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4. CHROMIUM

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CONTENTS

INTRODUCTION

Most of the new inorganic and coordination chemistry of chromium published during 1981 has been concerned with the (III) oxidation state, although much of the work is routine. Except for an account of a few organometallic compounds which resemble classical chromium(III) complexes in some of their properties, the organometallic chemistry of chromium has not been included. The photochemistry of chromium(III), and the synthesis and study of quadruply bonded chromium(II) dimers, continue to be active areas.

4.1 CHROMIUM(VI), (V) and (IV)

Solvolysis of CrO_2Cl_2 and CrO_3 in chlorosulphuric acid produces chromyl chlorosulphate, $CrO_2(SO_3Cl)_2$, which has been characterised by analyses, its diamagnetism, and IR spectra [1]. From concentrated solutions of $K_2[CrO_4]$ and $K_2[Cr_2O_7]$ in chlorosulphuric acid, a green form of $CrO_2(SO_3Cl)_2$ separates at room temperature and a dark brown form at elevated temperatures. The double chromates $KLn(CrO_4)_2$ (Ln = La to Sm), $RbLn[CrO_4]_2$ (Ln = La to Nd), and $CsLa[CrO_4]_2$ are isostructural with each other and with crocoite,

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$Pb[CrO_4]$ [2]. $Rb_2[CrO_4]$ reacts with MoO_3 or $Cr_2(MoO_4)_3$ to produce the chromatomolybdates $Rb_2CrO_4.MoO_3$ or $Rb_2CrO_4.Cr_2(MoO_4)_3$, respectively [3]. New arsenatochromates, $[NH_4]_3[AsCr_4O_{16}]$ and $K_3[AsCr_4O_{16}]$ [4], and the heteropoly salts $[NH_4]_3[CrMo_6O_{24}].10H_2O$ and $K_2[CrV_6O_{19}].12H_2O$ [5], have been prepared. Crystallographic and IR studies have been carried out on the hydroxychromates $M^IM_3^{III}(OH)_6[CrO_4]_2$ (where M^I = Na, K, or NH_4; M^{III} = Fe, Al) [6], and thermogravimetric and ^1H NMR spectral studies [7] indicate that one hydroxyl group is present in $4ZnO.4CrO_3.K_2O.3H_2O$. The heats of solution of $K_2[Cr_2O_7]$ in water, aqueous nitric acid or sodium hydroxide have been measured at 25 °C [8]; from these data, the heats of formation of $[HCrO_4]^-$, $[CrO_4]^{2-}$, and $K_2[Cr_2O_7](s)$ were found to be -879.5, -881.7 and -2061.9 kJ mol^{-1}, respectively.

Ammonium salts efficiently catalyse the oxidation of alcohols to carbonyl compounds by CrO_3 in organic solvents at room temperature [9], and *t*-butylchromate can be safely and rapidly synthesised by the addition of aqueous CrO_3 to *t*-butanol, followed by extraction of the ester with carbon tetrachloride [10].

Resonance Raman (RR) spectra have been obtained for the short-lived blue intermediate formed by the Cr(VI)-H_2O_2 reaction in strongly acidic solutions [11]. Several excitation wavelengths were used and the spectra showed a number of bands which could be assigned to the different ν(Cr-O) modes and the ν(O-O) mode within $CrO_5.H_2O$. The RR band intensity profiles indicate that the resonance effect is associated with the absorption band at 590 nm, which is ascribed to an O→Cr(VI) charge transfer transition. The instability of the blue intermediate is reflected in the low ν(Cr-O) and high ν(O-O) values.

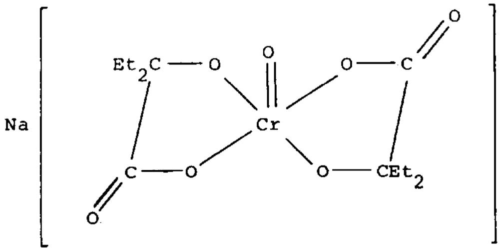
From thermodynamic considerations, the amount of Cr(VI) in sea water is expected to be more than 10^9 times greater than that of Cr(III), however, appreciable amounts of Cr(III) can be found in sea water even under oxidative conditions. This discrepancy could be due to the reduction of Cr(VI) by organic substances, or to the lack of specificity in the analytical procedures. A useful development in this respect is the co-precipitation of Cr(III) with the Co(II) complex of 1-pyrrolidinecarbodithioate, which allows [12] the selective analysis of Cr(VI) in artificial sea water in the presence of Cr(III).

The three equilibrium phases in the non-condensed system $CaO/Cr_2O_3/O_2$ - the ternary compound, thought to have the chromate chromite formula $Ca_9(Cr_4^{VI}Cr_2^{III})O_{24}$, calcium chromate and monocalcium chromite - have been investigated by solid state IR, diffuse reflectance, and EPR spectra [13]. Comparisons of the spectra of the different phases strongly suggest that Cr^{III} is not present in the ternary compound but that the tetraoxoanion $[Cr^VO_4]^{3-}$ is.

Hence, the solid ternary phase is best described as tricalcium orthochromate $Ca_3(Cr^VO_4)_2$, rather than $Ca_9(Cr_4{}^{VI}Cr_2{}^{III})O_{24}$. The latter represents the composition when the ternary phase is dissolved in acid, where Cr(V) disproportionates into Cr(VI) and Cr(III).

The XPES of powdered Cr_2O_5 has been compared with the corresponding spectra of related chromium compounds and it appears [14] that this compound is a mixed-valence compound containing Cr(III) and Cr(VI) in the ratio 1:2, as in KCr_3O_8.

The composition and structures of five types of Cr(V) complex, formed in non aqueous solution in the presence of oxalic acid, have been investigated by EPR spectroscopy [15]. The complexes were obtained by reduction of Cr(VI), or substitution of $Na_3[CrO_4]$ and [Hpy][$CrOCl_4$], by oxalic acid and/or organic solvent. The complexation of Cr(V) with several diketones has been studied [16] in a similar manner. The oxidation of alcohols by [H_2phen][$CrOCl_5$] and [(phen)$CrOCl_3$] [17], and of hydrazine by one of the new water-soluble and air-stable chromium(V) complexes [18], sodium bis(2-ethyl-2-hydroxobutyrato)oxochromate(V) (*1*), have been investigated [19].



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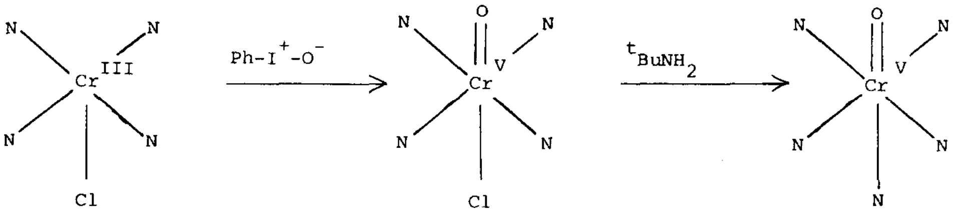
Reduction of [H_2bipy][$CrOCl_5$] takes place slowly in organic solvents, but, in general, the products have not been characterised; the reaction with ethanenitrile produces [$CrCl_3$(bipy)(NCMe)], which can be obtained similarly from [$CrOCl_3$(bipy)]. The nitrile ligand in [$CrCl_3$(bipy)(NCMe)] is readily replaced to give [$CrCl_3$(bipy)L] (where L = py, pyO or Ph_3PO). Reactions of [H_2bipy][$CrOCl_5$] with higher nitriles or with nitromethane all lead to the isolation of the known complex $[CrCl_3(bipy)]_n$ [20]. The heat capacity and other thermodynamic properties of $Cs_3[CrO_4]$ have been determined [21].

Further work on the chromyl(V) complex of 2,3,17,18-tetramethyl-7,8,12,13-tetraethylcorrole (H_3MEC) has been reported. Its redox chemistry and that of the tetraphenylporphin complexes [Cr(TPP)(OMe)] and [Cr(TPP)Cl] have been investigated by cyclic voltammetry and controlled-potential electrolysis. The compound [Cr(O)(MEC)] undergoes metal reduction more readily than the corresponding molybdenum compound. This has been attributed to extensive interaction between the chromium d_{xy} and ligand orbitals which tends to reduce the *d*-electron density at the metal and to raise the d_{xy} level. For [Cr(TPP)(OMe)], reduction first occurs at the heterocyclic ligand, but for [Cr(TPP)Cl] at the metal. The less easy reduction at the metal for the former was attributed to the covalent character of the Cr-OMe bond [22].

The oxidation of chlorotetraphenylporphinatochromium(III) with iodosylbenzene was reported previously [23] to produce (Cr^V=O)(TPP), by oxygen transfer to the metal and two electron oxidation of the chromium. However, EPR investigations have shown [24] that the oxidation occurs via an unstable paramagnetic species (*2*) which contains oxochromium(V), (d^1). The EPR spectra of the ^{17}O derivative and the *t*-butylamine adduct (*3*) also indicate the



(2) (3)

presence of chromium(V) and, therefore, oxidation of the metal; oxidation of the ligand occurs in analogous iron(III) complexes. The replacement of Cl in (*2*) by OH^- and F^- was also monitored by EPR spectroscopy. On standing at room temperature, (*2*) decomposed to a red diamagnetic oxochromium(IV) complex which is also produced via a μ-oxochromium(III) intermediate from Cr^{II}(TPP) by reaction with dioxygen [25]. The structure of [CrO(TPP)] is similar to those of other five co-ordinate oxometalloporphyrin complexes, with the metal atom ∿0.5 Å out of the porphyrin plane towards the oxygen atom. The chromium(II) complex was prepared by zinc amalgam or $Cr(acac)_2$ reduction of [CrCl(TPP)], and its oxidation monitored spectrophotometrically.

4.2 CHROMIUM(III)

4.2.1 Complexes of simple ligands

The hexafluorochromates $M_3[CrF_6]$ (where M is NH_4, Na, K, or Rb) have been prepared in high yield by a new and convenient method - the reduction of an aqueous solution of CrO_3 with hydrazine hydrate in the presence of an excess of equimolar amounts of MOH and 40% HF. The lithium complex $Li_3[CrF_6].H_2O$ was prepared from Li_2CO_3. The excess of HF presumably prevents the formation of hydroxo or hydrated chromium(III) species. The complexes are stable in water and the room temperature magnetic moments are typical of octahedral chromium(III) complexes. Bands in the IR spectra at *ca.* 535 and 524 cm^{-1} have been assigned to ν(Cr-F) vibrations [26].

Spin density data for $K_2Na[CrF_6]$ have been re-analysed [27] and the magnetic properties of $NaMn[CrF_6]$ investigated [28]. Of the complex fluorides, $M^{II}M^{III}F_5.7H_2O$ (where M^{II} = Mn, Fe, Co or Ni, and M^{III} = Cr, V, Mn or Fe) those containing Cr(III) have the highest decomposition temperatures [29].

There are *trans*-$[CrCl_2(OH_2)_4]^+$ ions in the complex chloride $Cs_2CrCl_5.4H_2O$; the Cr-Cl and Cr-O bond lengths are 2.302 and 1.925 Å, respectively, and there is extensive hydrogen bonding in the crystal. The polarised crystal spectra have been assigned [30]. Detailed optical absorption and Zeeman effect measurements have been made [31] on the exchange coupled chromium ions in $Cs_2[Cr_2Cl_9]$.

Some evidence has been obtained for the electrochemical fixation of dinitrogen to ammonia and hydrazine on a *p*-type gallium phosphide photocathode in non-aqueous electrolytes containing chlorides such as $CrCl_3$, and a trace of water [32].

X-ray structure determinations have been carried out on a series of caesium alums and in $CsCr(SO_4)_2.12H_2O$ the Cr-O distance is 1.959 Å [33]. In $Cr(OH)SO_4.H_2O$, each Cr atom is bonded to 2 OH groups, 3 oxygen atoms of SO_4 groups, and one water molecule, and infinite Cr-OH-Cr chains connected by SO_4 groups form a three dimensional network [34]. The structure [35] of $Cr_4H_2(SO_4)_7.24H_2O$ contains two independent Cr octahedra; in one, six water molecules are coordinated but, in the other, one water molecule is substituted by a sulphate oxygen atom.

