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6. CHROMIUM

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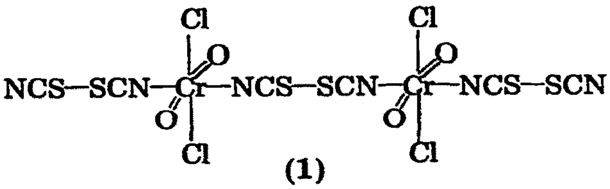
CONTENTS

As usual, most of the new chemistry of chromium published in 1979 concerns the (III) oxidation state, although the story of the chromium(II), and other, quadruply bonded dimers continues to unfold.

6.1 CHROMIUM(VI), (V) AND (IV)

The reactions of ICN and $(SCN)_2$ with CrO_2Cl_2 in dry carbon tetrachloride give [1] the easily hydrolysed compounds, $CrO_2Cl_2(ICN)_2$ and $[CrO_2Cl_2(SCN)_3]_2$. From their IR and Raman spectra, it is concluded that the former has a *cis*-structure with *N*-bonded ICN, and the latter is the dimer (1).



(1)

Some adducts of $K[CrO_3X]$ (X = Cl, Br, IO_3 or F) with primary and secondary aliphatic amines, pyridine, and aniline have been characterised by UV and IR spectroscopy [2].

The reaction of anhydrous sodium dichromate with tertiary α-hydroxy-

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carboxylic acids RR′C(OH)CO_2H (R = R′ = Me, Et or Bu; R = Me, R′ = Et; R = Me, R′ = Ph; R, R′ = $(CH_2)_n$, n = 4 or 5) in propanone has provided a simple, generally applicable route [3] for the synthesis of unexpectedly heat-stable, water-soluble chromium(V) complexes.

$$Na_2[Cr_2O_7] + 5\ RR'C(OH)CO_2H = 2\ Na[OCr(O_2COCRR')_2] + RR'CO + CO_2 + 5\ H_2O$$

The method is an improvement on an earlier one which required the use of CrO_3 in aqueous solution. Higher alkyl groups stabilise, and phenyl groups de-stabilise, the complex anions towards hydrolysis and disproportionation to chromium(VI) and chromium(III). The ionisation energies in the photoelectron spectrum [4] of $CrOCl_3$ are reproduced better by configuration interaction than ΔSCF calculations, and only the former predict the correct ground state for $[CrOCl_3]^+$. The electronic spectrum at 4.2 K of $[CrO_4]^{3-}$ doped in $Sr_5(PO_4)_3Cl$ has been interpreted in detail [5]. Oxidations of triphenylphosphine or sulphite (and some organic substrates) by $[R_4N][CrOCl_4]$ (R = Et or Bu) have been studied [6]; triphenylphosphine oxide and $[Cr_2Cl_9]^{3-}$ or sulphate, are formed by transfer of the oxo-ligand. Fully-labelled $H_2{}^{18,18}O_2$ has been used to demonstrate that exchange of peroxide between H_2O_2 and $[Cr(O_2)_4]^{3-}$ is reversible, and takes place without scrambling of oxygen atoms; the integrity of the exchanging peroxide group is preserved [7].

6.2 CHROMIUM(III)

6.2.1 Complexes of simple ligands

The crystal structure of $NaCrF_4$ is of the $NaNbO_2F_2$ type and contains puckered layers formed by octahedra each of which shares two *trans* and two *cis* corners [8]. There is much less distortion of the octahedra than in the niobium compound. The bridging angles Cr—F—Cr are about the same for *cis* and *trans* linkages, and close to the mean value (147°) found in the chain structure of $KCrF_4$, which is similarly a weak antiferromagnet.

When introduced, even at doping levels less than one part per thousand, into crystals of $CsMgCl_3$, $CsMgBr_3$ or $CsCdCl_3$, M^{3+} ions (M = Cr or Mo) cluster in pairs and behave as magnetic dimers [9]. The EPR spectra have been analysed, and $J \simeq 1\ cm^{-1}$ for the Cr—Cr species. The unexpected pairing arises from the need not to upset the overall charge balance of the linear chains of face-sharing $\{MX_6\}^{4-}$ octahedra in the host lattices, and to do this pairs of trivalent ions occupy the two divalent ion sites on either side of a divalent ion vacancy.

The chromium ions in $[Cr(H_2O)_6][Cr(C_2O_4)_3]$ can be radioactively labelled in either cation or anion, and exchange of label in the crystal lattice takes place as a thermal reaction [10] at or above room temperature. The exchange kinetics, unlike those in solution, can be interpreted in terms of a first order process with either a continuous spectrum of energies of activation, or with a small group of closely spaced energies of activation. The exchange isotherms are formally similar to those found in exchange reactions where the same element is found in different oxidation states, and in annealing reactions in solids.

The complexes *trans*-$[Cr(Me_2SO)_2(NH_3)_4][ClO_4]_3$, *cis*-$[Cr(OCHNMe_2)_2(NH_3)_4][ClO_4]_3$, and *cis*-$[Cr(Me_2SO)(OCHNMe_2)(NH_3)_4][ClO_4]_3$ have been characterised [11], and $[Cr(O_2CCH_3)(NH_3)_5][ClO_4]_2$ is among several carboxylato-transition metal complexes prepared by the general reaction of acylation of hydroxo-complexes [12], a reaction superior to the anation of aqua complexes.

A number of isothiocyanato-complexes, $[CrL_3(NCS)_3]$, $[CrL_3(NCS)(OH)_2]$, and $[CrL_2(NCS)_3(OH_2)]$ (where L is imidazole or various 1- or 2-substituted imidazoles) have been found to be typical chromium(III) complexes. Imidazole is higher in the spectrochemical series than its derivatives [13].

Chromium(III) shows strong affinity for *O*-donors, but the ambidentate cyanate ion is predominantly *N*-bonded to transition metals. It was hoped, therefore, that cyanate linkage isomers could be prepared with chromium(III), but attempts at direct synthesis were unsuccessful [14]. However, oxidation of *mer*-$[Cr(py)_3(NCS)_3]$ by potassium bromate in pyridine (py) has been found to give $[Cr(py)_3(NCO)_3]$ in good yield. It is believed to be the *mer*-isomer, and this novel oxidation has been used to prepare cyanato-*N* complexes from *trans*-$[Cr(en)_2(NCS)_2]^+$ and *trans*-$[Cr(pn)_2(NCS)_2]^+$. *Fac*- and *cis*-isomers give uncharacterised mixtures, and thiocyanato-*S* complexes are oxidised quite differently by bromate. The oxidations must be carried out in small quantities because of their potentially explosive nature.

$$mer\text{-}[Cr(py)_3(NCS)_3] + 4\ [BrO_3]^- \rightarrow [Cr(py)_3(NCO)_3] + 4\ Br^- + 3\ SO_3$$

The low symmetry of complexes $[Cr(NH_3)_5X]^{2+}$ splits the lowest excited doublet ^2E_g (O_h) into $^2B_1$ and $^2A_1$ levels. Experimentally, two intense zero phonon bands separated by 100—300 cm^{-1} are observed, but conventional ligand field calculations can account [15] only for splittings of less than 50 cm^{-1}. It has been argued that the assignments are incorrect, the splitting of ^2E_g being indetectable for most pentaammines; and the two bands have been assigned [16] to transitions to ^2E_g and the lowest component of $^2T_{1g}$. Inconsistencies have now been found [17] in the latter assignments, and analysis of the vibronic and far IR spectra of $[Cr(NH_3)_5(NCO)]^{2+}$, which are well resolved, confirms the earlier assignments and strengthens the belief that the ligand field calculations are inadequate.

Thermal decomposition of $[NH_4][Cr(NH_3)_2(NCS)_4]$ produces [18] $Cr(NH_2)(NH_3)(NCS)_2$ and eventually $Cr(NH)(NH_2)$. Isothermal heating at 150°C of mixtures of $[Cr(NH_3)_6]X_3$ (X = Cl, I, SCN or NO_3) and L-α-alanine (ala) gives [19] $[CrCl(NH_3)_5]Cl$ (X = Cl), $[Cr(NH_3)_3(NCS)_3]$ (X = SCN), $[Cr(ala)_3]$ (X = NO_3), and a green substance said to be $[Cr(NH_3)_6]I_2$ (X = I).

This is more likely to be an amido-compound than a chromium(II) salt.

