a dissociative mechanism is thought to apply in both systems there are significant differences in $S^{\ddagger}_{298}$ which gives rise to the different rates. In addition, the rates of exchange of the *sec*-N-H protons were observed by monitoring the N-H stretch for *trans*-RR,SS-$[CrX_2(3,2,3\text{-tet})]^+$ (X = F,Cl,Br; K_{exch} = 1×10^2, 1×10^3 and 3.5×10^2 respectively) [79]. The synthesis and resolution of *cis*-β-(RR,SS)-$[Cr(ox)(N_4)]^+$ (N_4 = 2,3,2-tet) has been described and from these the preparation of various racemic or chiral *cis*-$[CrXY(N_4)]^+$

($X = Y = Cl, NCS, OH_2$) is possible [80]. In addition, the previously known *trans*-$[CrCl_2(N_4)]^+$ was assigned the (RS)-*sec*-NH configuration. The kinetics for the first stage of hydrolysis in both acid and basic media were studied [80].

Reaction of a *cis/trans* mixture of $[CrCl_2cyclam]ClO_4$ with NaCN in dmso gives exclusively *trans*-$[Cr(CN)_2cyclam]^+$. *Trans* cyclam complexes of chromium(III) are usually difficult to prepare and this complex presents a possible route to other *trans* complexes as it hydrolyses (very slowly) to give *trans*-$[Cr(H_2O)_2cyclam]^{3+}$ which in turn reacts with CNS^- to give *trans*-$[Cr(NCS)_2cyclam]^+$ [81].

Complexes of chromium(III) with the two hexamethylcyclams, C-meso and C-racemic 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (teta and tetb respectively (10)) have been prepared [82]. The ligand teta is difficult to fold, but tetb does it readily. Hence reaction of $CrCl_3(dmf)_3$ with the ligands gives *trans*-$[CrCl_2(teta)]Cl$ and *cis*-$[CrCl_2(tetb)]Cl$. The ionic and coordinated halides can be replaced by other ligands (NCS, Br, NO_3 etc) but the stereochemistry, deduced from IR and visible spectra, remains unchanged. Very similar results have been reported independently for complexes of tetb [83].



(10)

The electrochemical reduction of Cr(TPP)Cl in a variety of solvents has been investigated [84], the solvents being classified as follows;-

a) non-coordinating (CH_2Cl_2, 1,2-$Cl_2C_2H_4$). Cyclic voltammograms suggested that the reactions occurring were

$$(TPP)CrCl \xrightarrow{e^-\ irrev} (TPP)Cr + Cl^-$$

$$(TPP)Cr \rightleftharpoons [(TPPCr)]^-$$

b) weakly coordinating (PrCN, PhCN, Me_2CO, thf). In these solvents the initial reduction was different but the second reduction was the same as in the previous example. Thus it is postulated that the complex is first solvated

$$\mathrm{(TPP)CrCl(S)} \xrightarrow{e^-\ \text{irrev}} \mathrm{(TPP)Cr} + \mathrm{Cl^-} + \mathrm{S}$$

$$\mathrm{(TPP)Cr} \rightleftharpoons \mathrm{[(TPP)Cr]^-}$$

c) strongly coordinating (oxygen donors, dma, dmf, Me_2SO). The reversible cyclic voltammograms observed in these solvents are interpreted in terms of the reactions

$$\mathrm{(TPP)CrCl(S)} \rightleftharpoons \mathrm{(TPP)Cr(S)} + \mathrm{Cl^-}$$

$$\mathrm{(TPP)Cr(S)} \rightleftharpoons \mathrm{[(TPP)Cr]^-} + \mathrm{S}$$

With strong nitrogen donors such as py the electrochemical behavior is more complicated with evidence for both mono and bis pyridine adducts.

A new edta complex of chromium(III), $Na_3[Cr(CN)_2(edta)H_2O].4H_2O$, was prepared by the interaction of NaCN and $[Cr(edtaH)H_2O]$. The edta ligand is thought to be terdentate with three of its carboxylate groups non-coordinating. The complex undergoes a pH dependent aquation of the cyano groups and the kinetics of the displacement of these ligands for both the thermal and photochemical reaction are in accord with the reactions

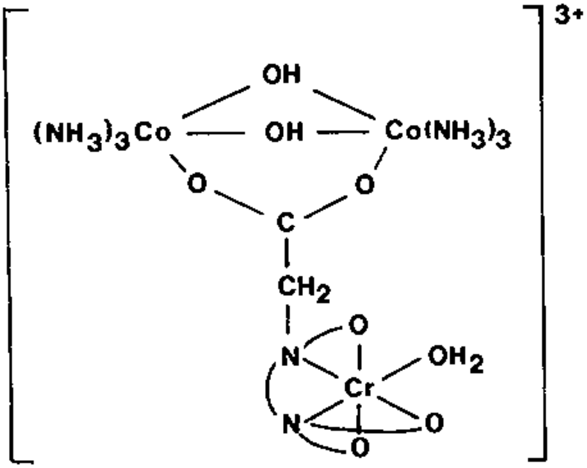
$$\mathrm{[Cr(CN)_2(edtaH)H_2O]^{2-}} \rightleftharpoons \mathrm{[Cr(CN)_2(edta)H_2O]^{3-}} + \mathrm{H^+}$$

$$\mathrm{[Cr(CN)_2(edtaH)H_2)]^{2-}} \rightleftharpoons \mathrm{[Cr(CN)(edtaH)H_2O]^-} + \mathrm{CN^-}$$

$$\mathrm{[Cr(CN)(edtaH)H_2O]^-} \rightleftharpoons \mathrm{[Cr(edtaH)H_2O]} + \mathrm{CN^-}$$

Loss of the first cyanide group is the rate determining step followed by rapid loss of the second cyanide [85].

The properties of $[Cr(edta)H_2O]^-$ and $[Cr(edta)H_2O]$ (where the free carboxylate is protonated) are well known. The anation rate constant for the replacement of H_2O is less (1 order of magnitude) when the carboxylate is protonated and much less (2-4 orders of magnitude) if the carboxylate is replaced by H or Me. The rapid rate is interpreted as being due to transient coordination of the free carboxylate. This has now been nicely utilized by coordinating the free carboxylate to cobalt(III) by replacement of one of the hydroxy bridges in $[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3]^{3+}$ by reaction with $[Cr(edtaH)H_2O]$ to give (11) [86]. The IR spectrum confirms loss of free carboxylate and shows bands due to bridging and monodentate CO_2^-. The water molecule on chromium is now very inert to replacement in comparison with $[Cr(edta)H_2O]$.



(11)

The kinetics of the oxidation of $[Cr(edtaH)H_2O]$ by periodate have been studied [87]. The overall stoichiometry is

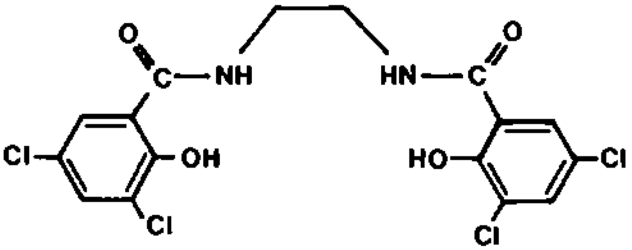
$$2Cr(III) + 3I(VII) \longrightarrow 2Cr(VI) + 3IO_3^-$$

The reaction exhibits first order dependence on each reactant concentration. The second order rate constant k_2 varied with $[H^+]$ according to the equation

$$1/k_2 = a + b[H^+] + c[H^+]^2$$

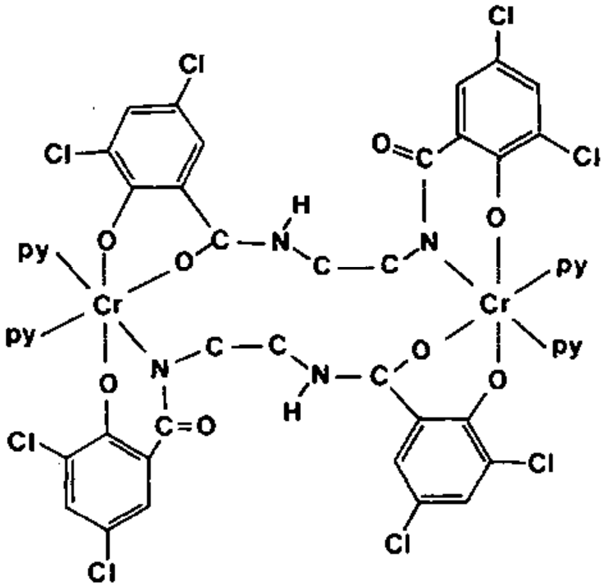
The rate law is consistent with deprotonation of the complex $[Cr(edta)OH]^{2-}$ and OH bridging to IO_4^- (or $H_3IO_4^{2-}$) to facilitate electron transfer by an inner sphere mechanism.

The ligand 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane (H_4chba-Et) (12)



(12)

reacts with $CrCl_3$ in pyridine solution to give $[Cr\{H(chba\text{-}Et)\}py_2]_2.2py$ [88]. A crystal structure determination shows the dimeric nature of the cation with the two pyridines on each chromium being *cis* (13). On each chromium there is



(13)

coordination to a phenoxy oxygen and carbonyl oxygen of one ligand and phenoxy oxygen and amide nitrogen of the other ligand. Thus the ambidentate nature of the ligand is obvious. Bond lengths are

Cr-N (amide)	2.030(6)Å
Cr-O (phenoxy)	1.915(5)
	1.931(5)
Cr-O (carbonyl)	1.976(5)
Cr-N (py)	2.145(6) (*trans* to N)
	2.097(6) (*trans* to O)

The Cr-O bond lengths to the phenoxide oxygens are of normal length, but those to the carbonyl oxygens are rather long. The Cr-N (py) bond lengths clearly indicate the greater *trans* influence of *N* over *O*-coordinated amide.