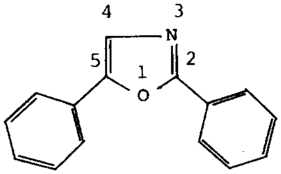
The enthalpies of solution of $[NH_4]Cr(SO_4)_2.12H_2O$, in aqueous perchloric acid, have been determined by direct calorimetry at 25 °C, and the thermodynamic constants for hydration of Cr^{3+} have been calculated [36]. Further crystalline modifications of $CrPO_4.6H_2O$ have been obtained [37] by precipitation from cold water, and $TlCr(CO_3)_2$ and $Tl_3Cr(CO_3)_3$ have been prepared from molten Tl_2CO_3 under pressure [38].

Further details have been given [39] of the electrochemical synthesis of $[Cr(dmso)_6][BF_4]_3$, $[Cr(NCCH_3)_6][BF_4]_2$, and $[Cr(NCCH_3)_4][BF_4]_2$ by the use of the metal as a sacrificial anode in dmso-HBF_4 and CH_3CN-HBF_4 solutions. The last complex is new and possibly contains bridging $[BF_4]^-$ anions as the IR spectrum shows significant distortion from T_d symmetry. The salts $[Cr(dmso)_6]X_3$ (X = Br, I [40] or $[ClO_4]$ [41]) and the dihexylsulphoxide (dhso) complex $Cr(NO_3)_3.3dhso$ have been prepared [42], as have $[Cr(NH_3)_5L]^{3+}$, *trans*-$[Cr(NH_3)_4LCl]^{2+}$ and *trans*-$[Cr(NH_3)_4L_2]^{3+}$ (where L = dmf or dmso) [43]. Some thiosulphate [44] and hydroxymethylthiosulphate [45] salts of $[Cr(ur)_6]^{3+}$ have been prepared, and a crystal structure investigation [46] shows that in $[Cr(urea)_6]Cl_3.3H_2O$ the ligand molecules are *O*-bonded. The *N*-oxide complexes $[Cr(LH)_2(C_2H_5OH)_2(OClO_3)_2](ClO_4)$ (where LH is purine N(1)-oxide [47] or adenine N(1)-oxide [48]) have been isolated.

The trirutile compounds MCr_2O_6 (where M = Te or W) exhibit a complicated variation of magnetic susceptibility in the temperature range 4.2-350 K. The magnetic behaviour can be explained at the higher temperatures in terms of magnetic interaction in quasi-isolated binuclear units $(Cr_2O_{10})^{14-}$ {J = -33.2° (M = Te) and -44.5° (M = W)}. The Cr-Cr distance is smaller (2.936 Å) in the W compound than in the Te compound (2.984 Å) and the latter manifests the weaker interaction. At lower temperatures, coupling between the binuclear units becomes important and is ferromagnetic for W and antiferromagnetic for Te; the intercluster exchange parameters are 1.4° and -4.5°, respectively. Mössbauer spectra of samples doped with ^{57}Fe confirm the existence of the long range order shown by neutron diffraction at 4.2 K [49].

Few structures of complexes of the type $[CrL_4F_2]X$ are known. The Cr-F bond distance in *trans*-$[Cr(NH_3)_4F_2]I.H_2O$ is 1.894 Å and in *cis*-$[Cr(NH_3)_4F_2]ClO_4$ is 1.887 Å. The Cr-N bonds *trans* to fluorine in the latter compound are significantly shorter than those which are *cis* (2.051 versus 2.062 Å), but the difference is too small to be indicative of a structural *trans* effect. The ν(Cr-F) absorptions are at 505 cm^{-1} (*trans*) and 515 and 490 cm^{-1} (*cis*) [50].

Some amine complexes containing dodecahydrodicarbaundecaborate(1-) anions, $[Cr(NH_2R)_5X](C_2B_9H_{12})_2$ (where R = Me, X = Br or Cl; R = Et, X = Cl) have been prepared and their thermolysis investigated [51]. The methylpyridine complex, $CrCl_3(4\text{-mepy})_3.0.5$ 4-mepy, is isomorphous with the corresponding molybdenum(III) compound which has the *trans* stereochemistry [52]. Chromium(III) forms a thermally stable, probably monoazido-complex, on the addition of potassium azide to a chromium(III) salt in molten KCNS [53]. Complexes of 2,5-diphenyloxazole {L, (*4*)} of the general formula $[CrL_nX_3].mH_2O$ (where X = Cl, Br, I or NO_3; n = 1-3, m = 0-6) are hexacoordinate, generally with monodentate *N*-bonded ligand [54]. The reduction of $[H_2bipy][CrOCl_5]$ has been used [20] in the preparation of the mixed ligand complexes $[CrCl_3(bipy)L]$ (where L = MeCN, py, pyO, or Ph_3PO).



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Several investigations of cyano-complexes have been reported. Earlier methods for the preparation of cyano-hydroxo- and aqua-cyano-chromate(III) complexes have been based on the aquation of the $[Cr(CN)_6]^{3-}$ ion, and have given poor yields. The hydroxo-complex $K_3[Cr(CN)_5(OH)].H_2O$ has now been obtained crystalline in good yield by the reaction of $[CrCl(NH_3)_5]Cl_2$ with KCN, followed by separation on a Sephadex gel column [55]. The IR and Raman spectra of $[(NMe_4)_2(M)][Cr(CN)_6]$ (M = Rb or Cs) have been determined [56], and a non-cubic modification of water-free $Zn_3[Cr(CN)_6]_2$ has been prepared [57]; the structure of $Cd_3[Cr(CN)_6]_2.14H_2O$ has been investigated [58] and a neutron diffraction study of $K_3[Cr(CN)_6]$ at 4.2 K has been carried out [59]. The loss of 1.5 HCN molecules accompanies the thermal dehydration of $[Co(NH_3)_5(OH_2)][Cr(CN)_6]$ [60]. The thermal decomposition of a series of chromium(III) compounds $[Cr(NH_3)_6]X_3$, $[CrX(NH_3)_5]Z_2$, and *trans*-$[CrX_2(NH_3)_4]Z$ (where X and Z are Cl and/or Br) has been investigated under quasi-isothermal and -isobaric conditions (Q-conditions) and under dynamic conditions (D-conditions) [61]. The complexes were finally converted into new *mer*-triamminetrihalo-complexes, containing mixed halides in Q-conditions, but decomposed in complicated ways under D-conditions.

Dinuclear complexes of the formula $[(aa)_2FCrNCM(CN)_3]$ (where *aa* = en or 1,3-pn, and M = Ni, Pd or Pt) result on heating *trans*-$[CrF(OH_2)(aa)_2][M(CN)_4]$ [62].

The XPES spectra of a number of cyanide and 1,2-diaminoethane complexes, including $K_3[Cr(CN)_6]$ and $[Cr(en)_3]Cl_3$, have been measured in order to obtain the difference ΔE between the N 1*s* and C 1*s* binding energies [63]. For the complexes of 1,2-diaminoethane, the ΔE values are related to σ-donation; for the cyanide complexes, they are controlled mainly by the nitrogen charge which depends on the π-back-donation. MO calculations of the DV-Xα type applied to $[M(CN)_6]^{3-}$ ions (where M = Cr, Mn, Fe or Co) give good correlation with the XPES results [63,64].

S-trityl-*L*-cysteine (HL) is only *N*-bonded in $[Cr(HL)_3Cl_3]$ [65]. The apparent molal volumes, viscosity coefficients, and conductivities in water at

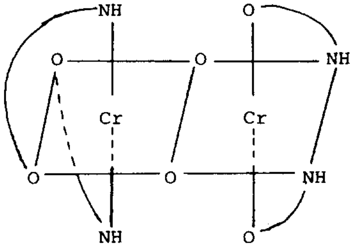
25 °C of $[CrL_6]X_3$ (where L = NH_3, H_2O, urea; L_2 = en, $CH_2(CH_2NH_2)_2$, tn, or biguanide; X = Cl or NO_3) have been determined [66]. The Reinekate anion $[Cr(NH_3)_2(NCS)_4]^-$ has been used to obtain crystals suitable for single crystal X-ray investigations of a binuclear tungsten cation containing a bridging formazanido(3-) ligand [67].

4.2.2 Hydroxo-bridged complexes

Hydrolysis and polymerisation produce mixtures of various species in aqueous solutions of metal ions. With inert ions such as Cr(III) interconversions are sufficiently slow for identification of many species to be possible, and, in addition to the known doubly bridged chromium(III) dimer $[(H_2O)_4Cr(OH)_2Cr(OH_2)_4]^{4+}$, the singly bridged dimer $[(H_2O)_5Cr(OH)Cr(OH_2)_5]^{5+}$ [68] and a green trimeric species [69] have been identified. Solutions containing the doubly bridged dimer were separated by ion exchange techniques, making use of displacement elution, from aqueous solutions prepared by aerial oxidation of chromium(II) perchlorate, or reflux of aqueous chromium(III) nitrate. The singly bridged dimer was obtained by repeated evaporation of perchloric acid solutions of the doubly bridged dimer. The formula of the singly bridged dimer was established through measurements of equilibria and freezing point depression and its antiferromagnetic behaviour shown similar to that of other hydroxo-bridged dimers. The green trimer contains the unit $[Cr_3(OH)_4]^{5+}$, but analysis of magnetic and EPR data did not distinguish between the possible linear or triangular hydroxo-bridged arrangements of the metal atoms.

The nature of the variation of the antiferromagnetic exchange parameter J with the Cr-O-Cr bridging angle Φ in μ-hydroxo-dimers remains uncertain through lack of magnetic and structural data. The value of J (obtained by fitting the magnetic susceptibility data to various models) for the new dimer *trans*-$[(H_2O)(NH_3)_4Cr(OH)Cr(NH_3)_5]Cl_5.3H_2O$ is approximately 35 cm^{-1}, and $\Phi = 155.1°$ [70], both values being similar to those reported for $[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$ ($J \sim 31$ cm^{-1}, $\Phi = 154\text{-}166°$) but larger than for *cis*-$[(HO)(NH_3)_4Cr(OH)Cr(NH_3)_5]^{4+}$ ($J \sim 21$ cm^{-1}, $\Phi = 142.8°$). It is believed that the increased value of the angle Φ is partly responsible for the stronger coupling compared with the *cis* dimer, although the position of the hydroxo-hydrogen may be important, as it is 0.5 Å above the plane of the bridge in the *cis* dimer. Magnetic data do not appear to be available for $[(HO)(en)_2Cr(OH)Cr(en)_2(OH)]^{3+}$, which has a much smaller bridging angle of 135.4°.

The reaction of hexaamminechromium(III) nitrate with *L*-proline in water produces a purple compound which was thought to be either *mer*-tris(prolinato)chromium(III) $[Cr(L\text{-}pro)_3].6H_2O$ {only *fac*-isomers of tris(aminoacidato)chromium(III) complexes which are pink to red are known} or a dimeric hydroxo-compound $[Cr(L\text{-}pro)_2(OH)]_2.4H_2O$. Although the purple compound is soluble in MeOH or dmso, unlike other di-μ-hydroxochromium(III) dimers, the electronic absorption spectrum did not support the *mer* structure. Crystal structure analysis has shown [71] that it is the di-μ-hydroxo compound, with the N atoms of the amino acid *trans* in one octahedral unit and *cis* in the other giving a Δ-trans(*N*), Δ-trans(*O*) isomer (*5*). From considerations of



(5)

steric hindrance between prolinato-ligands and intramolecular hydrogen bonding, this appears to be the most stable of the many possible isomers. The metal-metal separation (2.983 Å) and the geometry of the bridging unit are similar to those in $[Cr(gly)_2(OH)]_2$ and other di-μ-hydroxo-compounds.

The IR spectrum of $[CrL_2(OH_2)(OH)]_2$ (where HL = salicylic acid) shows that some salicylate groups are monodentate and others chelating [72]. The structure of di-μ-hydroxobis[bis{(*S*)-1-(2-pyridyl)ethylamine}chromium(III)] dithionite dihydrate and the absolute configuration of the cation have been determined [73]. The molecules in di-μ-hydroxo-bis{bis[(*S*)-alaninato]chromium(III)} trihydrate contain octahedrally coordinated Cr atoms in which there is a *cis-cis-cis* arrangement of two hydroxo *O* atoms, and two *O* and two *N* atoms of alanine [74]. The burgundy coloured crystals were hand picked from the solid {also containing pink crystals of $[Cr(S\text{-}Ala)_3]$} which separated from the aqueous reaction mixture containing (*S*)-alanine and $[Cr(NH_3)_6][NO_3]_3$. The $Cr_2(OH)_2$ bridging unit shows the same features as in the corresponding glycine compound, and the Cr-OH-Cr angles are 97.6° and 99.4°.