The reactions of $[Cr(NH_3)_5N_3]^{2+}$ with $H^{18}OF$ [20] and $[H^{18}OOSO_3]$ [21] proceed by direct *O*-transfer to produce $[Cr(NH_3)_5N^{18}O]^{2+}$, although partial exchange of nitrosyl during isolation leads to slightly low enrichment.

The violet salt $[Cr(N_2H_4)_2(ClO_4)_2][ClO_4]$ contains monodentate hydrazine; unlike similar compounds it is not friction- or impact-sensitive but decomposes explosively at 240° C [22].

Many complexes of some phosphate esters and amine-oxides with various transition metal ions have been isolated. The Cr(III) complexes are $[Cr(TTP)_4(OClO_3)_2][ClO_4]$, $[Cl_3(TTP)Cr(TTP)_2Cr(TTP)Cl_3]$ (TTP = tri-4-tolylphosphate) [23], $Cr(tipp)_3$ (tipp = tri-isopropylphosphate) [24], $[CrL_6][ClO_4]_3$, $[CrL_4(OClO_3)(OH_2)][ClO_4]_2$ (L = 3-methylisoquinoline *N*-oxide) [25], $[CrL_2(LH)(OH_2)][ClO_4] \cdot 4\ H_2O$ (LH = picolinic acid *N*-oxide) [26], $Cr(ClO_4)_3L_2 \cdot 12\ H_2O$, and $[Cr(ClO_4)_3]_2L \cdot 12\ H_2O$ (L = phenazine-5,10-dioxide) [27]. Spectroscopic, conductance and magnetic data show that these complexes all contain six coordinate chromium(III), and in many cases bridging ligands.

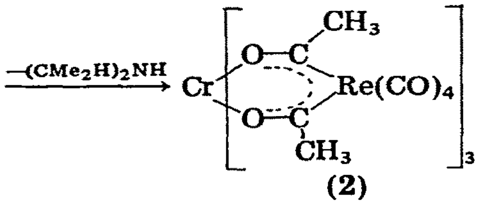
The electronic spectra of the trinuclear clusters $[Cr_3O(CH_2ClCO_2)_6(H_2O)_3]Cl \cdot 3\ H_2O$ and $[Cr_3O(CHCl_2CO_2)_6(H_2O)_3]Cl \cdot 2\ H_2O$ [28], and $[Cr_2FeO(CH_3CO_2)_6(H_2O)_3]Cl \cdot 4\ H_2O$ and $[CrFe_2O(CH_3CO_2)_6(H_2O)_3]Cl \cdot 6\ H_2O$ [29] have been analysed.

Further examples of the use of a metal as a sacrificial anode in the syntheses of anhydrous salts and complexes have been published, and preparations of anhydrous $CrBr_3$, $[Cr(en)_3]Br_3$, $[Cr(Me_2SO)_6]Br_3$, $K_3[Cr(C_2O_4)_3]$ [30], $[Cr(Me_2SO)_6][BF_4]_3$ and $[Cr(bipy)_3][BF_4]_3$ [31] are now available. The use of mixed aqueous/organic (Me_2SO) solutions of tetrafluoroboric acid [31] has permitted the isolation of many complex cations as tetrafluoroborates rather than as possibly dangerous perchlorates. Electrochemical oxidation of chromium [31] in a mixture of concentrated aqueous HBF_4 and ethanenitrile yields $[Cr(CH_3CN)_6][BF_4]_2$, whereas when dimethylsulphoxide is used chromium(III) complexes are obtained.

6.2.2 Complexes of bidentate ligands

Metalla-β-diketonate complexes of metal ions have not been known for long, and the first complexes containing transition metals as the central, coordinating ion have been obtained [32] by elimination of small molecules, other methods being unsuccessful. The dark green chromium(III) complex $[cis\text{-}(OC)_4Re(CH_3CO)_2]_3Cr$ (2) is air-stable, with a magnetic moment of 3.9

cis-$[(OC)_4Re(CH_3CO)_2]H + [Cr\{N(CMe_2H)_2\}_3]$

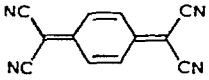


(2)

μ_B at 22°C. The positions of the *d—d* transitions show diacetyltetracarbonylrhenate(I) to be a somewhat weaker ligand than pentane-2,4-dionate.

Some organoseleninato- and dithioacetato-complexes, $[M(O_2SeR)_3]$ {M = V, Cr or Fe; R = Me or Ph} [33] and $[M(S_2CCH_3)_3]$ {M = Cr, Fe, Co or Rh} [34] have been isolated. The chromium(III) complexes show typical magnetic and spectroscopic behaviour.

Tetracyanoquinodimethane (3, TCNQ) in ethanenitrile reacts with tricarbonyltoluenechromium to form dark purple $[Cr(TCNQ)_2(MeCN)_2]$. It is formulated as Cr^{3+}, $TCNQ^{\cdot -}$, $TCNQ^{2-}$, and the effective magnetic moment (4.08 μ_B at 298 K) is considered to be due to the d^3 metal ion, and a small contribution from the TCNQ radical anion. A considerable decrease in μ_{eff} as the temperature is lowered is ascribed to antiferromagnetism [35].



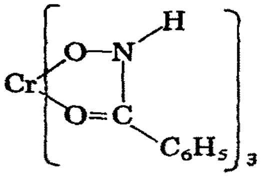
(3)

Attempts to prepare mixed metal dinuclear cyano-bridged complexes containing chromium(III) by heating doubly complexed salts of the type $[Cr(OH_2)(NH_3)_5][Co(CN)_6]$ were unsuccessful because of loss of water and ammonia, but by using 1,2-diaminoethane (en) instead of ammonia, *cis*-$[(en)_2FCrNCNi(CN)_3] \cdot 2\ H_2O$, *cis*-$[(en)_2ClCrNCNi(CN)_3] \cdot 2\ H_2O$ and *cis*-$[(en)_2BrCrNCNi(CN)_3] \cdot 2\ H_2O$ have been obtained [36]. The IR spectra show that bridging and terminal cyanide are present, and the *cis*-configuration has been assigned from the preparative method and the symmetrical nature of the $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ absorption band of chromium(III).

The reaction of dimethylformamide with *trans*-$Na[Cr(C_2O_4)_2(OH_2)_2]$ at 90°C leads to *cis*-$Na[Cr(C_2O_4)_2(OCHNMe_2)_2]$ as major product [37]. The stability constants for combination of 2-hydroxy-1-naphthaldehyde with Cr^{3+} at 30°C in 75% (v/v) dioxan/water containing 0.1 M $NaClO_4$ are log K_1, 8.70 and log K_2, 7.20. Log K_3 could not be determined [38].

Cis—trans isomerisation has been investigated [39] and found to be one-way (*trans* to *cis*) and exothermic in the mixed bis(diamine) complexes *trans*- and *cis*-$[CrX_2(aa)(bb)]X \cdot n\ H_2O$ {where X = Cl or Br, and aa and bb are different diamines selected from 1,2-diaminoethane (en), 1,2-diaminopropane (1,2-pn) and 1,3-diaminopropane (1,3-pn)}. The intermediates *mer*-$[CrBr_3(en)(1,2\text{-}pn)] \cdot 2\ H_2O$ and *mer*-$[CrBr_3(1,2\text{-}pn)(1,3\text{-}pn)] \cdot 2\ H_2O$ were isolated during isomerisation of *trans*-$[CrBr_2(en)(1,2\text{-}pn)]Br \cdot 2\ H_2O$ and *trans*-$[CrBr_2(1,2\text{-}pn)(1,3\text{-}pn)](H_5O_2)Br_2$, respectively, so that bond rupture takes place during this process.