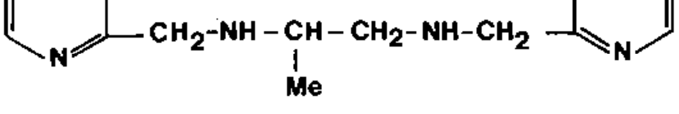
3.4.4 Dinuclear complexes

The spectrum of Cr^{3+} pairs in crystalline $Rb_3Cr_2Cl_9$ has been studied using high resolution optical absorption and Zeeman spectroscopy in high magnetic fields [89]. The results were interpreted in terms of a recent theory which adequately describes transitions from the $(^4A_2 \times {}^4A_2)$ pair ground manifold to the singly excited pair manifold $(^4A_2 \times {}^2T_1)$. The vibronic spectrum associated with pair transitions to the $(^4A_2 \times {}^2T_1)$ manifold was also measured. The absorption, luminescence and far IR spectra of $[(NH_3)_4Cr(\mu\text{-}OH)_2Cr(NH_3)_4]Br_4$ were recorded at various temperatures and for the first time the vibronic spectrum has been assigned using an energy level scheme for the coupled $(^4A_{2g}, {}^4A_{2g})$ and $(^4A_{2g}{}^2E_g)$ manifolds [90].

The behavior of $[Cr_2(OH)_2]^{4+}$ in high concentrations of perchloric acid has been investigated by the NMR inert probe method, using *p*-dioxane and observing the broadening of its ^1H NMR lines. Dioxane is not a ligand in the first coordination sphere, so there is no exchange phenomena and proton broadening is dependent only on gross structural change [91]. It has been suggested previously that the colour change from blue to green at high perchloric acid concentrations is due to opening of one of the hydroxy bridges. This work does not support this suggestion as there are no breaks in plots of line width broadening against $[ClO_4^-]$, so no major structural change is involved. It is now suggested that an inner sphere perchlorate complex is formed which causes the colour change:-

$$[(H_2O)_4Cr(OH)_2Cr(H_2O)_4]^{4+} + ClO_4^- \rightleftharpoons [(H_2O)_4Cr(OH)_2Cr(H_2O)_3OClO_3]^{3+} + H_2O$$

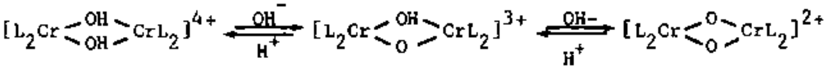
Binuclear complexes of the type $[LCr(\mu\text{-}OH)_2CrL]^{4+}$ have been prepared where L is NN'-bis(2-pyridylmethyl)-1,2-propanediamine (14)



(14)

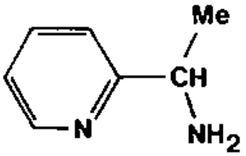
with the ligand in both racemic and optically active forms [92]. Various optical isomers of the chromium complexes were obtained, separated and resolved. Their structures were determined by decomposition to mononuclear *cis*-α-dichloro complexes with established structures. Circular dichroism spectra of the optically active complexes were reported. Magnetic measurements indicated antiferromagnetic exchange coupling giving rise to singlet-triplet separations of between 44 and 50 cm^{-1}.

All three complexes in the pH dependent equilibrium



$$[\mathrm{L_2Cr}\begin{smallmatrix}\mathrm{OH}\\ \mathrm{OH}\end{smallmatrix}\mathrm{CrL_2}]^{4+} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} [\mathrm{L_2Cr}\begin{smallmatrix}\mathrm{OH}\\ \mathrm{O}\end{smallmatrix}\mathrm{CrL_2}]^{3+} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} [\mathrm{L_2Cr}\begin{smallmatrix}\mathrm{O}\\ \mathrm{O}\end{smallmatrix}\mathrm{CrL_2}]^{2+}$$

have been isolated for the series L = 2-pyridylethylamine (15)



(15)

and the crystal structure of the oxo-hydroxy bridged complex has been investigated [93]. Each chromium is approximately octahedrally coordinated with the ligating atoms being two py N's, two amine N's (*trans* to the two bridges) and two O's from the bridges. Bond distances are

Cr-N (amine)	2.057(5), 2.084(5)Å	(*trans* to OH)
	2.107(5), 2.130(6)	(*trans* to O)
Cr-N (py)	2.060(6) - 2.079(6)	
Cr-OH	1.950(4), 1.960(4)	
Cr-O	1.869(4), 1.878(4)	

The Cr-N (amine) bonds *trans* to the oxo bridge are very long and no such lengthening is observed for those *trans* to the hydroxy bridge indicating a significant *trans* effect for the oxo group. Also, the Cr-O bond distances are short while the Cr-OH distances appear to be normal. The Cr-Cr separation of 2.883(2)Å is substantially shorter than that for the di-μ-hydroxy compound and the Cr_2O_2 bridging unit is significantly non-planar. The magnetic susceptibility of the complex shows a maximum near 100 K and leads to a triplet energy of 46.45 cm^{-1}.

Recent work reported last year showed that exchange coupling between chromium atoms in di-μ-hydroxy complexes of chromium(III) depends upon

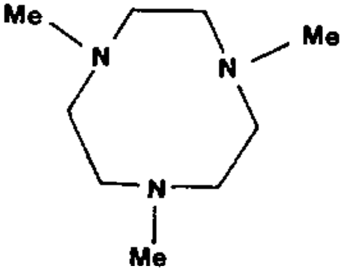
a) the Cr-O-Cr angle (ϕ)
b) the Cr-O distance (r)
c) the dihedral angle between the OH vector and the bridge plane (θ)

although the details of the interaction were not fully understood at that time. In order to obtain more quantitative data the crystal structures have been determined for the dithionate and chloride salts of the $[(NH_3)_4Cr(OH)_2Cr(NH_3)_4]^{4+}$ cation [94]. In both compounds the cation has the expected type of structure but there is also extensive hydrogen bonding throughout the lattice in each case. Important bond distances and angles are

	$S_2O_6^{2-}$ salt	Cl^- salt
Cr-Cr	3.045(1)Å	3.023(1)
Cr-O	1.968(1)	1.980(1)
	1.962(1)	1.969(1)
Cr-N	2.078(2)-2.082(2)	2.074(1)-2.089(2)
Cr-O-Cr	101.54(5)°	99.92(3)°
θ	24°	41°

The magnetic susceptibility of both compounds was measured over the temperature range 1.8 - 290 K and in neither case is the behavior described by the simple Van Vleck model. However, the fit between theory and experiment was improved by the introduction of biquadratic terms. A theoretical treatment has now been developed [95] which incorporates the empirical relationships between structure and magnetic properties noted above.

The magnetic properties of the tris-μ-hydroxy complex $[LCr(OH)_3CrL](ClO_4)_3.3H_2O$ have been measured [96] where L = 1,4,7-trimethyl-1,4,7-triazacyclononane (16)



The susceptibilty data reflects antiferromagnetic exchange coupling interactions with $J = -64(1)\ cm^{-1}$. This is the largest exchange coupling constant yet found for binuclear chromium(III) and probably results from both the symmetry and the number of the OH bridging groups. A detailed comparison between the results for mono-, di- and tri-hydroxy bridged chromium(III) species was also made [96].

The hydrolysis in acid solution of the recently synthesized μ-oxo complex $[(H_2O)_5Cr(O)Cr(H_2O)_5]^{4+}$ has been investigated. The only product is $[Cr(H_2O)_6]^{3+}$

$$[(H_2O)_5Cr(O)Cr(H_2O)_5]^{4+} + 2H^+ + H_2O \longrightarrow 2[Cr(H_2O)_6]^{3+}$$

but the kinetic data shows there are two pathways. The rate law is

$$-d[\{(H_2O)_5Cr\}_2O^{4+}]/dt = (k_o + k_1[H^+])/[\{(H_2O)_5Cr\}_2O^{4+}]$$

$$\text{with } k_o = 5\pm2 \times 10^{-5}S^{-1} \text{ and } k_1 = (1.61\pm0.05) \times 10^{-3}M^{-1}S^{-1}$$

so the acid dependent pathway carries most of the hydrolysis reaction [97]. The acid independent step involves an initial rate determining cleavage of the oxygen bridge

$$[(H_2O)_5Cr(O)Cr(H_2O)_5]^{4+} + H_2O \longrightarrow [Cr(H_2O)_6]^{3+} + [Cr(H_2O)_5O]^+$$

$$[Cr(H_2O)_5O]^+ + 2H^+ \longrightarrow [Cr(H_2O)_6]^{3+}$$

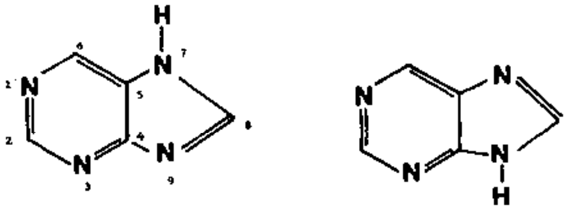
while the acid dependent route involves a rapid pre-equilibrium followed by structural change at the bridging oxygen (analogous to that known for the acid rhodo ion $[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$)

$$\begin{tikzcd}[(H_2O)_5Cr(O)Cr(H_2O)_5]^{4+} + H^+ \arrow[r, leftrightharpoons] & {[(H_2O)_5Cr(OH)Cr(H_2O)_5]^{5+}} \arrow[d, "slow"] \\ & {[(H_2O)_5Cr(OH)^{*}Cr(H_2O)_5]^{5+}}\end{tikzcd}$$

$$[(H_2O)_5Cr(OH)^{*}Cr(H_2O)_5]^{5+} + H^+ + H_2O \xrightarrow{\text{fast}} 2[Cr(H_2O)_6]^{3+}$$