The dimer $[Cr(EDDA)(OH)]_2.4H_2O$ [75] (where $EDDAH_2$ is *N*,*N'*-ethylenediaminediacetic acid) has now [76] been prepared by a new synthetic route from [Cr(EDDA)(acac)].$2H_2O$ [77] and its magnetic susceptibility determined in the range 3.0 to 79 K. The data have been fitted by the Van Vleck equation for pairs of exchange coupled $S={}^3/_2$ ions, including a biquadratic term to yield the parameters $J = -9.3\ cm^{-1}$, $j = -0.2\ cm^{-1}$ and $g = 1.96$. This complex has the smallest ratio of Φ (angle at bridging oxygen atom) to r (the chromium-bridging oxygen distance) of the di-μ-hydroxo-bridged chromium(III) complexes of known structure and analysis [76,78] of the available data shows that the singlet-triplet separation reaches a maximum when Φ/r is about 50°/Å. The dependence of the magnetic properties of the known di-μ-hydroxo-bridged complexes on Φ and r, and the Cr-Cr separation, has been discussed in some detail [78]. The data for some alkoxo-bridged complexes, including $[Cr(3\text{-}Cl\text{-}acac)_2(OMe)]_2$, suggest that increased electron density on the bridging oxygen enhances the exchange coupling.

Some further hydroxo-complexes are referred to in Sections 4.2.3, 4.2.4 and 4.2.5.

4.2.3 Complexes of bidentate ligands

The thermal, magnetic and spectral properties of $[Cr_3O(O_2CCH_3)_6(OH_2)_3]Cl.6H_2O$ have been re-examined in terms of a model which includes spin exchange between equilateral triangular clusters, as well as the intramolecular exchange [79]. Two inequivalent pairs of trimer sites with different inter-cluster exchange parameters are required to obtain agreement between experimental and theoretical heat capacities, magnetic susceptibilities, and optical spectral data. Intercluster spin exchange is associated with the hydrogen bonding between the trimers.

Soluble alkoxy soaps of chromium(III), with the general formulae $Cr(OR)_2(O_2CR')$, $Cr(OR)(O_2CR')_2$, and $Cr(O_2CR')_3$ (where R = Me or Et, $R' = C_7H_{15}$, $C_{13}H_{27}$, $C_{15}H_{31}$ or $C_{21}H_{43}$) have been prepared by the reaction of $Cr(OR)_3$ in benzene with stoicheiometric amounts of the fatty acids [80]. Molecular weight determinations showed that the three types of compound are polymeric, dimeric, and monomeric, respectively. The solid state electronic spectra are typical of chromium(III) complexes. Thermogravimetry of the product of metathetical reaction of sodium stearate and a chromium(III) salt has indicated that the product is not a chromium(III) tristearate, but a mixture of stearic acid (HX), $[CrX_2(OH)]$, and $[CrX(OH)_2]$ [81]. The acid impurity can be removed with ethanol. Stepwise formation constants, $\log K_1 = 2.7$ and $\log K_2 = 1.1$, have been reported [82] for the Cr(III)-propionic acid system.

A number of benzene seleninato-*O*,*O'* complexes, $[Cr(O_2SeC_6H_4X)_3]$ (where X = H, 4-Cl, 3-Cl, 4-Br, 3-Br, or 4-Me) have been carefully characterised [83]. The pyrophosphato-complex $[Cr(OH_2)_4HP_2O_7].3H_2O$ has been separated by ion exchange from various substances, including other polyphosphate complexes in a mixture of $Na_4P_2O_7$ and $[Cr(OH_2)_4Cl_2]Cl$, and crystallised [84]. An X-ray structure determination has shown that it contains bidentate pyrophosphate ligand with the six membered chelate ring in a boat conformation. This, and the extensive hydrogen bonding, may be important in the binding of enzymes to this complex and to Cr(ATP).

When $CrCl_3$ is heated with methyl methylphenylphosphinate, MeOP(O)MePh chloromethane is eliminated and $[Cr(O_2PMePh)_3]$ formed [85]. This complex has a magnetic moment at room temperature slightly below the spin-only value and may be a triply bridged linear polymer. A similar reaction occurs between triethyl phosphonoformate $C_2H_5OP(O)C(O)OC_2H_5$ and $CrCl_3$, whence $[Cr(C_2H_5OPO_2C(O)OC_2H_5)_3]$ and chloroethane are produced [86]. This chromium(III) complex is also thought to be a polymer. From the corresponding reaction with chromium(IV) perchlorate, $[Cr(C_2H_5OPO_2C(O)OC_2H_5)_2(ClO_4)]$ is obtained [86], and triethylthiophosphate (L) forms $[CrL_2(OH_2)_2(OClO_3)_2][ClO_4]$, in which it is coordinated as the thiol isomer $[(C_2H_5O)_2P(O)(SC_2H_5)]$ [87].

Typical chromium(III) complexes have been obtained from 2-hydroxy-3-(3-methyl-2-butenyl)-1, 4-naphthoquinone [88], 1-(2-furyl)-1,3-butanedione, 4,4,4-trifluoro-1-(2-furyl)-1,3-butanedione [89], and 4,4,4-trifluoro-1-(3-pyridyl)-1, 3-butanedione [90]. Unlike other metal acetylacetonates, [Cr(acac)$_3$] does not react with cyanogen at ambient conditions in CH_2Cl_2 [91]. Decomposition of [Cr(hfacac)$_3$] (and of complexes of other metals with the hexafluoro β-diketonate) takes place by fluorine rearrangement to the metal, accompanied by elimination of CF_2 and, ultimately, CrF_3 [92]. Some HF is also lost and this reaction replaces the elimination of metal fluoride with $[Cr(CF_3COCHCOR)_3]$ (where R = Me, Et, ^{i}Pr, ^{t}Bu, Ph, or C_4H_3S). It is possible that softening of the metal environment, by substitution of one CF_3 by R, weakens its ability to compete with hydrogen for the fluorine. The bromination of [Cr(tfacac)$_3$], with Br_2 in $CHCl_3$ below 30 °C, has been found to produce a mixture, analysed by GC/MS, which contains [Cr(tfacac)$_2$L], [Cr(tfacac)L$_2$], and [CrL$_3$], where L is monobrominated tfacac, but the position of substitution was not conclusively determined [93]. The complex [Cr(ℓ-moac)$_3$], in which ℓ-moac is the anion of 1-ℓ-menthoxy-3-acetylacetone, has been synthesised, and found [94] from NMR, electronic absorption, and CD spectra to have the cis-Λ-configuration. The stereoselectivity is attributed to the inter-ligand hydrophobic interaction between the ℓ-menthyl and methyl groups.

The thermal decomposition of tris(*N*-benzoyl-*N*-phenylhydroxylaminato)-chromium(III) has been investigated using radiometric methods by labelling the complex with ^{51}Cr [95]. The thermal decomposition of some chromium oxalates and their hydrazine adducts has been studied [96].

There have been extensive studies of difluorochromium(III) complexes, like $[CrF_2(OH_2)_4]^+$ and $[CrF_2(N)_4]^+$, but no such complexes of dicarboxylates were known previously. *cis*- and *trans*-$[CrF_2(ox)_2]^{3-}$, *cis*- and *trans*-$[CrF_2(mal)_2]^{3-}$ (where mal is malonate), and *cis*-$[CrF_2(ox)(en)]^-$ and *trans*-$[CrF_2(mal)(en)]^-$, have now been isolated [97]. The complexes were characterised by their IR, electronic, and CD spectra, and their elution behaviour. The absorption spectra were analysed in terms of the angular overlap model.

Typical chromium(III) chelates have been obtained from *N*-methyl-, *N*-ethyl- [98a] and α-iodo-acetoacetanilides [98b], 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one [99], 4-benzoyloxime-3-methyl-1-phenyl-2-pyrazoline-5-one [100], and some triazolinethiones [101]. Complexes of the nitrogen-oxygen and nitrogen-sulphur donor ligands, phenylpyruvic acid semicarbazone and (4-methylphenyl)pyruvic acid, and phenylpyruvic acid thiosemicarbazone and (4-methylphenyl)pyruvic acid thiosemicarbazone, have the general composition [Cr(Ligand-H)$_2$] (X = Cl, Br, I, or NO_3) [102].

Compared with cobalt(III), few chromium(III) complexes of optically active amino acids are known, particularly of the type $[CrL(N)_4]^{2+}$. The complexes $[CrL(en)_2]^{2+}$ (HL = glycine, alanine or phenylalanine) have been prepared and resolved into their optical isomers [103]. From absorption and CD spectroscopic investigations, it has been found that $[CrL(en)_2]^{2+}$ (HL = *L*-alanine or *L*-phenylalanine) exist as two pairs of diastereomeric, not enantiomeric, isomers.

When aqueous or alcoholic solutions of chromium(III) chloride react with glycine in the presence of sodium or lithium ethoxides, the products are $[Cr_2(OH)_2(OH_2)_4(gly)_2]Cl_2.H_2O$, $[Cr_2(OH)_2(OH_2)_2(gly)_3]Cl.H_2O$, $[Cr_3O(gly)_6(OH_2)_3]Cl.2H_2O$, and $[Cr_3O(gly)_6(OH_2)_3]Cl.3H_2O$ [104]. These compounds exhibit antiferromagnetic behaviour.

In order to determine the nature of the products of reaction between chromium(III) and α- and β-alanine, the emission spectra of chromium(III)-alanine complexes have been compared with those of the chromium(III) *fac*- and *mer*-tris(glycinato) complexes [105]. Only the binuclear complex $[(ala)_2Cr(OH)_2Cr(ala)_2].nH_2O$ and the monodentate *N*-bonded complexes were formed with α-alanine; with β-alanine monodentate *N*-bonded complexes were the only products. The complexes Na[Cr(*L*-cys)$_2$].$2H_2O$ and [Cr(*DL*-met)$_3$].$2H_2O$ have been reported [106].

A determination of the crystal and molecular structure of the tris(pentamethylenedithiocarbamato)chromium(III) 1:2 chloroform adduct has shown that the CrS_6 coordination octahedron is trigonally distorted, and channels within the structure contain $CHCl_3$ molecules hydrogen-bonded to the sulphur atoms [107]. The spectroscopic and magnetic properties of this and several related complexes have been reported [108]. Investigations of the complexes of the thiosemicarbazide (HL) complexes, $[Cr(HL)_3]Cl_3.3H_2O$ and CrL_3, suggest that the ligand bonds through the sulphur and hydrazine nitrogen atoms and that the complexes are the *cis* isomers [109].

The anhydrous complexes of mixed amines, $[Cr(en)_2L]Br_3$ [where L = 1, 2-pn, 1,3-pn, 2-methyl-1,2-propanediamine(I), or *trans*-1,2-cyclohexanediamine(II)] and $[CrLL'_2]Br_3$ (where L = I and L' = 1,2-pn, or 1,3-pn; L = II and L' = 1,2-pn) have been prepared by substitution reactions of *cis*-dichlorobis(diamine)chromium(1+) or tris(diamine)chromium(3+) complexes [110]. There are several advantages in the use of the *cis* complexes as reactant: the solvent is eliminated, anhydrous reagents are not required, reaction times are shorter, and there are improved yields in some cases. The tris(diamine)chromium(III) reagent is useful when the dichloro-complex is difficult to obtain.

The CD spectra of the series of complexes $[Cr(en)_{3-x}(1,3\text{-pn})_x]^{3+}$ (x = 0 to 3) have been measured over the range 500-1000 nm [111]. The optical activity associated with the quartet-doublet chromium(III) transitions may be assigned within an effective D_3 symmetry, irrespective of the actual symmetry of the chromophore. Measurements of the axial single crystal CD spectra of $[(+)_D\text{-}Cr(en)_3]^{3+}$ doped in $2[Ir(en)_3]Cl_3.KCl.6H_2O$ have been carried out under high resolution between 7 and 293 K, and transitions to the excited states $^4T_2$, $^4T_1$, ^2E, $^2T_1$ and $^2T_1$ have been observed [112].

The thermal behaviour of $(+)_{589}\text{-}[Cr(en)_3]Cl_3.2H_2O$, $(+)_{589}\text{-}Cr[(en)_3]Cl_3.1{\cdot}7H_2O$, and $(\pm)\text{-}[Cr(en)_3]Cl_3.3H_2O$ [113] has been investigated and differences related to the crystal structures.