Investigations of tris(benzohydroxamato)chromium(III) (4), tris(*N*-methylthiobenzohydroxamato)chromium(III) (5), and salts of tris(thiobenzohydroximato)chromate(III) (6) are in progress because ligands of these types are found in microbial iron transport compounds. Unlike the iron(III) complex,



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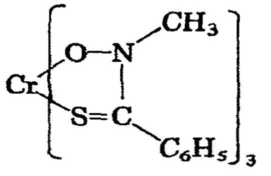

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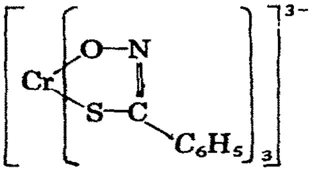
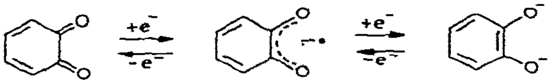


(6)

which crystallises as the *cis*-isomer, complex (4) was found to exist in solution as *cis* and *trans* isomers, characterised by their chromatographic and spectroscopic properties, and the isomers have now been crystallised [40]. The *cis* isomer is stable to isomerisation in $CHCl_3$, and the *trans* in alcohols, but both are unstable in $CHCl_3/MeOH$. Single crystal X-ray methods have confirmed the configuration of the bis(2-propanol) adduct of the *trans* isomer. The coordination octahedron is trigonally distorted, but is less distorted and the Cr—O bond lengths are much more nearly equal than in the iron(III) complex; this is thought to be due to the ligand field stabilisation of the chromium(III) complex. Complex (5) was predicted to have a *cis*-octahedral structure from its circular dichroism spectrum and physical properties, and this has been confirmed by a single crystal determination which shows that there is considerable trigonal distortion [41]. It is isostructural with the manganese, iron and cobalt complexes. The crystal structure of a salt of (6), $Na_2[(C_2H_5)_3(CH_3)N][Cr(C_6H_5C(S):N(O))_3]$ 0.5 $NaH_3O_2 \cdot 18\ H_2O$, has been determined [42]. There are only small differences in structural parameters between (6) and (5). Thus, the further deprotonation in (6) has little effect on complex or ligand geometry. This is the first structure of a thiohydroximato-complex, and the first observation of a discrete $[H_3O_2]^-$ anion (hydroxide hydrate) which has an unusually short hydrogen bond (2.29 Å), and is isostructural with $[HF_2]^-$.



(7) (8) (9)

Redox series involving 1,2-benzoquinone (7) (bq), 1,2-benzosemiquinone (8) (sq) and catecholate (9) (cat) complexes of chromium have been investigated because of their relation to biological and other chemical electron transfer systems, and their possible use as electroactive agents in the electrochemical reduction of small molecules such as nitrogen [43,44]. Cyclic voltammetry of the neutral tris(complexes) of 3,5-di-*tert*-butyl-1,2-benzoquinone, in CH_2Cl_2 [44] or ethanenitrile [43], 9,10-phenanthrenequinone, and tetrachloro-1,2-benzoquinone [44] has established the series

$$[Cr(bq)_3]^{3+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Cr(bq)_2(sq)]^{2+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Cr(bq)(sq)_2]^{+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Cr(sq)_3]^{0}$$

$$\underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [\mathrm{Cr(sq)_2(cat)}]^- \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [\mathrm{Cr(sq)(cat)_2}]^{2-} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [\mathrm{Cr(cat)_3}]^{3-}$$

It is considered that the metal remains essentially as Cr(III) while electrons are added to, or removed from, levels of primarily ligand character. Five reversible or quasi-reversible redox reactions were observed in the cyclic voltammogram of $[Cr\{O_2C_6H_2(CMe_3)_2\}_3]$, but the half-wave for the 2+/3+ couple could not be resolved. All six redox reactions were identified for $[Cr(O_2C_{14}H_8)_3]$, but only the three anionic reactions for $[Cr(O_2C_6Cl_4)_3]$. The latter occur at unusually positive potentials because of the electrophilic ligand, and were earlier assigned in error to oxidations of the neutral complex [44]. The kinetic stability of Cr(III) appears responsible for the redox series; the analogous Fe(III) complexes are irreversibly reduced.

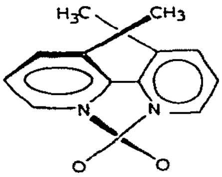
The three anionic redox couples have also been identified for $[Cr\{O_2C_6H_2(CMe_3)_2\}_3]$ in ethanenitrile [43], but irreversible oxidation waves were observed at high potentials; the anionic reactions have also been shown to be chemically reversible.

The neutral complex $[Cr\{O_2C_6H_2(CMe_3)_2\}_3]$ spontaneously resolved to the Λ-*cis* isomer on crystallisation, and comparisons of its C—C and C—O bond lengths with those in $[Cr(cat)_3]^{3-}$, catechol, and 1,2-benzoquinone suggest that the ligand retains considerable quinoid character [43]. Other crystallographic data have been similarly interpreted [44].

The neutral tris(quinone) complexes could be formulated as complexes of Cr(0) with three quinone ligands, of Cr(VI) with three catechol dianions, or as chromium(III) complexes in which there is intramolecular antiferromagnetic coupling between the metal d^3 electrons and the unpaired electrons of three semiquinone (sq) radical anions. One group [43] reports that $[Cr\{O_2C_6H_2(CMe_3)_2\}_3]$ is diamagnetic in solution and in the solid state, while another (see [44] and references therein) finds that $[Cr(O_2C_6Cl_4)_3] \cdot 4\,C_6H_6$ and $[Cr(O_2C_{14}H_8)_3]$ have magnetic moments decreasing from approximately 1.1 μ_B at 286 K to 0.3 μ_B at 4.2 K. It is possible that the third formulation, effectively $[Cr^{III}(sq)_3]$, is correct, and in $[Cr\{O_2C_6H_2(CMe_3)_2\}_3]$ strong coupling leads to population of the diamagnetic ground state only. The EPR spectra of the +1 and —1 members of the redox series show similar $\langle g \rangle$ and ^{53}Cr hyperfine values indicating substantial metal character in the ground states.

6.2.3 Optically active complexes

2,2′-Bipyridine-*N*,*N*′-dioxide (bpdo) forms a skew seven-membered ring on coordination, and since the skew chelate ring is chiral the complexes $[Cr(bpdo)_n(en)_{3-n}]^{3+}$ ($n = 1$, 2 or 3) should give a number of diastereoisomers, each of which has a pair of enantiomers. However, each bpdo complex gave only one pair of enantiomers, suggesting that the bpdo ring easily changes its conformation in solution [45]. The new ligand, 3,3′-dimethyl-2,2′-bipyridine-



(10)

N,N'-dioxide (dmbpdo) (**10**), has been synthesised [46] because rotation about the bond joining the heterocyclic rings should be prevented by the methyl groups: the ligand should exist in a pair of enantiomers, (R) and (S), and $[Cr(dmbpdo)_3]^{3+}$ should form a number of optical isomers. Three diastereoisomers have been obtained, (I), assigned to the pair of enantiomers Δ(RRR) and Λ(SSS), and (II) and (III) assigned to either a diastereoisomeric pair of Δ(RRS) and Λ(SSR) or Δ(SSR) and Λ(RRS). Optically active, free $(+)_{589}$- and $(-)_{589}$-dmbpdo were isolated by decomposing Λ(SSS)- and Δ(RRR)-$[Cr(dmbpdo)_3]^{3+}$, respectively, with ethylenediaminetetracetate. The active dmbpdo is optically stable, even in boiling water.

From circular dichroism spectroscopy, it was predicted that the (—) isomer of tris(pentane-2,4-dionato)chromium(III) would have the right-handed Δ configuration. Crystals of (—)-$[Cr(acac)_3]$ have been obtained via a partial asymmetric synthesis. The (—) isomer has the Δ configuration and a nearly regular CrO_6 coordination octahedron with similar intramolecular bond angles and distances to those in the racemic crystal [47]. The packing of the molecules in the active crystal has been compared with that of the enantiomeric pairs in the racemic crystal, and the more compact packing in the latter explains its poorer solubility in a range of common solvents, and the enantiomeric discrimination in its favour.

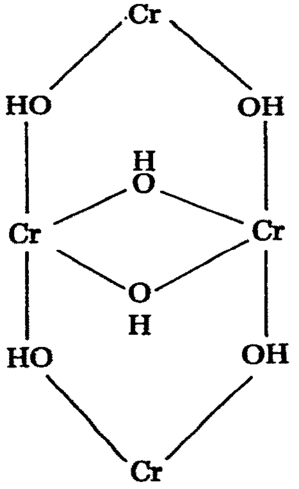
The Pfeiffer effect (n.b. this is the development of new optical activity which sometimes takes place when a racemic mixture of a labile metal complex like $[Cr(C_2O_4)_3]^{3-}$ or $[Co(phen)_3]^{2+}$ is mixed in solution with a certain chiral compound called an environment substance) of $[Cr(C_2O_4)_3]^{3-}$ has been compared with that of $[Co(phen)_3]^{2+}$ [48] by using the cinchoninium ion and some of its related chiral compounds as an environment substance in aqueous solution and mixed solvent. It has been proposed that negatively-charged $[Cr(ox)_3]^{3-}$ is electrostatically held to the cinchoninium ion and is subject to asymmetry around the C-8 atom, but that positive $[Co(phen)_3]^{2+}$ associates with the cinchoninium ion through hydrophobic interaction with the quinolyl group and is subject to asymmetry around the C-9 atom. The inversion rate of the Λ enantiomer of $[Cr(ox)_3]^{3-}$ enriched by the Pfeiffer effect is appreciably retarded by the cinchoninium ion, while the Δ enantiomer is kinetically little affected.