3.4.5 Polynuclear complexes

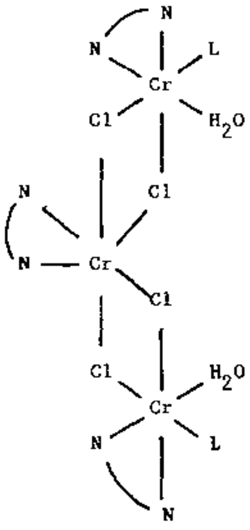
Reaction of $CrCl_3.6H_2O$ in ethanol/triethylformate mixture with purine (puH) or adenine (adH) (17) led to the isolation [98] of complexes $Cr_3L_5Cl_4.2H_2O$ (LH = puH, adH). The IR spectra of these insoluble compounds show bands characteristic of coordinated water. Bands associated with the vibrational modes of the imidazole and pyramidine fragments undergo change suggesting coordination through the ring nitrogens, but bands due to the exocyclic NH_2 of adenine do not change. The chromium-chlorine vibrations are low suggesting



purine adenine

(17)

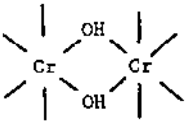
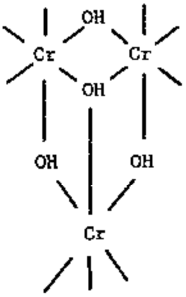
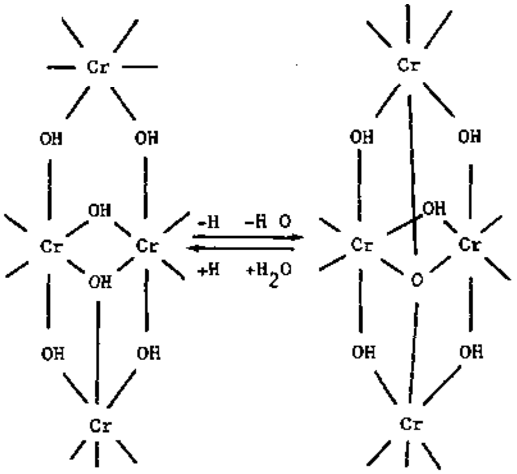
bridging chlorines. The proposed structure is (18)



(18)

(N-N is bidentate pu$^-$ or ad$^-$, probably through N2 and N9; L is terminal pu$^-$ or ad$^-$ and it is uncertain which N is coordinated)

The first few members of the series of hydrolytic polymers of chromium(III) formed upon addition of hydroxide to $[Cr(H_2O)_6]^{3+}$ have been separated on Sephadex SP C-25 [99]. Elution with sodium perchlorate (0.5 - 4M) gave the following fractions (only O and OH are given in the following formulae, the octahedral coordination of chromium in all cases being made up by water molecules).

Cr^{3+}	blue purple	
$[Cr_2(OH)_2]^{5+}$	greenish blue	
$[Cr_3(OH)_4]^{5+}$	green	
$[Cr_4(OH)_6]^{4+}$	olive	

The visible spectra of the monomer, dimer and trimer agreed with previously reported values. The tetramer has λ_{max} = 426nm (ϵ= 30.3) and 580nm (ϵ= 15.6). The order of robustness in acid solution is dimer<trimer>>tetramer, and the tetramer deprotonates to give $[Cr_4O(OH)_5]^{5+}$ as shown above. The proposed structures are in accord with the reactivities of the polymers. Thus the tetramer $[Cr_4(OH)_6]^{4+}$ was made by the addition of hydroxide to the dimer with formation of very little trimer. The compact trimer, in which each chromium is bound to two others by a total of three OH bridges, is more robust and more stable than the doubly bridged dimer. The tetramer cleaves to the monomer and trimer. Similar arguments and also ^{51}Cr labelling experiments serve to rule out many other possible isomeric species.

There has been a detailed criticism [100] of a recent explanation of the magnetic properties of $[Cr_3O(RCOO)_6(H_2O)_3]X$ species which invoked inter-cluster interactions to explain the experimental observations. Optical spectroscopy has shown [101] that below 211 K the structure of $[Cr_3O(CH_3COO)_6(H_2O)_3]Cl.6H_2O$ consists of equal numbers of two inequivalent trimers a and b . Dehydration produces an anhydrous phase also characterized by two trimeric species c and d. Selectively excited emission and excitation spectra, together with fluorescence lifetime measurements, gave evidence for energy transfer $d \rightarrow c$ and $a \rightarrow b$ by pure electronic energy transfer.

A complex $Na[Cr_3O(nicH)_6(H_2O)_3](ClO_4)_8.nicH.6H_2O$ has been prepared by the interaction of chromium(III) perchlorate, nicotinic acid (nic) and sodium perchlorate [102]. The structure includes the $[Cr_3O(nicH)_6(H_2O)_3]^{7+}$ cation, but the disposition of the other groups could not be determined because of severe disordering. The cation has a structure similar to that of the $[Cr_3O(CH_3COO)_6(H_2O)_3]^+$ cation with the nicotinic zwitterion bridging pairs of chromium atoms; the water molecules are *trans* to the central oxygen. Bond lengths are

Cr-O (nic)	1.98(2)Å
Cr-O (μ_3)	1.906(6)
Cr-O (H_2O)	2.05(2)

The mode of coordination of nicotinic acid, *via* the carboxylate oxygens, is different to that currently proposed for the glucose tolerance factor.

3.4.6 Photochemistry

The photochemistry of *trans*-$[Cr(CN)_2cyclam]^+$ has been examined [103]. Because CN^- has a greater ligand field strength than the in-plane N's of cyclam, N would normally be expected to be photolabilized. However, the polydentate nature of the ligand would prevent loss of ligand so the complex was expected to be photoinert. In fact it is, but it does show a very strong long lived (≃330 μsec) ${}^2E_g \rightarrow {}^4B_{1g}$ phosphorescence at 720 nm whose intensity is greatly enhanced (x5) by deuteration of the cyclam. Several explanations are possible for this deuterium effect but it is not possible at this stage to decide the mechanism. The luminescence of (TPP)Cr has been studied and compared with that of (TPP)Al [104]. The latter shows fluorescence at room temperature and the fluorescence spectrum shows the behavior expected for a diamagnetic metalloporphyrin complex. However (TPP)Cr does not behave in this way because the paramagnetic Cr^{3+} ion is a particularly strong perturber of the porphyrin ($\pi\pi^*$) excited state which causes it show only an extremely weak triplet fluorescence spectrum.

A review has appeared on the photochemical properties of chromium(III) polypyridyl complexes with a view to their use in photochemical solar energy conversion [105]. A pulsed-laser photochemical study of the reactions of $[Cr(bipy)_3]^{3+}$ in aqueous acidic and alkaline solution has been carried out using time resolved conductivity and visible optical detection methods. The overall reactions are

$$[Cr(bipy)_3]^{3+} + 2OH^- \xrightarrow{h\nu} [Cr(bipy)_2(OH)_2]^+ + bipy$$

(basic solution)

$$[Cr(bipy)_3]^{3+} + 2H_2O + H^+ \xrightarrow{h\nu} [Cr(bipy)_2(H_2O)_2]^{3+} + Hbipy$$

(acid solution)

and this study confirms that the lowest doublet excited states ($^2E/^2T_1$) are responsible for most of the chemical change. Data are consistent with a seven coordinate species $[Cr(bipy)_3(H_2O)]^{3+}$ being an intermediate in the reaction [106]. The thermal, photochemical and photophysical behavior of $[Cr(phen)_3]^{3+}$ in aqueous solution is very similar to that of $[Cr(bipy)_3]^{3+}$ and is interpreted in terms of analogous mechanistic steps [107]. Excitation with spin allowed states yields $^4T_2$ which undergoes efficient intersystem crossing to $^2T_1/^2E$ which can de-populate *via* non-radiative decay or interact with water and OH^- to yield an intermediate $[Cr(phen)_3(H_2O)]^{3+}$ which is the direct precurser of the aquation products [107].