The reaction of *trans*-$[Cr(1,3\text{-pn})_2FBr][ClO_4].0{\cdot}5H_2O$ with liquid ammonia produces only *trans*-$[Cr(1,3\text{-pn})_2F(NH_3)]Br[ClO_4]$, which, on recrystallisation from perchloric acid, gives the diperchlorate [114]. The ammination of *trans*-$[Cr(en)_2FBr]^+$ is known to produce a 60/40 ratio of *cis*- and *trans*-$Cr(en)_2F(NH_3)]^+$, but complexes of 1,3-pn generally are more resistant to stereochemical change than corresponding en complexes. Reaction of *trans*-$[Cr(1,3\text{-pn})_2F(NH_3)]^+$ with more liquid ammonia resulted in little additional ammination, but, in concentrated HBr, the fluoro-ligand was replaced by water.

Mixed ligand complexes of the imides, malonimide, glutarimide and phthalimide, and bipy and phen, have been prepared and characterised [115], as have the complexes $[CrL_2Q]Cl.1{\cdot}5H_2O$ and $[CrLL'(H_2NCSNH_2)_2]Cl_2$, in which L is the anion of 2-(2-pyridyl)benzimidazole, Q is biguanide, and L' is bipy or phen [116]. Similar mixed chelates containing dipicolinic acid have also been isolated [117].

The observation of optical activity in a racemic mixture of a labile complex on addition of a chiral compound (environment substance) is the Pfeiffer effect. Until recently, only chiral organic compounds have been used, for example, the chiral equilibrium of $[Cr(ox)_2(phen)]^-$ is greatly displaced towards its $(+)_{546}$- or $(-)_{546}$-enantiomers on the addition of *ℓ*-(8*S*,9*R*)-quinine or *d*-(8*R*,9*S*)-quinidine hydrochloride, respectively [118]. The Pfeiffer effect of $[Cr(ox)_3]^{3-}$ has been examined [119] using optically stable complexes of the type *cis*-$[M(diamine)_2XY]^{n+}$ (where M = Cr^{3+} or Co^{3+}, diamine = en or 1,3-pn, and X and Y = anionic monodentate ligand). It was found that the chiral equilibrium of $[Cr(ox)_3]^{3-}$ was always displaced in favour of its Δ enantiomers in the presence of Λ enantiomers of those complexes added as an environment substance. It seems that Λ-*cis*-$[M(diamine)_2XY]^{n+}$ complexes associate preferably with Δ-$[Cr(ox)_3]^{3-}$, its inversion rate being retarded relative to that of its antipode. It is proposed that the absolute configuration of *cis*-$[M(en\ or\ 1,3\text{-}pn)_2XY]^{n+}$ and related complexes can be inferred from the equilibrium shift induced in racemic $[Cr(ox)_3]^{3-}$. Resolved $[Cr(en)_3]^{3+}$ has been used to induce optical activity in a terbium complex [120].

4.2.4 *Photochemistry*

The hydridopentaaquachromium(III) ion $[(H_2O)_5CrH]^{2+}$, previously prepared by pulse radiolysis [121], has now been prepared by UV flash photolysis of chromium(II) perchlorate in dilute perchloric acid [122]. This ion has a short lifetime, owing to a rapid reaction with H_3O^+ to evolve hydrogen. It might be considered related to the general family of alkylchromium(III) cations $[(H_2O)_5CrR]^{2+}$ but it is much more reactive.

The photoaquation of *trans*- and *cis*-$[Cr(NH_3)_4F_2]^+$ in acidic aqueous medium at 22 °C produces efficient ammonia aquation (ϕ = 0.36 and 0.45, respectively) for irradiation in the lowest quartet state, with minor yields of fluoride [123] and there was little wavelength dependence. The observed products from the *trans* complex were the 1,6-difluoro-2-aquatriamminechromium(III) and 1,2-difluoro-6-aquatriamminechromium(III) ions in the ratio 1:2.5. The *cis* compound yielded these products in a 1:1.5 ratio, together with small, wavelength dependent amounts of the 1,2-difluoro-3-aquatriamminechromium(III) ion. The stereochemistry of photolysis of the *trans* complex is consistent with both the edge displacement model and the Vanquickenborne-Ceulemans (VC) theory. The results for the *cis* complex do not fit the former model but can be accommodated by the latter.

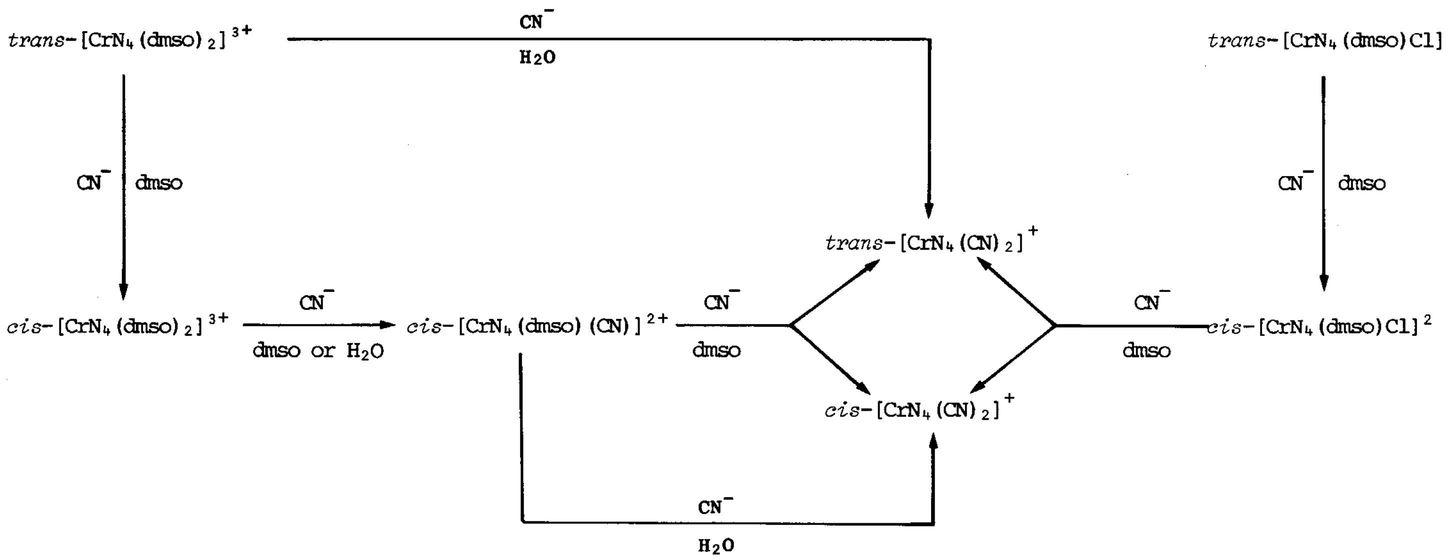
The VC model has now been extended to the photolabilisation of complexes of D_{2h} symmetry [124]; previously the complexes considered were of real or effective D_{4h} symmetry. It has been shown that the leaving ligand is the one characterised by the smallest value of the bond index I*(ML) [125], and this is compatible with the almost exclusive photodissociation of en from *cis*-$[Cr(en)_2(NCS)Cl]^+$.

Photoaquation reactions of $[Cr(NH_3)_5X]^{2+}$ (where X = Cl, Br, or NCS), $[Cr(NH_3)_6]^{3+}$ [126], $[Cr(NCS)_6]^{3-}$, and $[Cr(CN)_6]^{3-}$ [127] in aqueous solution have been studied as a function of pressure up to 1500 bar.

Upon ligand field irradiation in acidic solution, the *trans*-$[Cr(NH_3)_4(dmf)Cl]^{2+}$ cation undergoes simultaneous loss of dmf, Cl^-, and NH_3 [128]. Photosolvation of dmf predominates at all excitation energies, and from the wavelength dependence of quantum yields, it is inferred that the lower lying ^4E state and the upper $^4B_2$ state are the main precursors to aquation of the axial ligands and of NH_3 respectively.

The question of doublet versus quartet reactivity in the photoanation of $[Cr(NH_3)_6]^{3+}$ by Cl^- and Br^- [129], and in the photochemistry of $[Cr(en)_3]^{3+}$ [130], has been considered. A series of Cr(III)-alkylamine complexes with CrN_6 skeletons have been synthesised in order to study the role of hydrogen vibrations in the radiationless deactivation of the complexes in their lowest doublet state [131]. The complexes have similar electronic properties but from 8 to 18 N-H bonds. Measurements of absorption spectra, relative phosphorescence quantum yields, and phosphorescence decay times at liquid nitrogen temperature showed a good correlation between radiationless transition rate and the number of active hydrogen atoms attached to the donor atoms.

A procedure that is proving useful in the synthesis of cyano-complexes, is cyanide anation in dmso, since cyanide ion displaces coordinated dmso cleanly but deprotonates rather than displaces coordinated water. The preparation [132] of *trans*- and *cis*-$[Cr(NH_3)_4(CN)_2]^+$ perchlorates starts from the recently characterised complexes [43] *trans*- and *cis*-$[Cr(NH_3)_4(dmso)_2]^{3+}$, although *trans*- or *cis*-$[Cr(NH_3)_4(dmso)Cl]^{2+}$ can also be used (Scheme I). The insolubility of the perchlorate of *trans*-$[Cr(NH_3)_4(CN)_2]^+$ permitted its isolation from solution, but it was necessary to separate the *cis*- isomer by ion exchange. Rapid *trans*-to-*cis* isomerisation of *trans*-$[Cr(NH_3)_4(dmso)_2]^{3+}$ occurs on the addition of CN^-, before anation produces the dicyano-complexes



SCHEME I: Syntheses of cyano complexes; N=NH_3 [132].

in a stepwise manner, both apparently *via* *cis*-$[Cr(NH_3)_4(dmso)(CN)]^{2+}$ which, in an uncommon rearrangement, gives a mixture of *trans*- and *cis*-dicyano-complexes. The *cis*-monocyano-intermediate was isolated as the perchlorate salt. Cyanochloro-complexes could not be obtained by anation of $[Cr(NH_3)_4(dmso)Cl]^{2+}$, rather a mixture of the dicyano-isomers was obtained. Substitution of dmso by CN^- in water is stereoretentive. The $^2E_g \rightarrow {}^4A_{2g}(O_h)$ transitions have been identified in the luminescence spectra of the dicyano-isomers. As with related complexes, the IR spectra are not good criteria of geometry, since the *trans* complex shows a small splitting of the weak C-N stretching absorption, and the *cis* isomer does not. These isomers are inert in neutral or alkaline conditions at room temperature, but readily aquate stepwise in acid with retention of configuration. The cyanoaqua- and cyanohydroxo-complexes were characterised in solution.

There is little difference in the electronic absorption spectra of *cis*- and *trans*-$[Cr(NH_3)_4(CN)_2]^{2+}$, although the lowest energy band of the latter is slightly the less intense and less asymmetric. The splittings of the O_h levels in these complexes are the reverse of those found generally for other complexes $[Cr(NH_3)_4X_2]^{n+}$, because CN^- has a stronger field than other acido-ligands. This leads [133] to atypical photolabilisation patterns with *trans*-$[Cr(NH_3)_4(CN)_2]^+$, as compared with the other diacido-complexes. Photolysis in acidic aqueous solution at 10 °C results in NH_3 aquation ($\phi = 0.24$) as expected, with no release of CN^-, although the dark reaction is exclusively loss of CN^-. The results corroborate those obtained [134] with $[Cr(NH_3)_5CN]^{2+}$.

Photochemical substitution (ligand field irradiation) in $[Cr(NH_3)_6]^{3+}$, $[Cr(NH_2CH_3)_6]^{3+}$, and $[Cr(en)_3]^{3+}$ has been studied in acid solution [135]. In perchloric acid, photoaquation takes place, but when the solution contains a ligand capable of forming a stronger bond with Cr^{3+} than water, *e.g.* Cl^- from HCl, the amine is replaced by that ligand.