The resolution of the (+)-*cis*-fluoroaquabis(1,2-diaminoethane)chromium-(III) ion into its optical isomers [49] and the establishment of its absolute configuration by optical rotatory dispersion have confirmed the earlier *cis* assignment from electronic spectral data. The complexes $[Cr(acac)(1,3\text{-}pn)_2]^{2+}$ and $[Cr(acac)_2(1,3\text{-}pn)]^+$ (acac = pentane-2,4-dionato and 1,3-pn = 1,3-diaminopropane) have been resolved, and from their circular dichroism spectra $(+)_{589}$-$[Cr(acac)(1,3\text{-}pn)_2]^{2+}$ and $(-)_{589}$-$[Cr(acac)_2(1,3\text{-}pn)]^+$ were assigned the Λ configuration [50]. Single crystal studies [51] have confirmed the assignment for the latter complex. The amine ligand assumes a chair configuration, one acac ring is planar and the other is bent away from the plane defined by the Cr and two O atoms by intramolecular repulsion.

Improved methods of synthesis and resolution of tris(2,2′-bipyridine)- and tris(1,10-phenanthroline)-chromium(III) salts have been given [52].

6.2.4 Hydroxo-bridged complexes

The tetranuclear cation, hexa-μ-hydroxo-bis{tetraamminechromium(III)} bis{diamminechromium(III)} has the structure (11), omitting the NH_3 molecules. Its antiferromagnetic behaviour (ca. 1—250 K) can be reasonably reproduced in terms of dominant exchange parameters along the side and shorter diagonal of the planar rhombus formed by the four chromium atoms. Neutron inelastic scattering has been used to observe the exchange splittings of the ground electronic state and provide refined and additional exchange parameters. There is a sharp drop in magnetic moment below 10 K which requires that the lowest level of the ground state be a spin singlet with a low-lying triplet. The triplet, from the temperature dependence of the neutron inelastic scattering spectra, lies less than 4 cm^{-1} above the singlet. The exchange splittings of the ground state have also been observed through the temperature dependent intensities (<11 K) of transitions to the ^2E and $^2T_1$ levels [53].



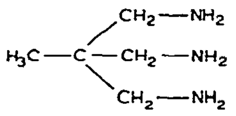
$[Cr_4(OH)_6(NH_3)_{12}]Cl_6 \cdot 4\,H_2O$

(11)

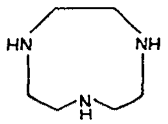
A linear dependence of exchange interaction on Cu—O—Cu bridging angle has been found in a series of copper(II) dimers $[Cu_2(OH)_2L_4]$ [54], but in chromium(III) dimers there is a complex dependence of the magnetic exchange parameter J on the Cr—O—Cr bridging angle in particular. Discrete di-μ-hydroxo structures have been established [55] for the complexes $[Cr(L_3)(OH_2)OH]_2 \cdot x\ H_2O$, {where L_3 is terdentate 4-hydroxo-2,6-dicarboxylatopyridine (complex A) or 4-chloro-2,6-dicarboxylatopyridine (complex B)}. In each complex the coordination around the metal is roughly octahedral and the bridging angles Cr—O—Cr are 99.5° (A) and 100.7° (B). The powder susceptibility data (4.95—291.2 K) for A and B fit the Van Vleck model with singlet—triplet splittings of 4.27 and 10.24 cm^{-1}, respectively, but an impurity contaminated B.

Further investigations [56] of the related complexes $[Cr_2(OH)_2(en)_4]X_4 \cdot x\ H_2O$ {$X_4 = Cl_4, Br_4, I_4$ or $Cl_2[ClO_4]_2$} have been carried out. The chloride and bromide contain dimeric di-μ-hydroxo cations in which the Cr—O—Cr angles are 102.4° (Cl) and 102.6° (Br). The ground state splittings for the four compounds have been determined not only from fitting the powder magnetic susceptibility data from 1.5 K to room temperature, but also by an analysis of the low temperature optical and photoluminescence spectra in the region where the transitions of the dimer between the ground state $^4A_2{}^4A_2$ and the lowest levels of the first singly excited state $^4A_2{}^2E$ occur. The exchange parameters J (singlet—triplet splittings) determined spectroscopically are 31.4 (Cl), 30.0 (Br), 24.3 (I) and 22.2 (Cl, ClO_4) cm^{-1}. These deviate by up to 10% from the values obtained from the magnetic data, indicating a few per-cent increase in J from room to liquid nitrogen temperature. These J values and bridging angles are larger than in the dicarboxylatopyridine complexes, and it may be that J increases with bridging angle; but this will not be the only factor [55,56] and more data are required.

The attempted preparation of dinuclear complexes of chromium(III) containing three μ-hydroxo bridges by condensation of $[Cr(OH_2)_3L]^{3+}$ in acidic media gave [57] only the di-μ-hydroxo complexes $[Cr_2L_2(H_2O)_2(OH)_2]^{4+}$ {where L = 1,1,1-tris(aminomethyl)ethane, (12), or 1,4,7-triazacyclononane, (13)}. More drastic conditions with L = (13) gave salts of the trinuclear cation $[Cr_3L_3(OH)_5]^{4+}$, in which there is a terminal OH ligand and two different pairs of bridges with Cr—O—Cr bond angles of 98° and 126°.



(12)



(13)

The structures of $[(en)_2Cr(OH)(SO_4)Cr(en)_2]_2(S_2O_6)_3 \cdot 2\ H_2O$ and $[(HO)(en)_2Cr(OH)Cr(en)_2OH](ClO_4)_3 \cdot H_2O$ have been reported [58,59]. The former compound is the first sulphato-bridged dinuclear chromium(III) complex isolated as a salt and may be a model for the poorly characterised sulphato-bridged species involved in chrome tanning.

The reaction of *meso*-diol, Δ, Λ-$[(en)_2Cr(OH)_2Cr(en)_2]^{4+}$ with carboxylic acids gives the first carboxylato-bridged chromium(III) complexes: Δ,Λ-$[(en)_2Cr(RCO_2)(OH)Cr(en)_2]^{4+}$ {where R = H, Me, $H_3\overset{+}{N}CH_2$ or H_2NCH_2} [60]. Spectroscopic and chemical properties show that the bridges are symmetrical, and strong base produces the μ-carboxylato-μ-oxo complexes.

6.2.5 *Photochemistry*

Studies of the photochemistry of chromium(III) complexes provide a model for the photochemical field. Progress has been summarised and the way ahead for inorganic photochemistry predicted [61].

A new ligand field model [62] of chromium(III) photochemistry accounts [63] for the production of mainly NCS^- in the photoaquation of *trans*-$[Cr(en)_2(NCS)F]^+$ in the ^4E excited state (^4E and $^4B_2$ derive from $^4T_2(O_h)$). Some ethylenediamine (en) is also produced, but no F^-, and complex ions optically or thermally excited to the higher $^4B_2$ state are thought to photoaquate with the production of en.

Experimental data summarised in the photoaquation (1), including the formation of *cis*-products, are at variance [64] with earlier theories but are explained [65] by the new model which uses spectroscopic parameters and five coordinate intermediates to account for the strong axial labilisation.

$$trans\text{-}[Cr(en)_2(NH_3)F]^{2+} + H_2O \xrightarrow[546nm]{h\nu} cis\text{-}[Cr(en)_2(H_2O)F]^{2+} + NH_3 \qquad (1)$$

However, the loss [66] of en from the excited state of *cis*- and *trans*-$[Cr(en)_2(NH_3)_2]^{3+}$ was larger than expected statistically, and the rate constant for en was 2.8 times that for ammonia. Thus, not only spectroscopic parameters, but also steric strain must be considered [66,67] in theories concerning ligand labilities from excited states.