The emission lifetimes of the excited $^2T_1/^2E$ states of $[Cr(bipy)_3]^{3+}$ and $[Cr(phen)_3]^{3+}$ ($[Cr(N\text{-}N)_3]^{3+}$) have been determined in pure water and in aqueous solutions of various anions as a function of the concentration of the ground state compounds in order to quantify the ground state quenching effect. The kinetics follow the rate law

$$k_{obs} = k_o + k_g[Cr(N\text{-}N)_3{}^{3+}]$$

where k_o ($= 1/\tau$) is the first order rate constant for the decay of $^2T_1/^2E$ and k_g is the second order rate constant for ground state quenching. For $[Cr(phen)_3]^{3+}$, τ in pure water does not vary with concentration of the ground state species, but does decrease on addition of anions such as $ClO_4{}^-$, $NO_3{}^-$, Br^- etc. No such effect was observed for $[Cr(bipy)_3]^{3+}$ at 22 °C, although it was observed at lower temperatures. An ion bridged excimer is proposed to account for the ground state quenching [108]. Iodide ion almost completely quenches the photoaquation reaction of $[Cr(bipy)_3]^{3+}$ (to give $[Cr(bipy)_2(OH)_2]^+$) in mildly alkaline solution, but at $[I^-] \approx 0.1M$ the quantum yield φ reaches a plateau value revealing a small non-quenchable photochemical pathway [109]. This pathway originates from a short lived excited state and several models were examined to reconcile the quenchable and non-quenchable modes with temperature and pH dependencies of the quantum yields. It was concluded that the unquenchable reaction arises from the $^4T_2$state, there is intersystem crossing to $^2T_1/^2E$ states and quenchable reaction from these long lived states. The quenching of the phosphorescence emission from ^2E_g of $[Cr(bipy)_3]^{3+}$ by some 16 complexes of cobalt(III) (all cationic, charges 1+ to 3+) has been investigated in 0.1M H_2SO_4 [110]. The bimolecular quenching constants are lower than diffusion and span a large range. On the basis of theoretical considerations, electronic energy transfer is the only plausible mechanism for the quenching. It is suggested that the energy transfer rate is controlled by electronic factors which depend upon the nephelauxetic ability of the ligands and on parameters which determine the characteristics of the encounter complex.

Preferential solvation data for $[Cr(bipy)_3]^{3+}$ in CH_3CN/H_2O solvent mixtures was measured by NMR line broadening methods and the results compared with earlier data for *trans*-$[Cr(NH_3)_2(NCS)_4]^-$. Both ions are preferentially solvated by CH_3CN [111]. Lifetimes, luminescence intensities and photosolvolytic reactivity for the lowest energy doublets ($^2T_1/^2E$) of $[Cr(bipy)_3]^{3+}$ were measured at various solvent ratios. The doublet excited state properties follow the preferential solvation curves for *trans*-$[Cr(NH_3)_2(NCS)_4]^-$ but not for $[Cr(bipy)_3]^{3+}$. This has been interpreted in terms of static effects of the solvent on those properties for the Reineckate and dynamic effects for $[Cr(bipy)_3]^{3+}$.

Because of disagreements in the recent literature, a re-investigation has been made of the wavelength dependence of intersystem crossing yield in $[Cr(en)_3]^{3+}$ on irradiation within a single absorption band [112]. It was concluded that the yield does not vary significantly with wavelength from 347 - 530 nm.

An investigation has been made of the effects of solid state irradiation of ligand field bands for some chromium(III) complexes and the results compared with solution measurements [113]. Irradiation of $[Cr(en)_3]Cl_3$ at the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition for 5 - 30 mins gave spectral changes with an increase in intensity at 453 nm and a corresponding decrease at 560 nm. The visible spectrum suggested formation of *cis*-$[Cr(en)_2Cl_2]Cl$ and this was confirmed by its isolation using ion exchange. Similarly, irradiation of $[Cr(NH_3)_6]Cl_3$ gave two complexes, one identified as $[Cr(NH_3)_5Cl]^{2+}$, and another, $[Cr(NH_3)_4XY]^+$, where X and Y could not be identified directly since the compound reacted further. During this reaction the charge changed to 2+ and *cis*-$[Cr(NH_3)_4(H_2O)Cl]Cl_2$ was isolated. It is likely therefore that *cis*-$[Cr(NH_3)_4Cl_2]Cl$ is the primary product. Somewhat similar studies have been reported on the photoinitiated ligand exchange reactions in the solid state of some chromium(III) ammine complexes by photolysis in a glassy matrix at low temperature [114]. Some of the reactions studied were

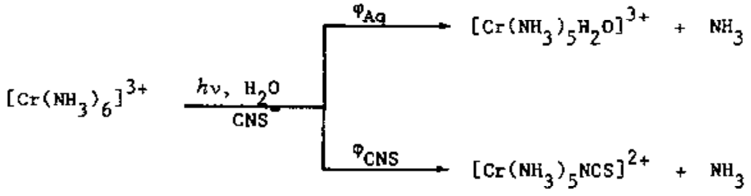
$$[Cr(NH_3)_6]^{3+} \xrightarrow[\text{5M LiCl}]{h\nu} [Cr(NH_3)_5Cl]^{2+} + NH_3$$

$$[Cr(NH_3)_6]^{3+} \xrightarrow[\text{5M,10M NaOH}]{h\nu} [Cr(NH_3)_5OH]^{2+} + NH_3$$

$$[Cr(NH_3)_5H_2O]^{3+} \xrightarrow[\text{5M,10M LiCl}]{h\nu} [Cr(NH_3)_4(H_2O)Cl]^{2+} + NH_3$$

No photoaquation was observed. Products were identified by difference spectroscopy (visible) and by EPR spectroscopy.

Previous studies of the photoanation of $[Cr(NH_3)_6]^{3+}$ by halide ions and photoanation of $[Cr(dmso)_6]^{3+}$ by CNS^- have shown different effects on the quantum yield by varying the anion concentration. Hence a study of the photoanation of $[Cr(NH_3)_6]^{3+}$ with CNS^- has been undertaken to investigate whether there are some special properties of CNS^- substitution [115]. There are two reaction pathways:-



In 0.01M $HClO_4$ the total quantum yield $\varphi_T = \varphi_{Aq} + \varphi_{CNS}$ increased from 0.49±0.04 to 0.70±0.07 with an increase of $[CNS^-]$ from 0 to 5M, but in alkali solution the quantum yield is independent of $[CNS^-]$. It was shown that CNS^- does not effect the lifetime of the phosphorescent ^2E_g state, so interaction with this species is eliminated. The conclusion was that there is some special reaction pattern for CNS^- and the mechanism of its photosubstitution of chromium(III) is not typical [115].

Upon ligand field irradiation in aqueous acid solution, *cis*-$[Cr(NH_3)_4(CN)_2]^+$ undergoes simultaneous aquation of NH_3 and CN^-, although the former occurs at a rate greater by an order of magnitude. Quantum yields and ratios of products are wavelength dependent. The product of NH_3 release, $[Cr(NH_3)_3(CN)_2H_2O]^+$, was isolated by ion exchange and shown to be a mixture of *mer* and *fac* although the proportions varied depending on which ligand field band was irradiated [116].

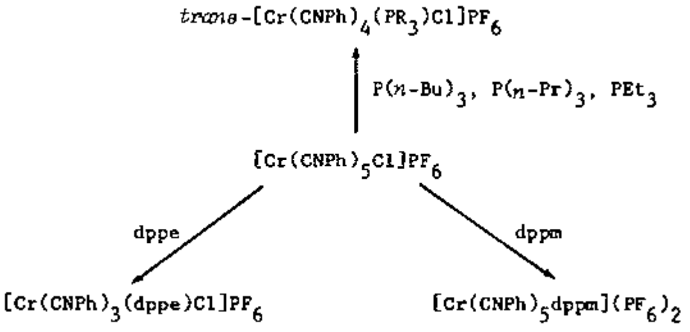
The photoracemization of $(-)_D$-$[Cr(ox)_2phen]^+$ has been investigated as a function of intensity of irradiation across the first quartet band. Photoracemization was the only reaction observed. The variation of quantum yield φ with intensity implies two reaction routes, an intensity independent one which is probably an intramolecular twist mechanism, and an intensity dependent pathway which probably involves an aquo intermediate with one oxalato group being monodentate [117].

Low temperature excitation spectroscopy has been used to measure the five components of the ^2E_g and $^2T_{1g}$ (O_h) states for *fac*-$[Cr(gly)_3]$. It was found that the doublet energies depend very strongly on the molecular geometry since the deviation of the chelate bite angles from 90°, reinforced by ligand field asymmetry, causes considerable splitting in the $^2E, ^2T_1$ manifold. An angular-overlap model analysis of the data was carried out [118].

3.5 CHROMIUM(II)

3.5.1 *Simple complexes of chromium(II)*

Treatment of chromium(II) in ethanol (made by reduction of $CrCl_3.6H_2O$ with Zn/Hg) with excess of phenylisocyanide in the presence of PF_6^- gave the complex $[Cr(CNPh)_5Cl]PF_6$, but *p*-tolylisocyanide gave the homoleptic derivative $[Cr(CN\textit{p}\text{-tol})_6]PF_6$. Treatment of $[Cr(CNPh)_5Cl]^+$ with various phosphines gave the reactions shown in the scheme

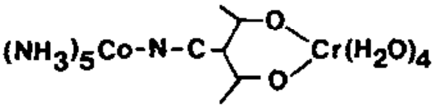


All the complexes were paramagnetic except for the seven coordinate $[Cr(CNPh)_5dppm](PF_6)_2$. $[Cr(CNPh)_5Cl]^+$ and $[Cr(CNPh)_4(PR_3)Cl]^+$ showed a reversible electrochemical oxidation and two irreversible reductions [119].