The 77 K excitation spectra of $[Cr(ox)_3]^{3-}$ in several crystal lattices have been reported [136]. The components of the $^2T_1$ and $^2T_2$ states can be located quite easily by this technique, and there are advantages over absorption measurements. The quenching of triplet states of organic donors by $[Cr(acac)_3]$ and $[Cr(bzac)_3]$ in benzene solution has been studied [137]. The reaction of chromium(II) with glycine yields four products, *fac*- and *mer*-$[Cr(gly)_3]$, the dimeric species, di-μ-hydroxotetraglycinatedichromium(III), and a series of complexes involving singly and *N*-bonded glycinate ligands [138]. The $^2E \rightarrow {}^4A_2$ luminescence spectra were recorded from 4 K to room temperature. The emission spectra are much more indicative of the type of complex than the absorption spectra. The splitting of the ^2E term in *fac*-$[Cr(gly)_2]$ was dependent upon its degree of hydration which varied with the crystallisation conditions.

On ligand field excitation, Λ-$[Cr(en)_3]^{3+}$ in acidic aqueous solution produces the Λ-*cis*, Δ-*cis*, and *trans* isomers of $[Cr(en)_2(enH)(OH_2)]^{4+}$, with quantum yields 0.10, 0.03, and 0.24, respectively, independent of the wavelength of irradiation [139]. It has been deduced that there is reactivity only from the lowest quartet state, with back intersystem crossing from the lowest doublet state to the quartet accounting for delayed reaction.

Investigations of the oxidation of $[Cr(bipy)_3]^{2+}$ and similar metal chelates by various oxidants in aqueous sulphuric acid provide evidence that chemiluminescent reactions involving coordination compounds will prove to be common and may be important for electronic display devices and lasers. Among the new chemiluminescent reactions are the oxidation of $[Cr(bipy)_3]^{2+}$ by $[S_2O_8]^{2-}$, Tl^{3+} [140], Ce(IV) and $[Ru(bipy)_3]^{3+}$ [141]. The emission is from the ${}^2E_g$ state of $[Cr(bipy)_3]^{3+}$. The rates of quenching of this excited state by various cobalt(III) complexes have been investigated [142]. Quantum yields of photoaquation and the lifetimes of the ${}^2T_1/{}^2E$ excited states have been determined in aqueous solution of tris(amine) complexes of bipy and phen and various substituted derivatives [143]. The quantum yield of luminescence of $[Cr(bipy)_3]^{3+}$ in aqueous solution is lowered by the presence of D_2O, but the lifetime of the emitting ${}^2E$ state remains unchanged [144]. This is considered to arise from the variation of efficiency of intersystem crossing from ${}^4T_2$ with solvent composition. The rigidity of phen in $[Cr(phen)_3]^{3+}$ leads to little variation of lifetime with D_2O concentration. A number of new tris(amine) complexes of substituted phenanthroline ligands have been prepared during investigations of the reductive quenching of the ${}^2E$ state of $[Cr(amine)_3]^{3+}$ by Fe^{3+} [145]. The luminescence spectra of Cr^{III}(TPP) and other metalloporphyrins have been investigated [146].

Various products of the UV photolysis of solutions of chromium(III)azide complexes $[CrL(N_3)]^{2-}$ (where L = edta, nitrilotriacetate or *d*-valine-*N*,*N*-diacetate) have been separated by ion exchange chromatography, and identified as chromium(V) nitride complexes by their EPR, absorption, and CD spectra [147]. The reactions are of the type:

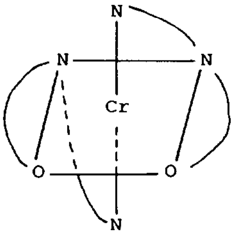
$$[LCr^{III}(N_3)(H_2O)]^- \xrightarrow{h\nu} [LCr^{V}N(H_2O)]^- + N_2$$

A detailed study of the ability of several metallophthalocyanines to photoreduce methylviologen using visible light in the presence of triethanolamine has been carried out [148]. Irradiation of the chromium(III) complex of tetra(octylsulphonamido)phthalocyanine ($ToPcH_2$) in the presence of cysteine produces the chromium(II) complex *in situ* which photoreduces the methylviologen.

4.2.5 *Complexes of polydentate ligands*

Comparisons of the visible and CD spectra in the spin-forbidden transitions of the new complex potassium (2*S*,4*S*)-2,4-pentanediaminetetraacetatochromate(III) monohydrate [149] with those of chromium(III) complexes of edta analogues show that the complex is formed stereospecifically with the Λ(ΛΔΛ) absolute configuration [150]. The stability constants of Cr^{3+} with iminodiacetic acid (log β_2 = 16.31) and nitrilotriacetic acid (log β_2 = 18.47) have been determined [151]. The structure of aqua(*N*,*N'*-ethylenediaminetriacetatoacetic acid)chromium(III) has been determined because it is unusually substitution-labile [152]. As in other reactive chromium(III) complexes, coordination around the metal atom is a distorted octahedron, and the distortion is likely to persist for the complex in solution. A number of mixed ligand complexes of the types $K[CrLL^1]$ or $K_2[CrLL_2{}^2]$ (where H_3L is nitrilotriacetic acid and HL^1 and HL^2 are amino acids such as histidine and nicotinic acid) have been characterised [153].

Octahedral bis complexes of tridentate *L*-histidine, in which the histidinato-ions coordinate facially, can assume the three isomeric forms (*6*, *7*, and *8*). The *trans*-imidazole and *trans*-carboxylate isomers of



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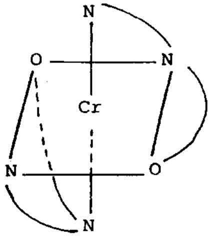

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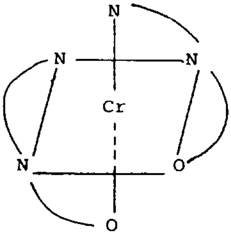

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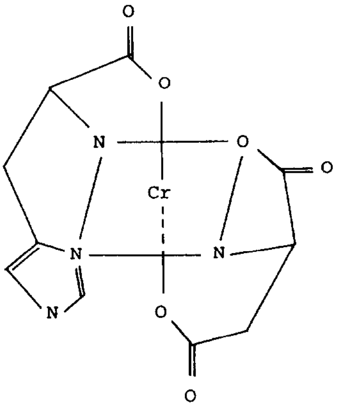
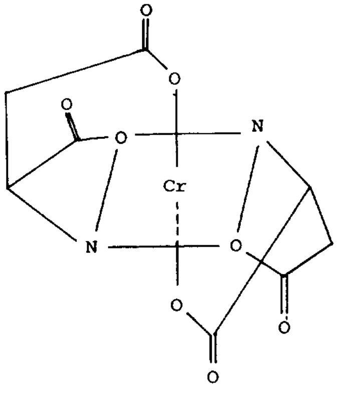
$[Cr(L\text{-his})_2]^+$, (*6*) and (*7*), have been isolated [154] as the nitrate and perchlorate salts, respectively. The assignments were based on the elution behaviour and the IR, VIS, CD, and luminescence spectra of the isomers.

Few chromium(III) complexes containing bis(tridentate) amino acidato-ligands are known, but the complexes [Cr(*L*- or *D*-asp)(*L*-his)] and $[Cr(L\text{-asp})_2]^-$ have now been prepared [155]. The former has six possible isomers: two meridional and one facial, each of which can contain *L*- or *D*-asp, and all have been isolated or detected. The meridional isomer containing *L*-asp is shown in (*9*), and this is the least stable apparently because, as in



(9)

the corresponding cobalt(III) compounds, the amino groups avoid being *trans* to each other. The preparation of the three isomers of $[Cr(L\text{-}asp)_2]^-$ has been refined {(*10*) is one of the two *cis* isomers}. The isomers were assigned



(10)

structures from their visible spectra and high speed chromatograms; this was aided by comparisons of elution behaviour and CD spectra between the chromium(III) and corresponding cobalt(III) complexes.

The perchlorate salt, $[Cr(sal_2en)(OH_2)_2][ClO_4].H_2O$, has been prepared by reaction of an aqueous solution of hexaaquachromium(II) perchlorate with sal_2enH_2 in acetone, but this method was not successful when attempted with

sal_2phenH_2 and $acac_2enH_2$ [156]. The sal_2en complex was also prepared by a template synthesis, which yielded sal_2phen and $acac_2en$ complexes in solution. The polymer, $[CrL(OH_2)_2]Cl$, in which L is the dianion of the Schiff base prepared by condensation of 5,5'-methylenebis(salicylaldehyde) with aniline [157], and the complexes [CrL(OAc)], where H_2L = $2\text{-}HOC_6H_5CH{:}NNHCO(CH_2)_nCONHN{:}CHC_6H_4OH\text{-}2$ (n = 0, 1, or 2), have been characterised [158]. Condensation of biacetyl monoxime with the appropriate acid hydrazide produces the acido-ligands HL and H_2L', where HL is MeC(:NOH)C(Me):NNHC(O)R, R=Ph, $3\text{-}ClC_6H_4$, $3\text{-}BrC_6H_4$, $2\text{-}NO_2C_6H_4$, Bu, and H_2L' is $MeC({:}NOH)C(Me){:}NNHC(O)(CH_2)_nC(O)NHN{:}C(Me)C({:}NOH)Me$ (n = 0 or 4); the complexes $[CrL(OH_2)_3]Cl_2$ and $[Cr_2L'(OH_2)_6]Cl_4$ have been prepared [159].

The kinetics of solvolysis of $[Cr(tren)Cl_2]Cl$ have been measured in the non aqueous solvents, dmso, dmf, formamide (form), and *N*-methylformamide (nmf). During these investigations [160], the complexes chloro(solvent)(tren)chromium(III)perchlorate were obtained, for which IR spectroscopic data indicate *O*-coordination of the solvent molecules: from visible spectra it was deduced that the ligand field strengths of the coordinated solvent are greater than those of chloro- or bromo-ligands, and are in the order nmf < form < dmso < dmf. Several oxalato-species, *e.g.* $[Cr(trenH)(ox)(OH_2)]^{2+}$, have been obtained in solution [161].

Three complexes $K[Cr(SCN)_4A]$, $[Cr(SCN)_3L]$, and $K_3[Cr(NCS)_2Q]$ (where A = dien, L = *N*-(2-aminoethyl)-1,3-diaminopropane, and Q = deprotonated *trans*-1,2-diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetraacetic acid) have been prepared by reactions with $K_3[Cr(SCN)_6]$ [162]. The values of 10 Dq are in the order Q > L > A. Two diastereoisomers, $(+)^{\mathrm{CD}}_{600}$ and $(-)^{\mathrm{CD}}_{600}$, of *cis*-α-$[CrCl_2$(*S*-picpn)$]^+$ (where *S*-picpn is (*S*)-*N*,*N'*-bis(2-pyridylmethyl)-1,2-diaminopropane) were assigned absolute configurations from their CD spectra. An X-ray structural analysis of the chloride of the more stable isomer $\{(+)^{\mathrm{CD}}_{600}\}$ has confirmed its Δ configuration [163]. This work has been extended [164] to complexes of the related ligands (*S*,*S*)-*N*,*N'*-bis(2-pyridylmethyl)-2,3-butanediamine(*SS*-picbn) and (*S*,*S*)-*N*,*N'*-bis(2-pyridylmethyl)-1,2-cyclohexanediamine(*SS*)picchxn), and $[CrCl_2$(*SS*-picbn)$][ClO_4].0.5H_2O$, $[CrCl_2$(*RR*-picchxn)$][ClO_4].0.5H_2O$, and the di-μ-hydroxo dinuclear complexes [{Cr(OH)(*S*-picpn}$_2$]$[ClO_4]_2.3.5H_2O$, [{Cr(OH)(*SS*-picbn)}$_2$]$.3H_2O$, and [{Cr(OH)(*RR*-picchxn)}$_2$]$[ClO_4]_2.4H_2O$ have been investigated. The dichloro-complexes were assigned the novel Λ-*cis*-α structure from CD spectral comparisons, and structures were also assigned to the dihydroxo-complexes. Steric repulsion is apparently responsible for the stereoselective formation of the Λ diastereoisomers and the limited number of isomers of the dinuclear hydroxo-complexes obtained. The CD and MCD spectra of salts of Δ- and Λ-*cis*-α-$[CrX_2(S\text{-picpn})]^+$ (where X = Br, Cl, or F) in the region of the pyridine ring absorption band have been analysed [163] using the recent structural information [165].