In (1), there is also some loss of equatorial en (quantum yield, $\phi_{NH_3} = 0.254$ at 546 nm; $\phi_{en} = 0.07$), and, from a comparison of the stereochemistry of photoaquation of *trans*-$[Cr(en)_2(NH_3)F]^{2+}$ and $[Cr(NH_3)_5F]^{2+}$, it has been deduced [67] that equatorial labilisation of NH_3 in the latter gives much *trans*-$[Cr(NH_3)_4(H_2O)F]^{2+}$. This stereomobility producing *trans*-products apparently conflicts with the new theory, and a call has been made [67] for a theory based on associative reactions between the excited complex and the solvent. However, in the latest theoretical paper an attempt [68] has been made to accommodate the stereomobility by suggesting an additional pathway for deformation of the five coordinate intermediate before reaction with H_2O.

The ligand field photolysis of *cis*-$[Cr(NH_3)_4Cl_2]^{2+}$ in acid results in both amine (quantum yield $\phi_{H^+} = 0.32$) and chloride ($\phi_{Cl^-} = 0.15$) labilization [69]. It has been confirmed that amine loss ($\phi_{H^+} = 0.13$) is the dominant photochemical reaction of *cis*-$[Cr(en)_2Cl_2]^+$ ($\phi_{Cl^-} = 0.02$), and found that *cis*-α-[Cr-

(trien)$Cl_2]^+$ displays negligible amine loss ($\phi_{H^+} = 0.015$) with predominant chloride aquation ($\phi_{Cl^-} = 0.10$). The photolyses proceed with retention of *cis* configuration. It is considered that diversity of behaviour, particularly the efficiency of chloride release in two cases, is not predicted by the available models, although the reactivity in the $CrCl_2$ plane follows from them. The total photochemical reactivity is linearly related to the rate of thermal aquation.

Opinion has varied as to which excited state, $^4T_2$ or ^2E, is photoreactive. Lifetimes and relative values of the intersystem crossing ($^4T_2 \rightarrow {}^2E$) efficiencies have been determined for $[Cr(NH_3)_2(NCS)_4]^-$ and $[Cr(NCS)_6]^{3-}$ in pure and mixed solvents [70]. Intersystem crossing is independent of solvent, and both excited states are thought to be significantly reactive in the photochemistry of these anions. In photolysis of aqueous $[Cr(en)_3]^{3+}$ there is [71] both a prompt and a delayed appearance of the primary photoproduct $[Cr(en)_2(enH)(H_2O)]^{4+}$. Analysis of the data indicates that the first quartet thermally equilibrated excited state Q_1^0 ($^4T_2$), formed with 70% efficiency, reacts with a yield of 0.17 to give the primary product, and the doublet state D_1^0 (^2E), produced with 30% efficiency in fast intersystem crossing, reacts to give the primary product with a yield close to unity. In the case of $[Cr(NH_3)_5Cl]^{2+}$ the appearance time of the primary photoproduct, *cis*-$[Cr(NH_3)_4(OH_2)Cl]^{2+}$, was too short to allow identification of the reacting state. Ligand and solvent effects on emission lifetimes of a number of Cr(III) ammines from D_1^0 (^2E) have been determined [72], and a set of rules for estimating emission lifetimes of Cr(III) complexes proposed. The effects of solvent composition on the lifetime and intersystem crossing efficiency of $[Cr(CN)_6]^{3-}$ have been determined for polyalcohol—water mixtures [73]. As for the isothiocyanato-complexes [70], intersystem crossing is independent of solvent.

Thermal and photochemical aquation (2) of $[Cr(bipy)_3]^{3+}$ proceed via direct association of the $^4A_2$ ground state and/or ^2E excited state, respectively, with H_2O to form the same seven coordinate intermediate. From temperature

$$[Cr(bipy)_3]^{3+} \xrightarrow{H_2O,\,OH^-} [Cr(bipy)_2(OH)_2]^+ + bipy \qquad (2)$$

dependence studies, the kinetic parameters for photoaquation have been evaluated and compared with those known for thermal aquation. The excited state reaction is 10^{10} times faster, has considerably lower enthalpy of activation, but exhibits the same entropy lowering in going to the activated complex [74]. The ^2E and $^2T_1$ excited states are in thermal equilibrium, and the latter has a vacant t_{2g} orbital. It is proposed that in photoaquation the empty orbital can accommodate the solvent molecule between the bipy ligands in the seven coordinate intermediate, leading to the rate enhancement. Factors such as increased acidity increase the stability of $[Cr(bipy)_3]^{3+}$ to photoaquation and a modified mechanism has been summarised [75].

Flash photolysis and luminescence techniques have been used to investigate the behaviour of the ^2E excited states of tris(amine) complexes of 2,2′-bipyridine, 1,10-phenanthroline and various substituted derivatives, and $[Cr(2,2',2''\text{-terpyridine})_2]^{3+}$ [76]. Oxygen quenches ^2E predominantly via energy transfer, and aqueous Fe^{2+} and I^- quench via reductive electron transfer. The (^2E) $[Cr(NN)_3]^{3+}$—$[Cr(NN)_3]^{2+}$ self-exchange rate is estimated to be 4×10^{-7} M^{-1} s^{-1}.

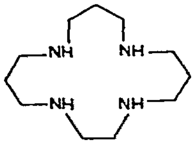
In de-aerated aqueous and alcoholic media, flash photolysis of $[Cr(bipy)_3]^{3+}$ produces $[Cr(bipy)_3]^{2+}$, identified by its spectrum, together with the thermally equilibrated excited ^2E $[Cr(bipy)_3]^{3+}$ transient [77]. Yield of $[Cr(bipy)_3]^{2+}$ increases with pH in the range 11—13, excitation wavelength, and alcohol concentration; the alcohol is oxidised during its formation, and the Cr^{3+}/Cr^{2+} self-exchange rate has been found to be close to the diffusion limit. Photolysis of $[Cr(bipy)_3]^{3+}$ in dimethylformamide in the absence of oxygen or oxidising impurities is followed by a secondary dark reaction with an induction period leading to rapid dissociation of the ligand. The evidence suggests that the chain carrier is a chromium(II) complex [78].

Photoracemisation of (+)-$[Cr(phen)_3]^{3+}$ is partially quenched by I^- and O_2 but the residual non-quenchable limit of reaction has been assigned to immediate reaction from the initially excited ^4T state preceding intersystem crossing to the quenchable ^2E state. At high quencher concentrations, quantum yields for racemisation increased slightly with increasing wavelength indicating that reaction from ^4T was competing with vibrational deactivation [79].

UV irradiation of β-diketonate complexes of most first-row transition metals results in a one electron reduction of the metal by the ligand, but chromium(III) appeared to be an exception, reactions in various non-aqueous solvents inducing isomerisation and decomposition, and substitution by water in aqueous ethanol [80]. It has now been found [81] that flash photolysis of *trans*-$[Cr(tfacac)_3]$ (tfacacH = 1,1,1-trifluoropentane-2,4-dione) in propan-2-ol/hexane yields, relatively efficiently, a metastable chromium(II) product, probably solvated $[Cr(tfacac)_2]$, and tfacacH. Thus, UV photochemistry of Cr(III) β-diketonates is, after all, qualitatively similar to that of corresponding first row complexes. Photolysis probably produces, by ligand-to-metal charge transfer, an excited Cr(II)-ligand radical species which forms tfacacH when a good hydrogen atom donor solvent like propan-2-ol is present, but regenerates the original complex or an isomer, or leads to decomposition in poor hydrogen donor solvents such as cyclohexane or aqueous mixtures.

6.2.6 Complexes of polydentate ligands

A new series of *trans*-monoalkyl complexes of chromium(III), $[RCr^{III}N_4(H_2O)]^{2+}$, where R = alkyl and N_4 is the macrocycle 1,4,8,12-tetraazacyclopentadecane (**14**), has been prepared by the second order reaction of $[Cr^{II}N_4(H_2O)_2]^{2+}$, which was not isolated, with alkyl halides RX, but not halobenzenes, in aqueous organic solvents [82]. The fifteen-membered macrocycle was chosen because it is water-soluble and able to accommodate the Cr^{2+} ion. The reaction is believed to take place in two steps: rate-limiting



(14)

halogen abstraction by the chromium(II) complex to form a carbon-centred free radical, followed by rapid coupling of the latter with a second molecule of chromium(II) complex to form approximately equal quantities of $[RCrN_4(H_2O)]^{2+}$ and $[XCrN_4(H_2O)]^{2+}$.