Treatment of $CrCl_2$.thf with two moles of dmpe yields yellow $CrCl_2(dmpe)_2$ which is paramagnetic (low spin d^4) with a magnetic moment of 2.76 BM. Treatment with LiMe yields red-orange *trans*-$CrMe_2(dmpe)_2$ (μ= 2.7 BM) which was confirmed by a crystal structure determination to be the first monomeric alkyl of chromium(II) [14]. Bond distances are Cr-C = 2.168(4)Å and Cr-P = 2.342(1) and 2.349(1)Å.

Reaction of $Cr_2(CH_3COO)_4$ with $NaB(C_2H_5)_2(2\text{-pyrazoyl})_2$ yielded bright orange mononuclear $Cr\{(pz)_2BEt_2\}_2$. A crystal structure determination showed the air stable compound to be a square planar chromium(II) complex with all Cr-N distances identical within experimental error (2.060(4)Å). The stability of the complex may be due in part to the fact that an ethyl group of each ligand blocks the fifth and sixth coordination positions [120].

The kinetics of the interaction between $[(NH_3)_5Co(NCacac)]$ and $[Cr(H_2O)_4]^{2+}$ have been investigated [121]. The reaction proceeds *via* an intermediate in which the chromium coordinates to the free oxygens to give the binuclear complex (19)



(19)

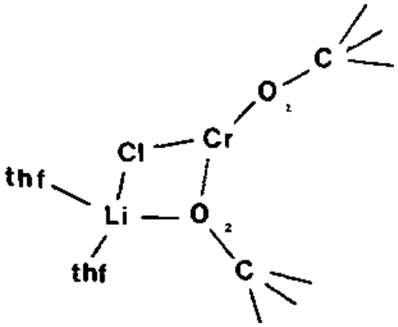
followed by Co-N bond breakage to give $[Cr(H_2O)_4(acacCN)]^{2+}$ as the final product.

The stepwise formation constants of the complexes formed by chromium(II) with en, mal, gly, β-alaninate, iminodiacetate, nitrilotriacetate and edta have been determined pH-metrically [122]. The formation of chromium(II) glycine complexes has also been studied by ^1H NMR relaxation methods [123]. The formation rate constant for $[Cr(gly)]^+$ was calculated to be $3.1 \times 10^9 M^{-1}s^{-1}$ and for $[Cr(gly)_2]$ $2.8 \times 10^8 M^{-1}s^{-1}$. A significant increase in the relaxation rate at higher glycinate concentration was interpreted as being due to the exchange

$$[Cr(gly)_2] + gly^* \rightleftharpoons [Cr(gly)(gly^*)] + gly$$

and the exchange rate constant was calculated to be $2.22 \times 10^7 M^{-1}s^{-1}$.

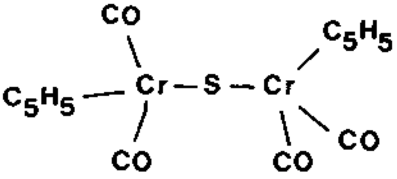
Reaction of *n*-BuLi in hexane with $t\text{-}Bu_3OH$ and $CrCl_2$ in thf (3:3:1) at room temperature gave emerald green crystals of $[Cr(OCt\text{-}Bu_3)_2LiCl(thf)_2]$. A crystal structure determination revealed the first structurally characterized three coordinate chromium(II) complex (20) which is best described as T shaped because of the large O-Cr-O angle of 157.9(2)°. The core atoms (Li, Cl, Cr, O_1, O_2) are all coplanar and the coordination at Li is severely distorted T due to steric effects. The Cr-O_1 bond distance of 1.881(4)Å is longer than those found in other chromium alkoxides due to the lower oxidation state of the metal. The bridging Cr-O_2 distance of 1.991(3)Å is similar to that found in



(20)

$[(C_5H_5)$ CrO -Bu$]_2$; the Cr-Cl distance is 2.324(2)A.[124].

Reaction of $[(\eta_5\text{-}C_5H_5)_2Cr(CO)_3]_2$ with 1/8 molar proportion of S_8 per dimer molecule at room temperature gives dark green $[(\eta_5\text{-}C_5H_5)_2Cr_2(CO)_4S]$ (21) and reaction with a 2/8 mole proportion of S_8 gave dark brown $[(\eta_5\text{-}C_5H_5)_2Cr_2(CO)_5S_2]$ (22) [125].



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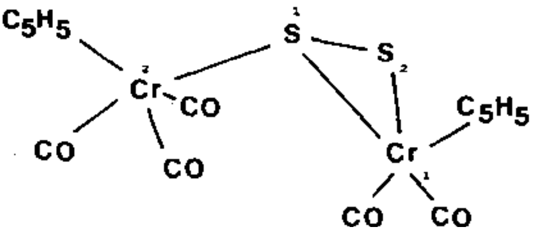


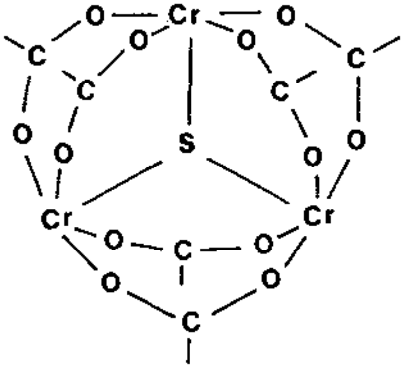
(22)

(21) has a single μ-S bridge and is the first example of a binuclear chromium complex linked by a single sulphur. The Cr-S-Cr angle is 174.4(2)°and the Cr-S bond distances are short at 2.067(2) and 2.076(2)Å. It is thought that there is probably some π interaction between Cr and S. **(22)** provides the first example of a Cr_2S_2 unit. The S_2^{2-} is a σ 2-electron donor to Cr_1 and a η_2 2-electron donor to Cr_2. Bond distances are

Cr_1-S_1 = 2.348(2)Å
Cr_2-S_1 = 2.466(2)
Cr_1-S_2 = 2.399(2)
S_1-S_2 = 2.009(2)

The geometry about Cr_2 is that of a four legged piano stool and it has an eighteen electron configuration. Cr_1 is a sixteen electron centre and has a three legged piano stool stereochemistry [125].

The complex $Cr_3S(OOCPh)_6$ **(23)** is produced by the reaction of benzoic acid



(23)

on $(CpCrSCMe_3)_2S$ or the adduct $(CpCrSCMe_3)_2S.Cr(CO)_5$ [126]. The IR spectrum of the soluble complex showed bands for bridging carboxylate groups only and it is antiferromagnetic with μ_{eff} decreasing from 2.60 BM at 298 K to 1.92 BM at 80 K. Similar species with one chromium replaced by Mn(II) or Fe(II) were also prepared by reacting the adducts $(CpCrSCMe_3)_2.Mn_2(CO)_9$ and $(CpCrS)_2(SCMe_3).Fe(CO)_3$ with benzoic acid. In contrast, heating $(CpCrS)_2(SCMe_3).Fe(CO)_3$ with trimethylacetic acid gave the heteronuclear cluster $Cp_3Cr_3(\mu_3\text{-}S)_4Fe(OOCCMe_3)$ which has a cubane type core with Cr-Cr bond distances in the range 2.828 - 2.848(3)Å and Cr - Fe distances of 2.721 -

2.787(3)Å. It is paramagnetic with two unpaired electrons for the Cr_3Fe core [126].

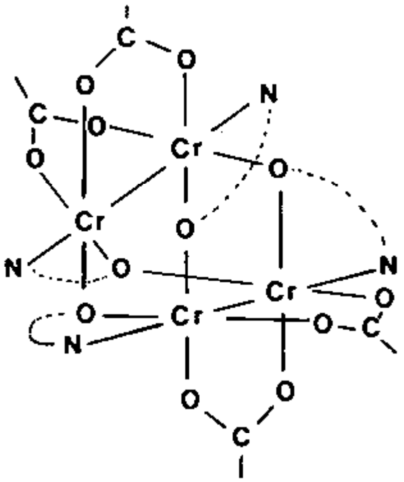
$CrZrF_6$ (which contains chromium(II) octahedrally coordinated to six fluorines) undergoes phase transitions between 100 - 450 K which are induced by packing effects. Ligand field, EPR and magnetic data are reported as well as Moessbauer studies of $^{57}Fe^{2+}$ doped Cr^{2+} sites [127].

The preparation and magnetic properties of some tetrachlorochromates(II) have been examined [128]. $(H_2pipz)[CrCl_4(H_2O)_2]$ (pipz = piperazine) and $(NPhH_3)_2[CrCl_4(H_2O)_2]$ obey the Curie Law with μ≃4.90 BM. The anhydrous compounds $[N(o\text{-}CH_3C_6H_4)H_3]_2CrCl_4$, $(NPhH_3)_2CrCl_4$ and $[H_3N(CH_2)_3NH_3]CrCl_4$ all obey the Curie-Weiss Law with positive intercepts on the temperature axis and μ_{eff} well above the spin-only value and which increased further as the temperature decreased; they are therefore ferromagnetic. The compounds $[H_2pipz]CrCl_4$, $(N_2H_6)_2CrCl_4$ and $(NEt_3H)_2CrCl_4$ are antiferromagnetic. Diffuse reflectance spectra of all the compounds show a broad asymmetric band near 12,000 cm^{-1} characteristic of octahedral chromium(II), which implies chlorine bridges in the tetrachloro compounds.