A number of chromium(III) complexes of macrocyclic ligands have been prepared: blue *cis*-$[Cr([12]aneN_4)Cl_2]Cl.H_2O$ was synthesised by refluxing $CrCl_3.6H_2O$ with $[12]aneN_4$ (1,4,7,10-tetraazacyclododecane) in absolute ethanol in the presence of activated zinc; violet *cis*-$[Cr([12]aneN_4)(NCS)_2]NCS.2H_2O$ was obtained from the blue complex in aqueous solution by the addition of $[NH_4][SCN]$; and green *trans*-$[Cr([15]aneN_4)Cl_2]Cl.2H_2O$ was obtained by the reaction of $CrCl_3.3thf$ with $[15]aneN_4$ (1,4,8,12-tetraazacyclopentadecane) in dmf [166]. A mixture of dark red *cis*- and green *trans*-$[Cr(1,4,7,11[14]aneN_4)Cl_2]Cl$ was produced by refluxing $CrCl_3.3thf$ with $1,4,7,11[14]aneN_4$ (1,4,7,11-tetraazacyclotetradecane) in dmf, and the isomers were separated by fractional crystallisation from methanol. The magnetic moments were as expected for chromium(III) compounds, and structural assignments were based on the UV-VIS and IR spectra of the complexes. The ranking of Dq^{xy} for various *trans* complexes is $1,4,8,11[14]aneN_4 > 1,4,7,11[14]aneN_4 > [15]aneN_4$, and $[12]aneN_4$ appears to be a relatively weak field ligand. In order to study the base hydrolysis of the cation, *trans*-$[CrCl_2(teta)][NO_3]_2$ (tet*a* = C-*meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) has been prepared [167] by mixing solutions of $CrCl_3.6H_2O$ and tet*a*.$2H_2O$ in dmf, after they had been dehydrated by boiling.

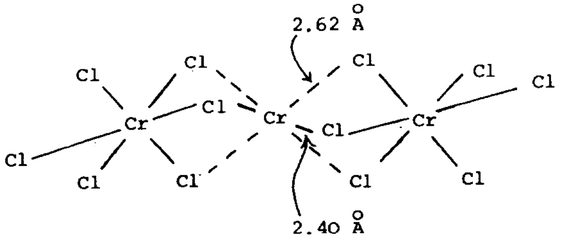
Electrochemical investigations [168] have suggested that two discrete paths of electron transfer are possible for the reduction of [Cr(TPP)ClL] (where L is a substituted pyridine). One of these involves the new complex $[Cr(TPP)L_2]^+$. The products of electron transfer are $Cr(TPP)L_2$ or $[Cr(TPP)ClL]^-$. The preparation of [(ToPc)Cr(III)OH] has been given [148]. The equilibria and kinetics of the reactions between *meso*-tetra(4-*N*-methylporphine)diaquachromium(III) and CN^- and NCS^- have been looked at in some detail [169].

4.3 CHROMIUM(II)

4.3.1 Complexes of simple ligands

Further structural investigations of the trihalochromates(II) have been reported. α-$CsCrCl_3$ and α-$CsCrI_3$ are hexagonal at 295 K and have a slightly distorted $BaNiO_3$ structure [170]. The distortion is predominantly related to the local Jahn-Teller effect which leads to elongated octahedra. The elongation can occur along one of the three principal axes of the octahedron. A new model is introduced, which takes into account the existence of octahedra with randomly distributed elongation directions. Neutron powder diffraction measurements show [171] that the linear chain structures of β-$RbCrI_3$ and γ-$RbCrI_3$ contain elongated octahedra. For β-$CsCrI_3$, the Curie temperature is equal to 27 K, but T_C could not be determined from the χ vs T curves of γ-$RbCrI_3$. From fits of the powder susceptibility data, J/k for $CsCrI_3$ and $RbCrI_3$ were estimated to be -14 and -11 K, respectively. Neutron powder diffraction studies [172] also show that α-$Tl_4[CrI_6]$ contains a random distribution of elongated octahedra, and there is a phase transition between 77 and 4.2 K. In β-$Tl_4[CrI_6]$ the directions of elongation of the octahedra are ordered, and three dimensional magnetic ordering takes place at 2.7 K.

The ferromagnetic tetrachlorochromate(II), $[1,3\text{-}pnH_2][CrCl_4]$, contains layers of chlorine-bridged $[CrCl_4]^{2-}$ units [173] about 9.3 Å apart, separated by the propane-1,3-diammonium cations. Chlorine bridges to adjacent $[CrCl_4]$ units complete a tetragonally elongated octahedron around each chromium ion. Each bridging chlorine atom lies closer (2.39 Å) to one chromium atom than the other (2.87 Å). The bridging angle is 165.3°, and the Cr-Cr separation 5.22 Å. As in $[dienH_3][CrCl_4]Cl$ [174] and Rb_2CrCl_4 [175], the tetragonal axes alternate at right angles in the chlorine-bridged layers. This type of cooperative Jahn-Teller distortion (antiferrodistortive order) is responsible for the ferromagnetism. Similar results have been found in a neutron diffraction investigation [176] of the structures of single crystals of $Rb_2[Cr_{1-x}Mn_xCl_4]$ $(0 \leqslant x < 1)$. For $x = 0.01$, the Cr-Cl bond lengths to the bridging chloride atoms in the layers are 2.40 and 2.74 Å, and the distortion in the $(Mn,Cr)Cl_6$ octahedra decreases with increasing x. The data are in reasonable agreement with those for $Rb_2[CrCl_4]$ [175]. The antiferromagnetic compound $[NMe_2H_2]_2[CrCl_4]$ has very different structure (*11*) containing isolated



(11)

$[Cr_3Cl_{12}]^{6-}$ anions, in which the chromium atoms are arranged linearly [173]. The central chromium atom can be considered surrounded by a tetragonally flattened octahedron of chlorine atoms which bridge to the terminal metal atoms. These form four short and two long Cr-Cl bonds.

A number of tetrabromochromates(II) have been synthesised [177] and, like the tetrachlorochromates(II) (see above and 1979 review), they exhibit various types of magnetic behaviour. The dihydrates $M_2[CrBr_4(OH_2)_2]$ (where M = Cs, Rb, NH_4, or Hpy) are magnetically dilute, high-spin compounds. The ammonium salt is isomorphous with the analogous copper(II) bromide which is known to contain *trans*-$[CuBr_4(OH_2)_2]^{2-}$ anions, with two short and two long Cu-Br bonds. The piperazinium salts $[H_2pipz]_2[CrBr_6].2H_2O$ and $[H_2pipz]_2[CrBr_6]$, and the quanidinium salt $[C(NH_2)_3]_2[CrBr_4].2MeCO_2H$, are also magnetically dilute. Their reflectance spectra are as expected for tetragonally distorted octahedral anions. Thermal dehydration gives the compounds $M_2[CrBr_4]$ (where M = Cs, Rb, NH_4, $NPhH_3$, or Hpy) but the monoalkylammonium salts $[NRH_3]_2[CrBr_4]$ (where R = Me, Et, Pr^n, n-C_5H_{11}, n-C_8H_{17}, or n-$C_{12}H_{25}$), $[NMe_2H_2]_2[CrBr_4]$ and $[C(NH_2)_3]_2[CrBr_4].2MeCO_2H$ have been crystallised from glacial acid, and $[NEt_4]_2[CrBr_4]$ from mixed organic solvents. Ferromagnetic behaviour is exhibited by $Cs_2[CrBr_4]$ and the monoalkylammonium salts, but the other tetrabromochromates(II) are antiferromagnetic. The reflectance spectra indicate tetragonal six coordination of Cr^{II} and hence polymeric structures. Like the analogous tetrachlorochromates(II), the magnetic data for the ferromagnetic tetrabromochromates from liquid nitrogen to room temperature can be reproduced by the high temperature series-expansion formula for a sheet ferromagnet with $S = 2$, and $J_{Br} > J_{Cl}$. The reflectance spectra contain very sharp bands at *ca.* 15,600 and 18,400 cm^{-1}, assigned to spin-forbidden transitions intensified by magnetic coupling. The magnetic behaviour of the antiferromagnetic complexes is reproduced by the high temperature series-expansion formula with appropriate changes of sign. The stretching vibrations of the short Cr-Br bonds occur near 250 cm^{-1}.

It is supposed that the ferromagnetic complex bromides have layer structures like $[1,3\text{-}pnH_2][CrCl_4]$ but structural data are as yet unavailable. The Curie temperatures of $[NRH_3]_2[CrBr_4]$ {where R = Me, n-Pr, or n-$C_{12}H_{25}$} are just below 60 K, and for $[H_3dien][CrCl_4]Cl$ T_C is approximately 38 K [178].

The use of the Jahn-Teller theorem in inorganic chemistry has been considered [179] and an explanation given [180] for the experimental observation that most Cu(II) and high spin Cr(II) complexes suffer tetragonal elongations.

Many attempts to isolate pure solids from the deep red solutions, formed from Cr^{2+} and aqueous potassium cyanide in excess and thought to contain low spin $[Cr(CN)_6]^{4-}$ ions, have been unsuccessful. Through careful control of concentration and pH, the green crystalline hexacyanochromates(II) $M_4[Cr(CN)_6].2H_2O$ (where M = Na or K), and the dark green, simple cyanide $Cr(CN)_2.2H_2O$, have been obtained [181]. Dehydration at 100 °C in vacuum gives the blue hexacyanochromates(II) and the brown chromium(II) cyanide, respectively. The ν(C-N) stretching frequencies of the hexacyanochromates(II) are characteristic of terminal cyano-groups but $Cr(CN)_2$ contains bridging, and $Cr(CN)_2.2H_2O$ bridging and possibly terminal cyano-groups. The complexes are all low spin, but the lower moments of the simple cyanides ($\sim 2.8\ \mu_B$) relative to those of the hexacyanochromates(II) ($3.1-3.5\ \mu_B$) may be due to less orbital contribution to the former because of planar configurations. X-ray powder data and reflectance spectra were also obtained.

Recently, the dark green sodium salt $Na_4[Cr(CN)_6].10H_2O$ was prepared by the reduction of $Na_3[Cr(CN)_6]$ with amalgamated aluminium sheet and, from a crystal structure determination, the anion has nearly octahedral symmetry [182]. Apparently, the decahydrate crystallises but the dihydrate is the stable phase [181]. In liquid ammonia, the hexacyanochromates(II) can be reduced to the chromium(0) complexes $M_6[Cr(CN)_6]$ by the appropriate alkali metal. These are all diamagnetic with a $(t_{2g})^6$ configuration.

4.3.2 *Complexes of N-donor ligands*

Chromium(II) complexes of adenine (ade) of the stoicheiometry $[Cr(ade)_2X_2]$ (where X = Cl, Br, or I) exhibit antiferromagnetic exchange [183]. The complexes were solvated to varying extents with 2-methoxyethanol. The preparation of $[Cr(NCCH_3)_6][BF_4]_2$ and $[Cr(NCCH_3)_4][BF_4]_2$ has been mentioned earlier [39].

The first stepwise formation constant of $[Cr(bipy)]^{2+}$ in hmpa, determined spectrophotometrically [184], is log $K_1 = 4.61 \pm 0.02$. Because log K_1 is slightly greater in hmpa than in water the chromium(II) species in hmpa was considered to be tetrahedral, but no other evidence was given.

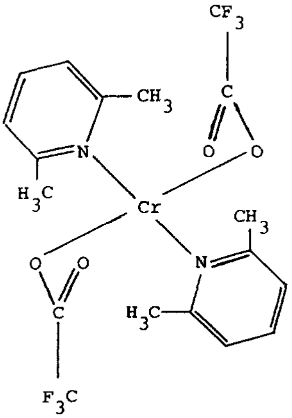
The chromium(II) ion is in an unusual *trans* planar environment in bis(2,6-dimethylpyridine)bis(trifluoroacetato)chromium(II) [185] (*12*). The complex is prepared by the reaction sequence (1):

$$[\text{thf.Cr}(BH_4)_2] \xrightarrow{CF_3COOH} \{[\text{thf.Cr}(O_2CCF_3)_2]_2\} \xrightarrow{2,6\text{-mepy}} [(2,6\text{-mepy})_2Cr(O_2CCF_3)_2], \qquad (1)$$

each ligand is monodentate (Cr-N = 2.111 Å and Cr-O = 2.028 Å). The methyl groups of the 2,6-dimethylpyridine (2,6-mepy) molecules are above and below the CrO_2N_2 plane and block further coordination.