Previously known organo-chromium derivatives are the cations $[(H_2O)_5CrR]^{2+}$, the recently prepared difunctional cation $[CrCH_2C_6H_4OC_6H_4CH_2Cr]^{4+}$ (aq) [83], some complexes containing ethylenediamine, and the perfluoroalkyls R_FCr(salen)py, but none of these was made by the above general method. The standard potential E^0 for $[CrN_4]^{3+}/[CrN_4]^{2+}$ has been estimated as —0.58 V showing that the chromium(II) complex is a more powerful reducing agent than the aqueous ion (E^0 = 0.41 V). This is apparently one factor which causes $[(H_2O)_2CrN_4]^{2+}$ to react with alkyl halides, although Cr^{2+}(aq) fails to react.

As solid salts of the $[RCrN_4H_2O]^{2+}$ cations could only be obtained impure ($[BPh_4]^-$) or in poor yield ($[ClO_4]^-$), the organometallic cations have been characterised mainly through their aqueous solution spectra and identification of the products of cleavage of the Cr—C bonds with halogens and mercury(II).

The difunctional organochromium cation $[CrCH_2C_6H_4OC_6H_4CH_2Cr]^{4+}$ (aq) has been prepared [83] from bis[3-(bromomethyl)phenyl]ether and excess chromium(II) in aqueous acetone, as deficiency of metal ion gives $[CrCH_2C_6H_4OC_6H_4CH_2Br]^{2+}$ (aq). The difunctional cations react about twice as fast as the monofunctional cations, suggesting little neighbouring group assistance. Primary organochromium cations in the series are stable towards molecular oxygen in aqueous solution, except the benzylchromium(III) ion which reacts indirectly by unimolecular homolysis; autoxidation of the isopropylchromium(III) cation [84] depends on its concentration to the power 3/2, and a radical chain mechanism accounts for the rate law and products.

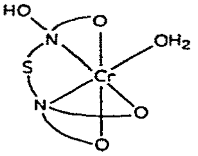
Equilibrium constants have been determined [85] for the reaction

$$PM^{III}—OH_2 \overset{K}{\rightleftharpoons} PM^{III}—OH + H^+$$

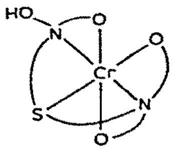
in which M = Cr, Mn, Fe, Co or Rh, and P = tetraphenylporphyrinsulphonate or haematoporphyrin. The magnitudes of K are in the order Cr > Co > Fe > Mn, as are the equilibrium constants for the binding of imidazole where they are known. This trend does not follow the simple Irving—Williams series, but has been explained by showing that the effective charge along the z axis decreases in the same order through the different occupancy of the d orbitals.

The magnitudes of the equilibrium constants are surprisingly independent of the porphyrin substituents.

Thiobis(ethylenenitrilo)tetraacetic acid $S[CH_2CH_2N(CH_2COOH)_2]_2$ (tedta) and $Cr(ClO_4)_3$ form [86] the *cis*-isomer (15) or the *trans*-isomer (16) (with respect to coordinated nitrogen) in solution, depending upon the reaction conditions, especially pH. Attempts to isolate solid (15) gave powders which did not exhibit the spectrum of pure (15) when re-dissolved. Isomers (15) and (16) can be inter-converted in solution, and they are separable from each other, and any bridged oligomers which may be present, by anion exchange. The pH titration and electrochemical behaviour of (15) and (16) are consistent with the assigned structures. In addition, (15) can be anated by N_3^- but (16) cannot, whereas (16) has the weaker and broader visible absorption bands as would be expected for a *trans*-chromium(III) species. There is also an intense absorption at 240 nm in its spectrum, which can be assigned to ligand-to-metal charge transfer involving the coordinated thioether group. Supporting evidence has been provided by comparisons with the behaviour of Cr(III) complexes of edta, oxybis(ethylenenitrilo)tetraacetic acid, and pentamethylenedinitrilotetraacetic acid. The tedta complexes were investigated in a search for substitutionally inert complexes which would adsorb strongly on mercury electrodes, and both isomers spontaneously absorb, (16) being extraordinarily strongly held.



(15, violet)



(16, pink)

6.3 CHROMIUM(II)

It is likely that electrochemical oxidation of metallic chromium, referred to under chromium(III) chemistry (Section 6.2.1), will prove generally useful in the synthesis of chromium(II) compounds [31].

6.3.1 Ferromagnetic tetrahalochromates(II)

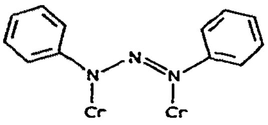
Most ferromagnetic substances are metals, but there are a few ionic transition metal compounds with this property. These have been listed in ref. 87, which is mainly concerned with the latest and largest class of compounds of this type, the tetrachlorochromates(II) A_2CrCl_4 {where A = K, Rb or Cs}. These compounds have been crystallised from the melt (although they can be obtained by crystallisation from ethanoic acid [88], and by thermal dehydration of the dihydrates [89]), and many techniques have been expertly deployed in their investigation. Magnetic susceptibility measurements indicate that the Curie temperatures T_c lie a little below liquid nitrogen temperature, and magnetization studies give values of T_c near 60 K. The ferromagnetic ordering has been confirmed and T_c obtained more accurately from the variation of neutron diffraction intensities with temperature. Besides the usual spin-allowed *d*—*d* transitions of Jahn—Teller distorted chromium(II), $^5B_{1g} \rightarrow {}^5A_{1g}, {}^5B_{2g}, {}^5E_g$, the solid state spectra of these compounds contain relatively intense spin-forbidden bands near 18700 and 15900 cm^{-1}. These bands all but vanish on cooling to 4.2 K. They correspond to transitions to the ^3E_g (^{3}H) and $^3A_{1g}$ (^{3}G) terms, and their intensity arises from the "hot band" mechanism — coincidently with the $\Delta S = -1$ change accompanying the optical excitation of one chromium(II) ion there occurs a $\Delta S = +1$ change at another magnetically-coupled ion which drops to a lower magnetic energy level. Effectively, $\Delta S = 0$ and the spin-forbidden absorptions gain considerable intensity. At low enough temperatures, when all the metal ions are in the ferromagnetic ground state (all spins parallel), the intensity of the optical transition becomes zero because no compensating $\Delta S = +1$ changes can occur. Almost up to T_c, which has also been derived from the data, the intensity follows a T^2 law, and this has been explained theoretically.

The ionic ferromagnets were thought to have the K_2NiF_4 structure in which there are sheets of chloride bridged $(CrCl_4)^{2-}$ units, separated by double layers of ACl from which chloride ions complete tetragonally-compressed $(CrCl_6)$ octahedra. Single crystal neutron diffraction has now shown [90] that the octahedra are elongated, not compressed, and the principal axes of the elongated octahedra lie in the sheets and are directed alternately at right angles. The Cr atoms are in two sites, and the Jahn—Teller distortion is fundamental to the ferromagnetism.

Nearest-neighbour coupling constants J (ca. 4 cm^{-1}) for exchange within the $(CrCl_4)^{2-}$ sheets have been calculated by fitting the magnetic data to the high-temperature series expansion formula for a two-dimensional ferromagnet; J values have also been derived from inelastic neutron scattering experiments which showed that the coupling between successive layers is essentially zero [87]. This presents a considerable theoretical problem, as a two-dimensional ferromagnet should not order above the absolute zero. Although the transparency in the visible of the tetrachlorochromates(II) could be of technological importance, because other ferromagnets are opaque, their relatively low Curie temperatures and air-sensitivity are severe limitations, but this does not detract from the considerable chemical and theoretical interest of these compounds. Tetrachlorochromate(II) salts of organic cations [91,92] have not yet been studied so extensively, but they often exhibit ferromagnetism, as do many tetrabromochromates(II) [93].

6.3.2 Complexes containing Cr—Cr quadruple bonds

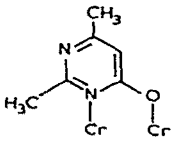
The binuclear nature of chromium(II) acetate $[Cr_2(O_2CCH_3)_4(H_2O)_2]$ has long been known, but only in recent years has it been realised what a variety of chromium(II) complexes can be prepared containing the very stable Cr—Cr quadruple bond. Compounds (18) to (23) [94—99] have either been prepared for the first time or discussed in some detail this year. They are all of the type $[Cr_2L_4]$, where L is generally a singly-charged, anionic ligand, but only one ligand has been shown in each formula. The complexes were obtained by reaction of anhydrous chromium(II) acetate with the lithium salt of the ligand in thf, except (18) which was prepared [94] from $Li(thf)_4[Cr_2(CH_3)_8]$ and (19) which was obtained from $Cr(CO)_6$ [95].