3.5.2 Metal-metal bonded species

There has been some interest in providing a theoretical understanding of the large variation in Cr-Cr distances in formally quadruple bonded dimeric species and the factors which effect these distances. One approach [129] using *ab initio* SCF and CI calculations showed that the nature of the bridging group is at least as important as the presence or absence of axial groups in determining the Cr-Cr distance. A different calculation [130] distinguished between those compounds with four carboxylate bridges and axial interactions (Cr-Cr = 2.283 - 2.541Å) and those for weaker acids which have infrequent axial interactions (Cr-Cr < 1.90Å). Calculations were performed on $Cr_2(O_2CH)_4$ (formato) and $Cr_2(NH(O)CH)_4$ (formamidato) complexes and it was shown that a major effect on the Cr-Cr bond strength is the donating power of the N atoms in the formamidato complex, again suggesting the bridging groups have an effect at least equal to those of any axial ligands. The gas phase core-electron ionization energies of a series of Cr_2L_4 complexes have been reported and it is shown that there is a correlation between metal electron ionization energies and variations in the metal-metal distance, which was then substantiated by *ab initio* calculations [131]. The conclusion was that it is the variation in electrostatic potential at the metal centre (due to variations in the ligand atoms) which leads to variation in the Cr-Cr distances.

Reaction of $Cr_2(OOCMe)_4$ with sodium (dimethylamino)ethoxide gave the tetranuclear species $Cr_4(OOCMe)_4(OCH_2CH_2NMe_2)_4$ [120]. The structure



(24)

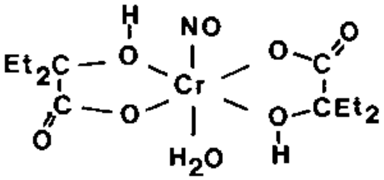
consists of two $Cr_2(OOCMe)_4$ units (in each of which the μ-acetate groups are *cis* and orthogonal to the Cr-Cr axis) linked by the four oxygen atoms of the alkoxide ligand (each bridging two chromium atoms) such that the metal atoms form a bisphenoid. The nitrogen atoms of the chelating aminoalkoxides are coordinated axially to the Cr-Cr bond. Bond distances are

Cr-Cr	2.5321(2)Å
Cr-O	1.999(4) to 2.033(4)
Cr-N	2.444(5)

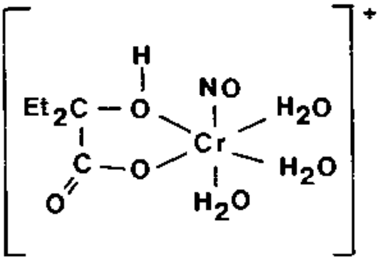
The chromium-chromium bond length is at the extreme edge of the range observed for quadruple bonded species.

3.6 CHROMIUM(I)

The chelated bis(carboxylato)oxochromium(V) species $CrOL_2$ (H_2L = 2-ethyl-2-hydroxybutyric acid) reacts smoothly with $[NH_3OH]^+$ at pH 3.6-4.7 in the presence of H_2L to form two products; one is not absorbed on a cation exchanger and is assumed to be neutral and the other has elution properties consistent with a 1+ charge [132]. They are formulated as (25) and (26). Each has ν_{NO} corresponding to NO^+ rather than NO^- and each has a magnetic moment corresponding to low spin d^5, both pieces of evidence suggesting chromium(I) rather than chromium(III). The overall stoichiometry of the reaction between chromium(V) and $[NH_3OH]^+$ is 1:1 and the mechanism is thought to involve a $Cr(V)-NH_2OH$ precursor with only one carboxylate, followed by a net 4e internal electron transfer. A one-pot synthesis of chromium(I) nitrosyl complexes



(25)



(26)

formulated as $[CrNO(CN)_4]^{2-}$, $[CrNO(CN)_3(H_2O)]^-$ and $[CrNO(CN)_2(L-L)]$ (L-L = bipy, phen) by hydroxylamine reduction of K_2CrO_4 in aqueous solution has been reported [133]. The complexes all have one unpaired electron and are clearly chromium(I) derivatives.

Reaction of $[CrNO(CNR)_5]X$ (R = CMe_3, $CHMe_2$, Me, X = PF_6, BF_4) with PR'_3 in 2-propanol gives *trans*-$[CrNO(CNR)_4(PR'_3)]^+$ (PR'_3 = PEt_3, $P(n\text{-}Pr)_3$, $P(n\text{-}Bu)_3$, PMe_2Ph) and with dppe gives *fac*-$[CrNO(CNR)_3dppe]^+$ [134]. These chromium(0) complexes could be reversibly oxidized electrochemically

$$[CrNO(CNR)_4(PR'_3)]^+ \rightleftharpoons [CrNO(CNR)_4(PR'_3)]^{2+}$$

and the chromium(I) cations were isolated using NO^+ oxidation.

3.7 CHROMIUM(0) AND MISCELLANEOUS SYSTEMS

Fourier transform far IR studies of bare Cr_3 clusters in Ar and Xe matrices have been reported [135]. Freshly deposited Cr_3 at 12 K in Xe shows a single band at 210 cm^{-1} assigned to the single IR active E' vibrational mode in D_{3h} (equilateral triangle) symmetry. In Ar matrices, this band is observed only after annealing to 40 K and in argon larger angled Cr_3 species tend to be preferred. A normal coordinate analysis of Cr_3 at different angles (60 - 180°) helped in assigning the IR spectra to different conformers. The species CrFe was prepared by co-condensation of Cr and Fe atoms in rare gas matrices at 4.2 K. The molecule was identified by Moessbauer techniques. SCF-Xα-scattered wave MO calculations were carried out on the diatomics Fe_2 and CrFe[136].

It has been found that $Cr(CO)_6$ may be adsorbed onto a porous Vycor glass without change of the electronic and IR spectra. On irradiation at 312 nm the pentacarbonyl species $Cr(CO)_5(ads)$ is formed which has an electronic spectrum identical to that of $Cr(CO)_5$ in a methane matrix. However, the lifetime of the pentacarbonyl adsorbed on glass is much longer, although there appears to be little reduction in its reactivity. $Cr(CO)_5(ads)$ gave no indication of unpaired electrons so it is thought to have singlet C_{4v} symmetry [137].

The crystal structure of $K[Cr_2(CO)_{10}H]$ has been determined [138]. There are three anions in the unit cell, two of which are related by a centre of symmetry. This equivalent pair of anions have the almost linear arrangement of the hydride bridge and eclipsed equitorial carbonyl groups found in previous studies of other salts of this anion. However, the third anion has a bent hydride bridge (Cr-H-Cr = 132(3)°) and staggered carbonyl groups. The Cr-Cr distance is 3.260(3)Å compared with an average value of 3.35Å for the linear arrangement. Lattice effects probably cause the distortion of the hydride bridge and the interaction between the potassium atom and the axial carbonyls may be dominant.

UV photolysis of $Cr(CO)_6$ in liquid Xe containing varying proportions of N_2 at 183 K gave the mixed carbonyl/dinitrogen species $Cr(CO)_{6-x}(N_2)_x$ (x = 1-5). The products were identified by IR spectroscopy and by their photochemical behavior, especially to narrow band photolysis at 367 nm which distinguishes between *cis*/*trans* and *mer*/*fac* isomers [139]. Two advantages of using liquid inert gas solvent systems rather than solid matrices are the total absence of IR absorptions and the absence of 'site splitting' which can be a major problem in solid matrices. Similar experiments in liquid xenon, but without added dinitrogen, led to the formation of $Cr(CO)_5Xe$ [140]. The species is relatively long-lived (half-life 2 sec) under these conditions which is partly attributable to the high concentration of xenon. The same product was observed in liquid Ar containing some dissolved Xe, but not in Ar alone, thus eliminating the possibility that the species may be some isomer of $Cr(CO)_6$, such as $Cr(CO)_5(OC)$.

Reduction of $CrCl_2(dmpe)_2$ with Na/Hg under a nitrogen atmosphere led to the isolation of the stable red complex *trans*-$[Cr(N_2)_2(dmpe)_2]$ [14]. A crystal structure determination showed it to be isomorphous with $CrMe_2(dmpe)_2$; bond distances are

Cr-N = 1.957(4)Å
Cr-P = 2.301(1), 2.307(1)
N-N = 0.985(4)

The N-N distance is shorter than that in N_2 itself (1.0971Å)! The Cr-N-N angle is 177.3°.

Deprotonation of $[Cr_2(CO)_{10}SH]^-$ to give deep green $[Cr_2(CO)_{10}S]^{2-}$ followed by treatment with $[Cr(CO)_5thf]$ in the presence of the PPN cation gave red $(PPN)_2[Cr_4(CO)_{17}S]$ [141]. The structure of the anion consists of a basal plane of Cr_3, each metal atom having three terminal carbonyl groups, and with each pair of metal atoms bridged by a highly asymmetrical carbonyl group. The $SCr(CO)_5$ group caps the basal triangle. Bond distances are

$$\begin{aligned} \text{Cr-Cr} &= 2.850(9)\text{Å (av)} \\ \text{Cr(base)-S} &= 2.305(8)\ \text{(av)} \\ \text{Cr(apex)-S} &= 2.468(3) \end{aligned}$$

All four Cr-S bond distances are in the range for a single bond, hence the S is regarded as an eight electron donor. The carbonyl groups in the basal plane are fluctional.