4.3.3 *Complexes containing $Cr^{II}-Cr^{II}$ quadruple bonds*

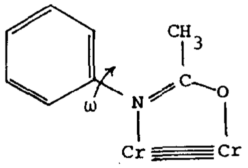
The length of the Cr-Cr quadruple bond in complexes Cr_4L_4 (only one of the



(12)

bridging anions L is shown in (*13*) to (*18*)) is principally dependent upon the presence or absence of axial ligands and, to a lesser extent, on the bridging ligands (see 1980 review). Axial ligands have been excluded by steric hindrance in complexes where L is an acetanilido-{complex (*13*) [186]}, or substituted acetanilido-anion as in complex (*14*) [187]. In compounds where L is carboxylate group, axial ligands such as R_2O or pyridine are present or, if not, the $[Cr_2(O_2CR)_4]$ molecules associate *via* the axial positions to form infinite chains. Dichromium(II) compounds of 2-phenylbenzoate (*15*,*16*) have now been synthesised [188], in the hope that the ortho phenyl groups would prevent intermolecular association, but this expectation was only half achieved in that the structure of (*15*) comprises the usual dinuclear units, but pairs of these units are linked by O → Cr bonds to form a dimer of dimers (*17*) where there are two free axial positions. Here, the four 2-phenyl groups are directed towards the same end of a $Cr\equiv Cr$ unit so that association with a similar dimer can occur at the other end. The formation of infinite chains is prevented, but carboxylates with substituents producing steric hindrance at both ends of the Cr-Cr unit are necessary for the formation of discrete $[Cr_2(O_2CR)_4]$ molecules. The molybdenum analogue of (*15*) does form isolated dimeric molecules [189].

Compound (*15*) was crystallised from a mixture of chromocene and 2-phenyl-benzoic acid in toluene as a ditoluene solvate. The reaction of anhydrous $[Cr_2(O_2CCH_3)_4]$ and 2-phenylbenzoic acid in thf with *n*-butyllithium in hexane produced (*16*), containing two axially coordinated thf molecules. The structure is similar to those of other $[Cr_2(O_2CR)_4A_2]$ molecules, and the Cr-Cr distance, as with (*15*), is within the range (approximately 2.28 to

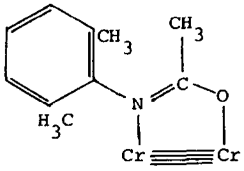


r(Cr-Cr) = 1.873 Å

ω = 48°

acetanilido

(*13*)



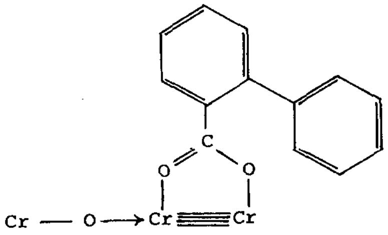
r(Cr-Cr) = 1.937 Å

$1.5C_6H_5CH_3$ (interstitial)

ω = 89.7°

2,6-dimethylacetanilido

(*14*)



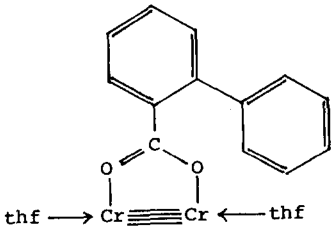
r(Cr-Cr) = 2.348 Å

r(O→Cr) = 2.309 Å

$2C_6H_5CH_3$ (interstitial)

2-phenylbenzoato

(*15*)

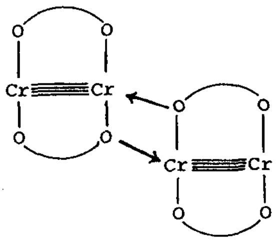


r(Cr-Cr) = 2.316 Å

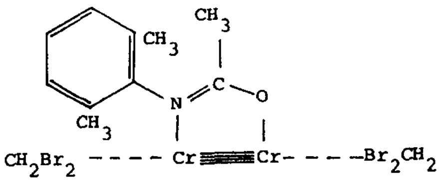
r(Cr-thf) = 2.275 Å

2-phenylbenzoato

(*16*)



(*17*)



r(Cr-Cr) = 1.961 Å

r(Cr-Br) = 3.554 Å and 3.335 Å

2,6-dimethylacetanilido

(*18*)

2.37 Å) previously established. In the structure two ortho phenyl groups are directed towards each end of the binuclear unit. It is not understood why the axial coordination at one end in (*15*) should lead to a longer Cr-Cr bond than in (*16*), where there is axial coordination at each end.

Complex (*14*), in which there are no axial ligands [187], was earlier [190] obtained with two molecules of dichloromethane positioned, as are the molecules of dibromomethane in the new complex (*18*) [187]. In the CH_2Cl_2 adduct, r(Cr-Cr) was found to be 1.949 Å, considerably longer than the value of 1.873 Å in the unsubstituted complex (*13*), the only complex of the acetanilido type without axial ligands available for comparison at the time. Since no significant difference was expected between the Cr-Cr bond lengths in (*13*) and (*14*), it was assumed that axial interaction Cl→Cr by CH_2Cl_2 molecules had caused the multiple bond to lengthen from 1.873 Å in (*13*) to 1.949 Å in the CH_2Cl_2 adduct. This interpretation is now doubtful because the bond length in (*14*), which has no axial ligands, is close to those in the CH_2Cl_2 or CH_2Br_2 adducts. However, since the chromium-halogen bond lengths decrease in going from dichloromethane to dibromomethane (van der Waals contacts should increase) there is still some evidence for axial interaction. Molybdenum(II) forms CH_2Cl_2 and CH_2Br_2 adducts isomorphous with (*18*).

It is possible that the Cr-Cr bond in (*14*) is *ca.* 0.07 Å longer than in (*13*) because the large dihedral angle ω in (*14*) reduces the conjugation between the phenyl and amide π-systems and hence the electron density between the Cr^{2+} ions.

From a consideration of the dissociation equilibria for chromium(II) and copper(II) acetates, it has been possible to estimate [191] the difference between the Cr$\equiv$Cr and Cu-Cu bond energies in the acetate system. The Cr-Cr interaction is usually described in terms of one σ, two π, and one δ components, and the weaker Cu-Cu interaction in terms of just one δ component. In spite of a difference of three units in bond order, the Cr-Cr bond is stronger than the Cu-Cu bond by only about 45 kJ mol^{-1}.

Measurements of their low energy photoelectron spectra have provided useful information on the electronic structure of dichromium(II) and dimolybdenum(II) complexes [192] and a correlation between the ionisation energies of the metal's valence electrons and the Cr-Cr separation suggests that the separation is influenced considerably by the Coulombic repulsion between the metal atoms [193]. The first measurements of the core level photoelectron spectra of dichromium(II) and dimolybdenum(II) complexes have been performed [194] using AlK_α-radiation. The complexes are M_2L_4 (where M = Cr, L = O_2CMe or mhp; M = Mo, L = O_2CH, O_2CMe, or mhp, and Hmhp = 2-hydroxy-6-methylpyridine). The oxygen core ionisation energies (I.E.'s) of $[Cr_2(O_2CMe)_4]$ and $[Mo_2(O_2CMe)_4]$ are the same within experimental error, as are the oxygen and nitrogen core I.E.'s of $[Cr_2(mhp)_4]$ and $[Mo_2(mhp)_4]$. Also, the decrease in binding energy of the chromium $2p$ levels from $[Cr_2(O_2CMe)_4]$ to $[Cr_2(mhp)_4]$ matches that of the molybdenum $3d$ levels in going from $[Mo_2(O_2CMe)_4]$ to $[Mo_2(mhp)_4]$. Therefore, it has been concluded that the charge distribution is probably the same within $[Cr_2(O_2CMe)_4]$ and $[Mo_2(O_2CMe)_4]$, and within $[Cr_2(mhp)_4]$ and $[Mo_2(mhp)_4]$. Consequently, the significant lengthening (0.40 Å) of the Cr-Cr separation in going from $[Cr_2(mhp)_4]$ to $[Cr_2(O_2CMe)_4]$ as compared with the smaller lengthening (0.03 Å) between the analogous molybdenum(II) complexes is *not* due to differences in the bonding of the ligands to the M_2^{4+} centres, but to the different nature of the Cr-Cr and Mo-Mo interactions, notably the shallower potential well for the former which leads to greater sensitivity to the Cr-Cr separation to changes in charge distribution within the Cr_2L_4 complex.

The known dichromium(II) complexes have been classified into three groups according to the metal-metal separations [195]. From calorimetric measurements at 25 °C of the enthalpies of oxidative hydrolysis in solution, the standard enthalpies of formation of crystalline $[Cr_2(mhp)_4]$ and $[Cr_2(dmp)_4]$ (where dmp is the dimethoxyphenyl anion) have been found to be $-(948.2 \pm 9)$ and $-(961 \pm 22)$ kJ mol^{-1}, respectively [196]. The enthalpies of formation in the gaseous state and the enthalpies of atomisation (ΔH_a°) have been evaluated from measured or estimated enthalpies of sublimation, and attempts made to quantify the contributions to ΔH_a° from the metal-metal, metal-oxygen, metal-nitrogen and metal-carbon bonds in these molecules.

4.4 MISCELLANEOUS CHEMISTRY OF CHROMIUM(II) AND (III)

In this section, reductions by chromium(II) complexes, electrochemical reactions, and some σ- and π-bonded organochromium(III) complexes are briefly and selectively reviewed. Although strictly organometallic compounds, the last have been included because they resemble, in oxidation state and other properties, classical chromium(III) coordination complexes.

The reduction of nitroamine with Cr^{2+} yields dinitrogen and ammonia, and a hydrazido-complex is postulated as an intermediate [197]. The use of low valent transition metal species including Cr(II) compounds in the reduction of organic compounds has been reviewed [198].

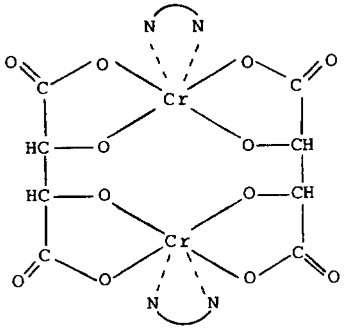
Pyrazine reacts with aqueous Cr^{2+} to form an intense green 1:1 species $[(H_2O)_5Cr(pzH\cdot)]^{3+}$, considered to be a complex of chromium(III) in which the radical anion is protonated at the remote nitrogen atom. Substituted pyrazines behave similarly, and the electrochemical behaviour of the "greens" derived from pyrazine, pyrazine-2-carboxamide, and pyrazine-2-carboxylic acid have been investigated [199]. Solutions of pyrazine green exhibit a single, composite polarographic wave which passes without inflection from anodic to cathodic currents. The anodic branch corresponds to oxidation to the chromium(III) cation $[(H_2O)_5Cr(pz)]^{3+}$, and the cathodic branch to two electron reduction to produce the dihydropyrazinium ion and Cr^{2+}. The corresponding set of reactions for the pyrazinecarboxylic acid green gives rise to separate oxidation and reduction waves, and the green is believed to contain a bidentate organic ligand. The more complex electrochemical behaviour of the pyrazine carboxamide green is ascribed to the presence of two isomers, one containing bidentate pyrazinecarboxamide, and the other monodentate pyrazinecarboxamide coordinated to Cr^{2+} by the 4-nitrogen atom. Interconversion of these isomers is catalysed by Cr^{2+}.

The dithiobenzoato-complexes $[Cr(S_2CC_6H_4R\text{-}4)_3]$ (where R = H, Me, MeO, Me_2N, or Et_2N) are reduced at a platinum electrode in a series of one-electron transfers [200]. The dithiobenzoate stabilises low oxidation states by involvement of the dianionic canonical form of the ligand in the structure of the initial complex. In the reduction of $[Cr(NH_3)_5L]^{n+}$ (n = 2 or 3; L = an amino acid, aminobenzoic acid, or Schiff base of an amino acid or aminobenzoic acid with benzaldehyde or 2-vanillin) at the dropping mercury electrode, the one-electron, irreversible reductions follow a mixed inner/outer sphere path, but reduction by Cr(II) follows an inner sphere path [201]. The voltammetric behaviour of the bis complex of chromium(III) with 2,6-bis(4-phenyl-2-pyridyl)-4-phenylpyridine was studied in ethane nitrile [202]. It shows four one-electron reductions to the +2, +1, 0 and -1 formal oxidation states. Comparisons with related ligands show that phenyl 4-substituents stabilise the low and the high oxidation states.

The reduction of CHX_3 (X = Cl, Br, or I) by Cr^{2+} proceeds *via* the primary products CrX^{2+} and $CrCHX_2^{2+}$ [203] and the reduction of NH_2OH, HN_3, and maleic acid has been investigated [204].