$r(CrCr) = 1.858$ A

1,3-diphenyltriazinato

(18)

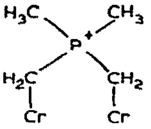


$r(CrCr) = 1.898$ Å, form I

$r(CrCr) = 1.907$ Å, form II

2,4-dimethyl-6-hydroxypyrimidinato

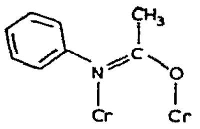
(19)



$r(CrCr) = 1.895$ Å

dimethylphosphoniumdimethylido

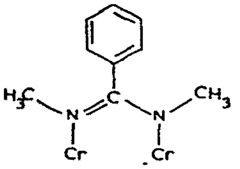
(20)



$r(CrCr) = 1.873$ Å

acetanilido

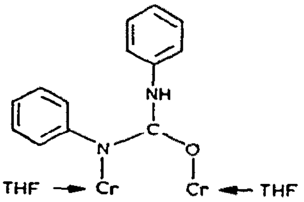
(21)



$r(CrCr) = 1.843$ Å

N,N'-dimethylbenzamidinato

(22)



$r(CrCr) = 2.246$ Å

carbanilanilido

(23)

The Cr—Cr bond distances, with the important exception of (23), are 1.90 Å or less so they are of the "supershort" category as compared [98,99] with the longer bonds (2.29—2.53 Å) found in chromium(II) carboxylates. The complexes have been synthesised and their structures determined to clarify which structural and electronic factors might be important or essential in determining the length of the Cr—Cr bond. Earlier work has shown that the formation of supershort bonds does not require the presence of a Cr—C bond, a Cr—O bond, or four carboxylates, and it is not necessary for the Cr_2L_4 unit to be neutral or for the donor atoms to be incorporated in an aromatic ring. Complexes (**18**) to (**23**) confirm these generalisations, (**20**) showing that aromatic rings need not be present at all. It now appears that exclusion of axial ligands is necessary for the formation of supershort bonds. Every known tetracarboxylate is either a disolvate with axial ligands, or, if unsolvated, has $Cr_2(O_2CR)_4$ molecules in infinite chains with intermolecular O····Cr bond distances of 2.22—2.44 Å, but the supershort bonds are in Cr_2L_4 units, from which axial donors are excluded by steric hindrance. For example, in (**21**) the acetanilido-groups are bonded with N *trans* to N and O *trans* to O and the bite of N—C—O is greater than the Cr—Cr distance. The PhN units prevent association and axial donation of separate donor molecules; in (**22**) the eight methyl substituents exert a similar influence. However, in (**23**), the same bridging system is present as in the acetanilido compound (**21**), but coordination of axial tetrahydrofuran occurs in a complex [99] with a much longer Cr—Cr bond, almost the length (~2.35 Å) found in typical carboxylates. This emphasises the importance of axial ligands. The thf molecules are relatively tightly bound, and from the bond distances the carbanilanilido ligand is more weakly bound than the acetanilido ligand.

The low temperature electronic spectrum of a crystalline powder of $[Cr_2\{(CH_2)_2P(CH_3)_2\}_4]$ (**20**) pressed in KBr pellets could not be obtained with certainty because of decomposition, but the spectrum of the molybdenum analogue has been analysed [100].

In order to clarify further the importance of axial ligands, carboxylates $[Cr_2(O_2CR)_4]$ containing R groups which would prevent axial coordination are being synthesised [97] and Cr—Cr bond lengths are being measured in the gas phase by electron diffraction. It is considered that if the Cr—Cr bonds in $[Cr_2(O_2CR)_4]$ molecules free of axial ligands are supershort, ab initio calculations will be shown to be inadequate as these predict maximum strength at a Cr—Cr separation of ca. 2.40 Å.

The theoretical description of the quadruple bond is very dependent on the quantum mechanical approach [101]. It is believed [102] that the competition between attractive *d*-electron forces and repulsive *s*- (*p*-) electron forces is the principal factor governing the stereochemistry of metal—metal bonds.

Calculations based on a $\sigma^2\pi^4\delta^2$ configuration for the metal—metal quadruple bonds in binuclear Cr(II)—Cr(II) and Mo(II)—Mo(II) carboxylates give a reasonable account of the photoelectron (PE) spectra of the latter but not the former. In order to obtain further information on the nature of these quadruple bonds earlier research has been extended. Photoelectron spectra have been obtained for solid $Cr_2(O_2CMe)_4$, solid and gaseous $[Cr_2(O_2CCF_3)_4]$, gaseous $[Cr_2(mhp)_4]$ and $[Mo_2(mhp)_4]$ {where mhpH = 6-methyl-2-hydroxypyridine} [103], gaseous $[M_2(O_2CR)_4]$ {where M = Cr or Mo and R = Me or Et}, $[CrMo(O_2CMe)_4]$, and $[Mo_2(O_2CCF_3)_4]$ [104]. Amongst these complexes is one, $Cr_2(mhp)_4$, with a supershort Cr—Cr bond (1.89 Å).

The PE spectra of the chromium carboxylates show at lowest energy a broad band which, it is believed, contains all the ionisation energies of the σ, π, and δ electrons, and at least three ionisations have been detected in the He(II) spectrum of $[Cr_2(O_2CEt)_4]$ [104]. It is suggested that calculations for $[Cr_2(O_2CH)_4]$ which differ in their detailed assignments and none of which accounts comprehensively for the experimental data, can be best reconciled if all three ionisations are assigned to this band. Solid and gaseous $[Cr_2(O_2CCF_3)_4]$ [103] have essentially the same PE spectra, although the lowest energy feature is displaced ca. 0.3 eV to lower energy for the solid, and solid and gaseous $[Cr_2(O_2CMe)_4]$ spectra show similar behaviour. This is consistent with a weakening of the Cr—Cr bond in the solid where axial intermolecular Cr—O interactions are present.

Unlike chromium carboxylates, molybdenum carboxylates have PE spectra in which the lowest energy feature is assigned to ionisation from the metal—metal δ-bonding orbital only, and the next highest energy feature to overlapping ionisations from the metal—metal π- and σ-orbitals {i.e. the δ-, π- and σ-orbitals lie much closer in the chromium compounds [104]}. It is therefore interesting that the PE spectra of the complexes $[M_2(mhp)_4]$ [103] have essentially the same profile, resembling that of the molybdenum carboxylates. The resolution of the δ- and (π, σ)-ionisations for $[Cr_2(mhp)_4]$ is considered to be due to the shorter and stronger quadruple bond in this complex. A review [105] of the PE spectroscopy of transition metal complexes includes some discussion of the chromium and molybdenum carboxylates.

The standard enthalpies of formation at 298.15 K of some crystalline molybdenum and chromium carboxylates have been determined by solution reaction calorimetry [106] in order to assess the contribution of the metal—metal bond to the binding energy. For $[Mo_2(O_2CMe)_4]$, $[CrMo(O_2CMe)_4]$, $[Cr_2(O_2CMe)_4]$, $[Cr_2(O_2CMe)_4(H_2O)_2]$ and $[Mo_2(O_2CMe)_2(acac)_2]$ (acac = pentane-2,4-dionato), the values are −1971, −2114, −2297, −2875 and −1805 kJ mol^{-1}, respectively. From these and other thermodynamic data, estimates of the metal—metal enthalpy contributions in the gaseous species have been made. These are $\bar{D}$(Mo—Mo) = 334, $\bar{D}$(Cr—Mo) = 249, and $\bar{D}$(Cr—Cr) = 205 kJ mol^{-1}. This order of multiple bond energies agrees with the ν(M—M) frequencies, and the magnitude of $\bar{D}$(Cr—Cr) confirms the presence of a reasonably strong Cr—Cr bond, but it has not been possible to distinguish between various theoretical treatments from the thermochemical data.

A value of 44 kJ mol^{-1} has been derived for the bond enthalpy contribution for the coordination of each water molecule in $[Cr_2(O_2CMe)_4(H_2O)_2]$, but this is a low estimate as the loss of water is likely to be accompanied by a strengthening of the Cr—Cr bond which is shorter in the anhydrous compound.