Atomic transition metal anions, including Cr^-, have been prepared in good yields in a Fourier transform mass spectrometer utilizing collision induced dissociation of anionic carbonyl complexes [142]. $Cr(CO)_5^-$ was formed by electron irradiation of $Cr(CO)_6$ and then subjected to a dissociation pulse using argon. The fragments $Cr(CO)_4^-$ to Cr^- were produced but their proportions depended on the excitation energy. Cr^- reacts with $Cr(CO)_6$ to form $Cr(CO)_5^-$ and $Cr_2(CO)_5^-$ and with Bronsted acids to form Cr-H bonds.

REFERENCES

1 M.V.N. Murty, V.M. Rao and M.N. Shastri, *J. Ind. Chem. Soc.* 59 (1982) 1343
2 A. Okumura, N. Takeuchi and N. Okazaki, *Inorg. Chim. Acta.* 74 (1983) 77
3 R.J. French, L. Hedberg, K. Hedberg, G.L. Gard and B.M. Johnson, *Inorg. Chem.* 22 (1983) 892
4 W.A. Nugent, *Inorg. Chem.* 22 (1983) 965
5 Y. Ravi Sekhar and H. Bill, *Chem. Phys. Lett.* 92 (1982) 349
6 J.E. Fergusson, A.M. Greenaway and B.R. Penfold, *Inorg. Chim. Acta.* 71 (1983) 29
7 H.K. Saha, S.K. Ghosh and T.K.R. Chaudhuri, *Ind. J. Chem.* 22A (1983) 346
8 M. Mitewa, P. Russev, P.R. Bontchev, K. Kabassanov and A. Malinovski, *Inorg. Chim. Acta.* 70 (1983) 179
9 J.T. Groves, T. Takahashi and W.M. Butler, *Inorg. Chem.* 22 (1983) 884
10 J.W. Buchler, C. Dreher, K-L. Lay, A Raap and K. Gersonde, *Inorg. Chem.* 22 (1983) 879
11 T.L. Siddal, N. Miyaura, J.C. Huffman and J.K. Kochi, *J. Chem. Soc. Chem. Commun.* (1983) 1185
12 N. Miyaura and J.K.Kochi, *J. Am. Chem. Soc.* 105 (1983) 2368
13 B.L. Chamberland, *J. Solid State Chem.* 48 (1983) 318
14 G.S. Girolami, J.E. Salt, G. Wilkinson, M. Thornton-Pett and M.B. Hursthouse, *J. Am. Chem. Soc.* 105 (1983) 5954
15 C.J. Cardin, D.J. Cardin, J.M. Kelly, R.J. Norton, A. Roy, B.J. Hathaway and T.J. King, *J. Chem. Soc. Dalton Trans.* (1983) 671
16 O. Zakharieva-Pencheva and V.A. Dementiev, *J. Mol. Struct.* 90 (1982) 241
17 A. Marchaj and Z. Stasicka, *Polyhedron* 2 (1983) 485

18 D.A. Bohling and K.R. Mann, *Inorg. Chem.* 22 (1983) 1561

19 D.C. Bradley and M. Ahmed, *Polyhedron* 2 (1983) 87

20 A. Yamada, Y. Kato, Y. Nakabayashi and N. Tanaka, *Bull. Chem. Soc. Jpn.* 55 (1982) 3778

21 Yu.N. Shevchenko, N.I. Yashina, K.B. Yatsimirskii, R.A. Suitsyn and N.V. Egorova, *Russ. J. Inorg. Chem.* 28 (1983) 216