Oxidation by permanganate of the dibridged tartrate complexes (*19*) of chromium(III) $[H_2Cr_2(tart)_2L_2]$ and $[HCr_2(tart)_2L_2]^-$ (where L is bipy or phen) results in cleavage of the tartrate ligands to give bis(oxalato)-compounds [205]. When phen is present, further oxidation occurs to give diaqua(oxalato)-(phen)-chromate(III). Further studies of the co-oxidation of 2-hydroxy-2-methylbuteric acid and 2-propanol by chromic acid have been carried out [206].

Organic σ-bonded complexes of chromium(III) are generally prepared from aqueous chromium(II) solutions, but this does not give good yields of simple alkyl complexes. The penta-aquamethylchromium(III) ion is formed [207] in high yield by reactions (2) to (5), in which the Fenton reagent $H_2O_2/Cr(II)$ is



(19)

$$[Cr(OH_2)_6]^{2+} + H_2O_2 \longrightarrow [Cr(OH_2)_6]^{3+} + HO\cdot + OH^- \quad (2)$$

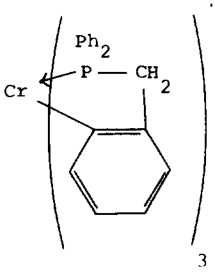
$$HO\cdot + (CH_3)_2SO \longrightarrow (CH_3)_2S(O\cdot)OH \quad (3)$$

$$(CH_3)_2S(O\cdot)OH \longrightarrow CH_3^\bullet + CH_3SO_2H \quad (4)$$

$$CH_3^\bullet + [Cr(OH_2)_6]^{2+} \longrightarrow [Cr(OH_2)_5(CH_3)]^{2+} + H_2O \quad (5)$$

used to generate hydroxyl radicals which in turn produce methyl radicals from dmso. These are then trapped as the ions $[Cr(OH_2)_5CH_3]^{2+}$ by the substitution labile excess of aqueous Cr^{2+} ions. It is considered that other alkyl chromium(III) ions can be obtained from the appropriate dialkylsulphoxide. Reactions of $[Cr(OH_2)_5CH_3]^{2+}$ with electrophilic reagents have been investigated kinetically [208].

The cationic organochromium complexes $[CrCH_2CN]^{2+}$, $[CrCH_2CH_2CN]^{2+}$, and $[CrCH_2CH(CH_3)CN]^{2+}$ have been prepared by the reaction of chromium(II) perchlorate with acidified solutions of hydrogen peroxide in water containing modest concentrations of the appropriate organic nitrile [209]. These complexes are stable in aqueous perchloric acid; they were separated by ion exchange chromatography, and characterised by their UV-VIS spectra, and the NMR spectrum of the organic bromide produced by reaction with aqueous bromine. These σ-bonded complexes differ from the hydroxymethylchromium(III) species in their unreactivity towards oxidants such as Fe^{3+} [210,211]. Kinetic investigations of the vanadyl(IV) oxidation of aqueous Cr^{2+} [212] and of the hydroxymethylchromium(III) ion have been reported [213], and further investigations of the aquation of σ-bonded organochromium complexes derived from 3- and 4-pyridineacrylic acids and maleic and fumaric acids have been carried out [214]. The reactions of $[RCr([15]aneN_4)(OH_2)]^{2+}$ with Hg(II) and HgMe have been investigated kinetically in aqueous perchloric acid [215]. By reaction of (2-lithiobenzyl)diphenylphosphine with $[CrCl_3(thf)_3]$ or $[CrBr_2(thf)_2]$, $[Cr(C_6H_4\text{-}2\text{-}CH_2PPh_2)_3]$ (*20*) has been obtained [216], and



(20)

$[Cr\{(CH_2)_2P(CH_3)_2\}_3]$ has been characterised [217].

The rhenaacetylacetonate complexes $[cis\text{-}(OC)_4Re(CH_3CO)_2]_nM$ {where M = Cr, Fe (n = 3), or Cu (n = 2)} have been examined by cyclic voltammetry [218], and the redox potentials of the central coordinating metal ions in the metalla- and analogous non-metalla-acac complexes were determined. The redox potential of the rhenaacetylacetonate complex was found the more positive, reflecting the higher electronegativity of the rhena moiety. Metallobis(phosphonates) can also act as chelating ligands since $(C_5H_5)M[\{P(OMe)_2O\}_2H]$, for example, where M = Ni or Pd, will react [219] with metal acetylacetonates and metal chlorides to give new tri- and tetra-nuclear complexes, *e.g.* $[((C_5H_5)M\{P(OMe)_2O\}_2)_3Cr]$.

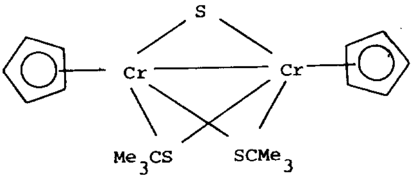
The existence of aquaorganochromium(III) complexes like those mentioned above shows that π-acceptor ligands are not needed to stabilise Cr-C σ-bonds. The ion $[(\eta^5\text{-}C_5H_5)Cr(OH_2)_n]^{2+}$, apparently containing π-bonded C_5H_5, has been prepared from chromocene, according to reaction (6) and isolated as the

$$Cr(\eta^5\text{-}C_5H_5)_2 + 2H^+ \xrightarrow[H_2O]{H[ClO_4]} [(\eta^5\text{-}C_5H_5)Cr(OH_2)_n]^{2+} + \tfrac{1}{2}H_2 + C_5H_6 \qquad (6)$$

slightly impure violet tetrafluoroborate $[(\eta^5\text{-}C_5H_5)Cr(OH_2)_3][BF_4]_2$ [220] so that the same seems true for π-bonded organochromium(III) species. The aqua cation has also been obtained in solution from $[NH_4][(\eta^5\text{-}C_5H_5)CrCl_3]$ and $[(\eta^5\text{-}C_5H_5)_2Cr]I$. Several halides and mixed halides $[(\eta^5\text{-}C_5H_5)CrX_2]$ have been characterised [221].

The complex $[(\eta^5\text{-}C_5H_5)_4Cr_4O_4]$ contains Cr atoms tetrahedrally disposed at four corners of a distorted cube, with the O atoms similarly arranged [222]. The Cr atoms are capped by the $[C_5H_5]^-$ anions, and so are formally six coordinate and in the (III) oxidation state. The Cr–Cr distances are markedly unequal (*ca.* 2.8 Å) and the complex is antiferromagnetic.

The photochemical reaction between the antiferromagnetic complex $[\{(\eta^5\text{-}C_5H_5)Cr(SCMe_3)\}_2S]$ {which contains (*21*) a Cr–Cr bond 2.689 Å long, and for which $-2J = 430\ cm^{-1}$ [223]} and $Fe(CO)_5$ results in the elimination of two carbonyl groups and one *t*-butyl radical to give $[(\eta^5\text{-}C_5H_5Cr)_2(\mu^2\text{-}SCMe_3)(\mu^3\text{-}S)_2Fe(CO)_3]$ [224]. The product contains a Cr–Cr bond of length 2.707 Å and one thiolate and two sulphide bridges. The iron atom is 2.726 Å from one chromium atom and 3.110 Å from the other. The exchange parameters (-2J) for the antiferromagnetic complex are Cr–Cr, 380 cm^{-1}, Cr(1)-Fe, 2600 cm^{-1}, and Cr(2)-Fe, 170 cm^{-1}, and direct exchange is considered the important factor determining the magnetism.



(21)

Complex (*21*) acts as an unusual antiferromagnetic ligand bound by a sulphide bridge in the heterotrinuclear complexes $[\{(\eta^5\text{-}C_5H_5)Cr(SCMe_3)\}_2S\cdot M(CO)_5]$ (where M is Cr, Mo or W [225]), and in $[\{(\eta^5\text{-}C_5H_5)Cr(SCMe_3)\}_2S\cdot Mn_2(CO)_9]$ [226]. The geometry of and magnetic interaction within (*21*) are little affected by complex formation. Reaction of (*21*) with $Co_2(CO)_8$ produces $[(\eta^5\text{-}C_5H_5)Cr(SCMe_3)Cr(\eta^5\text{-}C_5H_5)\cdot(\mu^3\text{-}S)_2Co(CO)_2]$ which is antiferromagnetic ($-2J = 530\ cm^{-1}$) and contains the CrCrCo metallacycle. Heating this compound in toluene in the presence of diphenylacetylene yields [227] the diamagnetic tetranuclear cluster $[(\eta^5\text{-}C_5H_5)_3Cr_3(\mu^3\text{-}S)_4\cdot Co(CO)]$ which contains a tetrahedral arrangement of metal atoms. The complexes $[\{(\eta^5\text{-}C_5H_5)Cr(SCMe_3)\}_2S\cdot Mn(CO)_2(\eta^5\text{-}C_5H_5)]$ and $[\{(\eta^5\text{-}C_5H_5)_3Cr_3(\mu^3\text{-}S)_4\}M(\eta^5\text{-}C_5H_5)]$ (M = Cr, V, or Nb) have also been obtained [228].

The reaction [229] of chromocene with trifluoroacetic acid affords, after various treatments, a series of compounds,

$[(\eta^5\text{-}C_5H_5)_2Cr][(\eta^5\text{-}C_5H_5)Cr(O_2CCF_3)_3]$, $[(\eta^5\text{-}C_5H_5)Cr(O_2CCF_3)_2\cdot thf]$, $[(\eta^5\text{-}C_5H_5)Cr(O_2CCF_3)\cdot py]$, and $[(py)_3Cr(O_2CCF_3)_3]$. The last, a typical chromium(III) complex, has been characterised by a complete X-ray analysis, and it can also be obtained from (*21*).

The nitrosylation [230] of (*21*) with NO in thf at room temperature forms $[(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2)]$ and the dimer $[(\eta^5\text{-}C_5H_5)(NO)Cr(\mu\text{-}SCMe_3)(\mu\text{-}S\text{-}S\text{-}CMe_3)Cr(NO)(\eta^5\text{-}C_5H_5)]$.

Some cationic thionitrosyl complexes have been isolated [231]. On reaction of a solution of $[NS][PF_6]$ in nitromethane, prepared *in situ* from $N_3S_3Cl_3$ and $Ag[PF_6]$, with $[(C_6H_6)Cr(CO)_3]$ in ethanenitrile, $[Cr(NS)(NCMe)_5][PF_6]_2$ was obtained. It is reduced to $[Cr(NS)(NCMe)_5][PF_6]$ in the presence of ^{t}BuNC and zinc powder, and is re-formed on oxidation with $[NO][PF_6]$ or $Ag[PF_6]$.

Improved conditions for the generation of the $[Cr(NO)]^{2+}$ species from $[CrO_4]^{2-}$ and aqueous hydroxylamine hydrochloride have been used [232] in the synthesis of the mononitrosyls $[Ph_4P]_3[Cr(NO)(NCS)_5]$, $[Cr(NO)(NCS)_2(bipy)]$, $[Cr(NO)(NCS)_2(phen)]$, and $[CrNO(Et_2dtc)_2]$. A number of derivatives of pentacyanonitrosylchromate, in which cyanide has been replaced by en, have been prepared from CrO_3, KCN and en in aqueous solution to which hydroxylamine was added as the source of the NO group [233]. The derivatives are $K[Cr(NO)(CN)_2(en)(OH)]\cdot H_2O$, $[Cr(NO)(CN)_2(en)(OH_2)]$, $[Cr_2(NO)_2(CN)_4(en)_3]$, $[Cr_2(NO)_2(CN)_2(en)_4]Cl_2\cdot 2H_2O$, and $[Cr_2(NO)_2(en)_5]Cl_4\cdot 6H_2O$. The last two were also obtained anhydrous as tetraphenylborate salts. These nitrosyls have temperature-dependent magnetic moments of approximately 2.0 μ_B. EPR, UV-VIS, and IR investigations were also carried out, and the last three nitrosyls are considered to contain bridging ethylenediamine ligands.

Well-defined "paired" chromium species in various oxidation states on silica and alumina catalyse propene hydrogenation efficiently at 195-263 K [234]. The catalyst was prepared by the reaction between $[Cr_2(\eta^3\text{-}C_3H_5)_4]$ and the surface OH groups of SiO_2 or Al_2O_3, and the surface structures were characterised by IR, UV diffuse reflectance, EPR, and photoluminescence spectroscopy, volumetrically, and by temperature programmed hydrogenolysis.

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