This review is not meant to cover the general organometallic chemistry of chromium, but as chromocene forms polymeric, pyrophoric chromium(II) alkoxides on reaction with primary and secondary alcohols in hydrocarbon solvents [107] or tetrahydrofuran (thf) [108], this work is included. The pale blue or pink alkoxides are insoluble and antiferromagnetic [108]:

$$[(C_5H_5)_2Cr] + 2\ ROH = [Cr(OR)_2]_x + 2\ C_5H_6\ ,$$

where R = Me, Et, CMe_2H, Me_3CCH_2 [107], Me, Et, Pr, CMe_2H, Bu, *i*-Bu [108]. Only partial replacement of cyclopentadienyl by R occurs with Me_3COH and silanols.

$$[(C_5H_5)_2Cr] + ROH = \tfrac{1}{2}[(C_5H_5)CrOR]_2 + C_5H_6\ ,$$

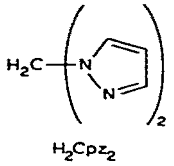
where R = Me_3C, Me_3Si, Ph_3Si [107].

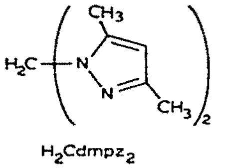
The product from Me_3COH is an antiferromagnetic, butoxy-bridged dimer with a non-planar central $(Cr\text{-}\mu\text{-}O)_2$ moiety and a Cr—Cr separation of 2.65 Å. The magnetic properties ($\mu_{eff} = 1.88\ \mu_B$ at 333.5 K) suggest that there is one unpaired electron per metal atom. It is thought that the compound may contain a Cr—Cr single bond. The dimer structure is preserved by reaction with CO, NO, and $CF_3C{\equiv}CCF_3$, but with CO_2 in thf, $[Cr(C_5H_5)_2]$ and $[Cr_2(O_2C\text{-}CMe_3)_4(thf)_2]$ are formed. The latter has the acetate structure with a typical Cr—Cr distance of 2.367 Å and axially coordinated thf.

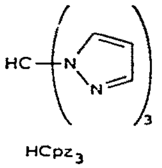
6.3.3 Complexes of N-donor ligands

Complexes of chromium(II) halides with 3-chloro-, 3-bromo, 3-iodo- and 3,5-dichloro-pyridine have been isolated [109]. Only pyridine and methylpyridine complexes of chromium(II) were known previously. Complexes of the type $Cr(X\text{-}py)_2Y_2$ (Y = Cl, Br or I) are antiferromagnetic and presumably linear halogen-bridged polymers like many analogous complexes of other bivalent transition metals. Bridging iodide is uncommon because of the greater size and polarizability of this halide, and the iodides (the first of this type to be established for chromium(II)) were more difficult to prepare than the other halides. The stretching vibrations of the "short" Cr—X bonds are thought to be near 320 (Cl), 260 (Br) and 240 (I) cm^{-1}. The ν(Cr—N) absorptions are also at ca. 260 cm^{-1} and cannot always be distinguished from the ν(Cr—Br) absorptions. The other complexes obtained, $[Cr(X\text{-}py)_2(H_2O)_2I_2]$ and $[Cr(3,5\text{-dichloropyridine})_4I_2]$ are six coordinate monomers.

The anionic poly(1-pyrazolyl)borates form chromium(II) complexes, and the neutral, isoelectronic poly(1-pyrazolyl)alkanes (24—26) do so also [110]. From the potentially tridentate ligand (26), $[Cr(HCpz_3)_2][BPh_4]_2$, a typical distorted six-coordinate chromium(II) complex has been obtained, but the potentially bidentate ligand (24) produces three complex types, exemplified by $[Cr(H_2Cpz_2)_2Br_2]$, $[Cr(H_2Cpz_2)Cl_2]_n$ and $[Cr(H_2Cpz_2)_2Cl][BPh_4]$. All three are believed from their electronic spectra to be six coordinate, and the halide bridging necessary to produce six coordination leads to antiferromagnetic behaviour with the second and third. The dimethyl-substituted ligand (**25**) forms complexes of the same stoicheiometry as (**24**), e.g. [$Cr(H_2Cdmpz_2)_2Br_2$] and [$Cr(H_2Cdmpz_2)_2Cl$][BF_4], but the cations are considered to be monomeric and five coordinate because the magnetic moments are essentially temperature independent, the complexes are 1 : 1 electrolytes in ethanenitrile, and their solution and reflectance spectra are not typical of six coordinate chromium(II). The pattern of bands is not typical of the few known trigonal bipyramidal or square pyramidal chromium(II) complexes either; there are two moderately intense absorptions in the ranges 14 700—17 000 and 11 100—12 500 cm^{-1}, which have been tentatively assigned to transitions to the $^5E'$ and $^5E''$ levels in C_{2v} symmetry. The relative intensity of the bands is the reverse of that found for known trigonal bipyramidal chromium(II) complexes. However, as these were of tetradentate tripod-like ligands which impose strict trigonal symmetry, the intensity difference is considered to be due to the lower symmetry of the trigonal bipyramidal [$Cr(H_2Cdmpz_2)_2X$]$^+$ ions.


(**24**)


(**25**)


(**26**)

The sublimation of β-[$Cr^{II}(Pc)$] (PcH_2 = phthalocyanine) can give a mixture of the α- and β-polymorphs, and pure β-[$Cr^{II}(Pc)$] in dry air or oxygen takes up slightly more than 0.5 O_2 per Cr to give a deep-blue product analysing as [CrO(Pc)] [111]. It is formulated as [(Cr^{IV}=O)Pc] from IR and Raman spectra {ν(CrO) = 1041 cm^{-1}} and mass spectra. Since its magnetic moment (1.9 μ_B at room temperature) is lower than expected for a chromium(IV) complex ($S = 1$), and temperature-variable, a double-sheet dimer structure with O atoms on opposite sides is proposed. This product was earlier thought to be [$Cr^{III}(Pc)OH$], and certain discrepancies in earlier work have been cleared up.

The low-spin complex bis(pyridine)(*meso*-tetraphenylporphinato)chromium(II), which combines irreversibly with oxygen, contains [112] two types of molecule in the solid, one with a two-fold axis and the other with a centre of symmetry. The Cr atoms are centred in the porphinato planes. The Cr—N distances to the axial pyridine molecules (ca. 2.13 Å) are considerably less than in the isoelectronic manganese(III) complexes, e.g. in high spin [MnClpy-(TPP)], the Mn — py bond distance is 2.444 Å. This is attributed to the depopulation of the $3d_{z^2}$ orbital in the low spin chromium(II) complex. The average Cr—N bond distance in the porphyrinato plane is 2.027 Å, comparable to that (2.033 Å) in [Cr(TPP)] · 2 (toluene) [113] which differs from [$Cr(py)_2(TPP)$] in being four coordinate and high spin. Addition of axial pyridine causes spin-pairing but little change in equatorial Cr—N distances.

6.4 MISCELLANEOUS COMPLEXES

The phosphites $CrHPO_3 \cdot H_2O$, $CrDPO_3 \cdot 2\ D_2O$, $CrH_4P_2O_6 \cdot H_2O$, and $CrD_2P_2O_6 \cdot D_2O$ are high-spin. Thermal decomposition under nitrogen occurs by loss of water followed by internal oxidation/reduction. Their Raman and IR spectra have been assigned [114].

Chromium(II) complexes, electrolytically generated from chromium(III) compounds in non-aqueous media, are useful in the reduction of unsaturated organic substrates. The ability of chromium(II) to catalyse inner-sphere ligand exchange is important, as well as its reducing ability. The presence of chromium(III) salts permits smooth electro-reduction of a variety of carbonyl compounds in dimethylformamide [115], and the species formed when chromium(III) salts are dissolved and electrochemically reduced in this solvent have been investigated [116,117].

Theoretical expressions have been derived to describe the magnetic properties of sandwich complexes including the d^4 case, which is expected to have a triplet ground state. Chromocene and the isoelectronic bis(mesitylene)-vanadium(I) cation have magnetic moments consistent with triplet ground states and the same has now been shown [118] for the air-stable chromium-(II) metallocarborane $[(C_2H_5)_4N]_2[Cr^{II}(C_2B_{10}H_{12})_2]$. The magnetic data follow the Curie—Weiss law, $\chi = C/(T - \theta)$, with $\theta = -1.7$ K and $g = 2.00$ over the range 1.8—90 K, but it has not proved possible to obtain a close fit to the available theoretical expressions. Structural data are needed so that the effects of distortion can be assessed.

The magnetic susceptibility of the d^3 metallocarborane, $Cs[Cr^{III}(C_2B_9H_{11})_2]$, obeys the Curie—Weiss law with $\theta = -1.5$ K and $g = 1.98$, in agreement with EPR data. This compound shows spin-only behaviour over the whole temperature range as predicted.

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