22 M.N. Bishnu, B. Chakravarti, R.N. Banerjee and D. Banerjea, *J. Coord. Chem.* 13 (1983) 63

23 C. Preti, L. Tassi, G. Tosi, P. Zannini and A.L. Zanoli, *Aust. J. Chem.* 35 (1982) 1829

24 M. Martinez and M. Ferrer, *Inorg. Chim. Acta.* 69 (1983) 123

25 T.W. Swaddle and M.K.S. Mak, *Can. J. Chem.* 61 (1983) 473

26 N.J. Curtis, G.A. Lawrance and A.M. Sargeson, *Aust. J. Chem.* 36 (1983) 1495

27 J.C. Chang, L.E. Gerdom, N.C. Baenziger and H.M. Goff, *Inorg. Chem.* 22 (1983) 1739

28 C.M. Mikulski, L. Mattucci, Y. Smith, T.B. Tran and N.M. Karayannis, *Inorg. Chim. Acta.* 80 (1983) 127

29 R.L. Carlin, R. Burriel, J. Pons and J. Casabo, *Inorg. Chem.* 22 (1983) 2832

30 A.D. Kirk and S.G. Glover, *Inorg. Chem.* 22 (1983) 176

31 K.K. Singh, P.R. Sarode and P. Ganguly, *J. Chem. Soc. Dalton Trans.* (1983) 1895

32 T.C. Gibb, *J. Chem. Soc. Dalton Trans.* (1983) 2031

33 H.Leiva, R. Kershaw, K. Dwight and A. Wold, *J. Solid State Chem.* 47 (1983) 293

34 Y. Sulfab, *Polyhedron* 2 (1983) 679

35 M. Bhattacharya and G.S. De, *Ind. J. Chem.* 21A (1982) 898

36 J.H. Espensen, P. Connolly, D. Meyerstein and H. Cohen, *Inorg. Chem.* 22 (1983) 1009

37 C.M. Mikulski, P. Sandford, N. Harris, R. Rabin and N.M. Karayannis, *J. Coord. Chem.* 12 (1983) 167

38 A. Terron and V. Moreno, *Inorg. Chim. Acta.* 80 (1983) 213

39 N.K. Graham, J.B. Gill and D.C. Goodall, *J. Chem. Soc. Dalton Trans.* (1983) 1363

40 J. Hasek, K. Huml, J. Jecny and R. Puffr, *Collect. Czech. Chem. Commun.* 47 (1982) 2403

41 P.G. Nelson and R.V. Pearse, *J. Chem. Soc. Dalton Trans.* (1983) 1977

42 M.K. Chaudhuri and N. Roy, *Synth. React. Inorg. Met-Org. Chem.* 12 (1982) 879

43 R.E. Sowden, J.M. Orza and S. Montero, *Polyhedron* 1 (1982) 475

44 C.A. Angell and A. Ellas, *J. Phys. Chem.* 87 (1983) 4704

45 R.L. Carlin and R. Burriel, *Phys. Rev. Condens. Matter* 27 (1983) 3012

46 A. Rahman, L.A.K. Staveley, C. Bellito and P. Day, *J. Chem. Soc. Faraday Trans. 2* 78 (1982) 1895

47 J.V. McArdle, E de Laubenfels, A.L. Shorter and H.L. Ammon, *Polyhedron* 1 (1982) 471

48 A.F. Zanoli, I.M. Vezzosi and G. Peyronel, *Transition Met. Chem.* 8 (1983) 113

49 P.J. Jones, A.L. Hale, W. Levason and F.P. McCullough,Jr., *Inorg. Chem.* 22 (1983) 2642

50 J.W. Vaughn, *Inorg. Chem.* 22 (1983) 844

51 M. Corbella, M. Serra, L. Martinez-Sarrion and J. Ribas, *Thermochim. Acta.* 57 (1982) 283

52 J. Ribas, M.L. Martinez, M. Serra, M. Monford, A Escuer and N. Navarro, *Transition Met. Chem.* 8 (1983) 87

53 S.K. Sharma, R.K. Mahajan, B. Kapila and V.P. Kapila, *Polyhedron* 2 (1983) 973

54 J.W. Vaughn, *J. Crystallogr. Spectrosc. Res.* 13 (1983) 231

55 L.R. Gray, A.L. Hale, W. Levason, F.P. McCullough and M. Webster, *J. Chem. Soc. Dalton Trans.* (1983) 2573

56 A.L. Hale and W. Levason, *J. Chem. Soc. Dalton Trans.* (1983) 2569

57 L. Kolosci and K. Schug, *Inorg. Chem.* 22 (1983) 3053

58 P.K. Biswas, M.K. Dasgupta, S. Mitra and N.R. Chaudhuri, *J. Coord. Chem.* 11 (1982) 225

59 M. Freni, A. Gervasini, P. Romiti, T. Beringhelli and F. Morazzoni, *Spectrochim. Acta.* 19A (1983) 85

60 G. Yuen, H. Heaster and P.E. Hoggard, *Inorg. Chim. Acta.* 73 (1983) 231

61 B. Singh and R.D. Singh, *Ind. J. Chem.* 21A (1982) 648

62 N.I. Buryak and S.V. Volkov, *Koord. Khim.* 9 (1983) 803

63 N. Bulc, L. Golic and J. Siftar, *Vestn. Slov. Kem. Drus.* 29 (1982) 211

64 A.M. Passaglia Schuch and A.G. Maddock, *Inorg. Chim. Acta.* 63 (1982) 27

65 A.K. Basak and C. Chatterjee, *Bull. Chem. Soc. Jpn.* 56 (1983) 318

66 A.F. Drake, J.M. Gould, S.F. Mason, C. Rosini and F.J. Woodley, *Polyhedron* 2 (1983) 537

67 R.D. Peacock, *J. Chem. Soc. Dalton Trans.* (1983) 291

68 H. Kanno, T. Shimotori, S. Utsuno and J. Fujita, *Chem. Lett.* (1983) 939

69 M.L. Morris and R.D. Koob, *Org. Mass Spec.* 17 (1982) 503

70 N. Sazuki, M. Itoh and H. Watarai, *Polyhedron* 1 (1982) 383

71 F. Wilkinson and C. Tsiamis, *J. Am. Chem. Soc.* 105 (1983) 767

72 T.W. Kallen and E.J. Senko, *Inorg. Chem.* 22 (1983) 2924

73 R.M. Buchanan, J. Claflin and C.G. Pierpont, *Inorg. Chem.* 22 (1983) 2552

74 H. Ohbu, H. Okazaki, K. Miyoshi and H. Yoneda, *Bull. Chem. Soc. Jpn.* 56 (1983) 1982

75 R.L. Martin, J.M. Patrick, B.W. Skelton, D. Taylor and A.H. White, *Aust. J. Chem.* 35 (1982) 2551

76 K-H. Hallmeier, R. Szargan, A. Miesel and A.Yu. Dukhnyakov, *Spectrochim. Acta.* 38A (1982) 1333

77 B.U. Nair, T. Ramasami and D. Ramaswamy, *Polyhedron* 2 (1983) 103

78 D.A. House and O. Nor, *Inorg. Chim. Acta.* 72 (1983) 195

79 D.A. House and O. Nor, *Inorg. Chim. Acta.* 70 (1983) 13

80 D.A. House and D. Yang, *Inorg. Chim. Acta.* 74 (1983) 179

81 N.A.P. Kane-Maguire, J.A. Bennett and P.K. Miller, *Inorg. Chim. Acta.* 76 (1983) L123

82 D.A. House, R.W. Hay and M.A. Ali, *Inorg. Chim. Acta.* 72 (1983) 239

83 J. Eriksen and O. Monsted, *Acta. Chem. Scand.* A37 (1983) 579

84 L.A. Bottomley and K.M. Kadish, *Inorg. Chem.* 22 (1983) 342

85 Z. Chen, M. Cimolino and A.W. Adamson, *Inorg. Chem.* 22 (1983) 3035

86 P. Leupin, A.G. Sykes and K. Wieghardt, *Inorg. Chem.* 22 (1983) 1253

87 N.A. Al-Jallal and Y. Sulfab, *Transition Met. Chem.* 8 (1983) 51

88 T.J. Collins, B.D. Santarsiero and G.H. Spies, *J. Chem. Soc. Chem. Commun.* (1983) 681

89 N.J. Dean and K.J. Maxwell, *Mol. Phys.* 47 (1982) 551

90 M. Morita, T. Schouherr, R. Linder and H-H. Schmidtke, *Spectrochim. Acta.* 38A (1982) 1221

91 I. Ostrich and A.J. Leffler, *Inorg. Chem.* 22 (1983) 921

92 K. Michelson and E. Pedersen, *Acta. Chem. Scand.* A37 (1983) 141

93 K. Michelsen, E. Pedersen, S.R. Wilson and D.J. Hodgson, *Inorg. Chim. Acta.* 63 (1982) 141

94 S.J. Cline, D.J. Hodgson, S. Kallosoe, S. Larsen and E. Pedersen, *Inorg. Chem.* 22 (1983) 637

95 J. Glerup, D.J. Hodgson and E. Pedersen, *Acta. Chem. Scand.* A37 (1983) 161

96 D.E. Bolster, P. Gutlich, W.E. Hatfield, S. Kremer, E.W. Muller and K. Wieghardt, *Inorg. Chem.* 22 (1983) 1725

97 R.F. Johnston and R.A. Holwerda, *Inorg. Chem.* 22 (1983) 2942

98 C.M. Mikulski, S. Cocco, N. de France and N.M. Karayannis, *Inorg. Chim. Acta.* 80 (1983) L71

99 H. Stunzi and W. Marty, *Inorg. Chem.* 22 (1983) 2145

100 B.S. Tsukerblat, M.I. Belinskii and B.Ya. Kuyavskaya, *Inorg. Chem.* 22 (1983) 995

101 L. Dubicki, J. Ferguson and B. Williamson,*Inorg. Chem.* 22 (1983) 3220

102 E. Gonzalez-Vergara, J. Hegenauer, P. Saltman, M. Sabat and J.A. Ibers, *Inorg. Chim. Acta.* 66 (1982) 115

103 N.A.P. Kane-Maguire, W.S. Crippen and P.K. Miller, *Inorg. Chem.* 22 (1983) 696

104 A. Harriman, *J. Chem. Soc. Faraday Trans. 1* 78 (1982) 2727

105 M.Z. Hoffman and N. Serpone, *Isr. J. Chem.* 22 (1982) 91

106 J. Lilie and W.L. Waltz, *Inorg. Chem.* 22 (1983) 1473

107 F. Bolletta, M. Maestri, L. Moggi, M.A. Jamieson, N. Serpone, M.S. Henry and M.Z. Hoffman, *Inorg. Chem.* 22 (1983) 2502

108 M.A. Jamieson, N. Serpone, M.Z. Hoffman and F. Bolletta, *Inorg. Chim. Acta.* 72 (1983) 247

109 M.A. Jamieson, N. Serpone and M.Z. Hoffman, *J. Am. Chem. Soc.* 105 (1983) 2933

110 M.T. Gandolfi, M. Maestri, D. Sandrini and V. Balzani, *Inorg. Chem.* 22 (1983) 3435

111 M.A. Jamieson, C.H. Langford, N. Serpone and M.W. Hersey, *J. Phys. Chem.* 87 (1983) 1004

112 A.D. Kirk and C. Namasivayam, *Inorg. Chem.* 22 (1983) 2961

113 B. Hajek and F. Benda, *Inorg. Chim. Acta.* 77 (1983) L77

114 A.Kh. Vorobiev and V.S. Gurman, *J. Photochem.* 20 (1982) 123

115 H.H. Krause and F. Wagestian, *Inorg. Chim. Acta.* 76 (1983) L295

116 P. Riccieri and E. Zinato, *Inorg. Chem.* 22 (1983) 2305

117 H. Kido and C.H. Langford, *J. Am. Chem. Soc.* 105 (1983) 1196

118 W.M. Wallace and P.E. Hoggard, *Inorg. Chem.* 22 (1983) 491

119 F.R. Lemke, D.E. Wigley and R.A. Walton, *J. Organomet. Chem.* 248 (1983) 321

120 F.A. Cotton and G.N. Mott, *Inorg. Chem.* 22 (1983) 1136

121 R.J. Balahura and A.J. Johnston, *Inorg. Chem.* 22 (1983) 3309

122 K. Micskei, F. Debreczeni and I. Nagypal, *J. Chem. Soc. Dalton Trans.* (1983) 1335

123 I. Nagypal, K. Micskei and F. Debreczeni, *Inorg. Chim. Acta.* 77 (1983) L161

124 J. Hvoslef, H. Hope, B.D. Murray and P.P. Power, *J. Chem. Soc. Chem. Commun.* (1983) 1438

125 L.Y. Goh, T.W. Hambley and G.B. Robertson, *J. Chem. Soc. Chem. Commun.* (1983) 1458

126 I.L. Eremenko, A.A. Pasynskii, B. Orazsakhatov, O.G. Ellert, V.M. Novotorsev, V.T. Kalinnikov, M.A. Porai-Koshits, A.S. Antsyshkina, L.M. Dikareva, V.N. Ostrikova, Yu.T. Struchov and R.G. Gerr, *Inorg. Chim. Acta.* 73 (1983) 225

127 C. Friebel, J. Pebler, F. Steffens, M. Weber and D. Reinen, *J. Solid State Chem.* 46 (1983) 253

128 M.A. Babar, L.F. Larkworthy and S.S. Tandon, *J. Chem. Soc. Dalton Trans.* (1983) 1081

129 R. Wiest and M. Benard, *Chem. Phys. Lett.* 98 (1983) 102

130 R.A. Kok and M.B. Hall, *J. Am. Chem. Soc* 105 (1983) 676

131 P.M. Atha, J.C. Campbell, C.D. Garner, I.H. Hillier and A.A. MacDowell, *J. Chem. Soc. Dalton Trans.* (1983) 1085

132 N. Rajasekar, R. Subramaniam and E.S. Gould, *Inorg. Chem.* 22 (1983) 971

133 R.G. Bhattacharyya, G.P. Bhattacharjee and N. Ghosh, *Polyhedron* 2 (1983) 543

134 D.E. Wigley and R.A. Walton, *Inorg. Chem.* 22 (1983) 3138

135 G.A. Ozin, M.D. Baker, S.A. Mitchell and D.F. McIntosh, *Angew. Chem. Int. Ed. Engl.* 22 (1983) 166

136 H.M. Nagarathna, P.A. Montano and V.M. Naik, *J. Am. Chem. Soc.* 105 (1983) 2938

137 R. Simon, H.D. Gafney and D.L. Morse, *Inorg. Chem.* 22 (1983) 573

138 J. Roziere, P. Teulon and M.D. Grillone, *Inorg. Chem.* 22 (1983) 557

139 J.J. Turner, M.B. Simpson, M. Poliakoff, W.B. Maier II and M.A. Graham, *Inorg. Chem.* 22 (1983) 911

140 M.B. Simpson, M. Poliakoff, J.J. Turner, W.B. Maier II and J.G. McLaughlin, *J. Chem. Soc. Chem. Commun.* (1983) 1355

141 M. Hoeffler, K-F. Tebbe, H. Veit and N.E. Weiler, *J. Am. Chem. Soc.* 105 (1983) 6338

142 L. Sallans, K. Lane, R.R. Squires and B.S. Freiser, *J. Am. Chem. Soc.* 105 (1983) 6352