

## 6. CHROMIUM

L.F. LARKWORTHY

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### INTRODUCTION

This review deals mainly with literature on the inorganic and coordination chemistry of chromium which appeared during 1980, but it includes some work published in 1979 usually in less accessible journals. The organometallic chemistry of chromium has not been covered. Chromium(III) chemistry has again been the most active area.

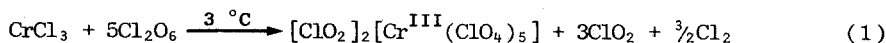
#### 6.1 CHROMIUM(VI)

Complex formation between  $\text{Ag}^+$  and  $[\text{CrO}_4]^{2-}$  in molten 1:1 (K,Na) $\text{NO}_3$  has been studied by measurements of EMF, solubility, and absorption spectra [1]. Weak complexes  $[\text{AgCrO}_4]^-$ ,  $[\text{Ag}_2\text{CrO}_4]$ , and  $[\text{Ag}(\text{CrO}_4)_2]^{3-}$  are formed. Absorption spectra of  $[\text{CrO}_4]^{2-}$  in melts with various cationic (K,Na) compositions show a shift to lower energy of the low energy band on association with  $\text{Ag}^+$  which has been attributed to considerable  $d_\pi$  back donation from  $\text{Ag}^+$  to  $[\text{CrO}_4]^{2-}$ . The new chromates  $\text{K}_4\text{Pb}_4[\text{CrO}_4]_6$  and  $[\text{NH}_4]_4\text{Pb}_4[\text{CrO}_4]_6$  and solid solutions formed from them have been studied [2]. Potassium chromate and dichromate

form the corresponding acids in a Na/KHSO<sub>4</sub> eutectic which decompose into water, dioxygen and Cr<sub>2</sub>O<sub>3</sub>, and this is converted into chromium(III) sulphate [3]. In a molten Li<sub>2</sub>CO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub>/K<sub>2</sub>CO<sub>3</sub> eutectic, dichromate produces chromate and CO<sub>2</sub>, and CrO<sub>3</sub> gives [Cr<sub>4</sub>O<sub>13</sub>]<sup>2-</sup>, [Cr<sub>3</sub>O<sub>10</sub>]<sup>2-</sup>, [Cr<sub>2</sub>O<sub>7</sub>]<sup>2-</sup> and finally [CrO<sub>4</sub>]<sup>2-</sup> as the temperature is increased [4]. The products were identified from their reflectance, IR and Raman spectra.

Investigations of the gas phase Raman and matrix IR spectra of CrO<sub>2</sub>F<sub>2</sub> have led [5] to an unambiguous assignment of the stretching vibrations in this molecule, and have confirmed earlier gas phase IR assignments. From the <sup>50</sup>Cr-<sup>52</sup>Cr isotopic shifts, the bond angles have been calculated to be O-Cr-O, 102.5° and F-Cr-F, 124° in agreement with the previous ED results, but not with the results from microwave spectroscopy. For SO<sub>2</sub>F<sub>2</sub> the angles are known to be O-S-O, 124.0° and F-S-F, 96.1°, and this is another example of the structural contrasts often found between related transition-metal and main-group compounds; only the latter follow the principles of the VSEPR theory.

Dichlorine hexoxide reacts with anhydrous chromium(III) chloride [6] according to equation (1), but there is some oxidation to Cr(IV) and formation



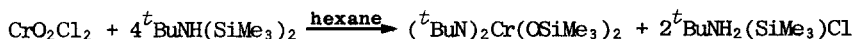
of [Cr<sup>VI</sup>O<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>] which can be removed under vacuum leaving [ClO<sub>2</sub>]<sub>2</sub>[Cr(ClO<sub>4</sub>)<sub>5</sub>]. On heating, this chloryl salt forms CrO<sub>3</sub>; its IR spectrum shows that mono- and bidentate [ClO<sub>4</sub>]<sup>-</sup> groups are present and contains bands at 1300 and 525 cm<sup>-1</sup> assigned to the ν<sub>as</sub> and δ vibrations of [ClO<sub>2</sub>]<sup>+</sup>. From its IR spectrum [CrO<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>] contains monodentate perchlorate groups so the chromium has a tetrahedral environment like CrO<sub>2</sub>Cl<sub>2</sub>.

Electron diffraction data for gaseous CrO<sub>3</sub> can be best interpreted by assuming that it consists of trimers and tetramers, with puckered rings in relative abundances of 30% and 70% [7].

An analysis of the spectra of CrO<sub>2</sub>Cl<sub>2</sub> in mixtures of carbon tetrachloride and acetone suggests that CrO<sub>2</sub>{OC(CH<sub>3</sub>)<sub>2</sub>}Cl<sub>2</sub> is formed [8]. The products of oxidation of 2,4,6-tri-*t*-butylphenol with CrO<sub>2</sub>Cl<sub>2</sub> are mostly quinones and diphenquinones. It was concluded [9] that CrO<sub>2</sub>Cl<sub>2</sub> is not a good model for the proposed ferryl intermediate in haem oxidase systems since it induces 1→3 rather than 1→2 halogen shifts and an NIH shift that is best explained by carbenium ion-like intermediates. The chromic acid cooxidation of 2-hydroxy-2-methylbutyric acid (HMBA) and 2-propanol is a two stage reaction; the first stage produces methylethylketone, acetone, CO<sub>2</sub>, Cr(V) and Cr(III) and, in the second slower stage, Cr(V) oxidises HMBA to acetone and CO<sub>2</sub> and

forms Cr(III). Unlike Cr(VI), Cr(V) selectively oxidises hydroxy acids [10]. Spectrophotometric, ESR and kinetic investigations have been used to identify Cr(V) and Cr(IV) intermediates in the oxidation of alkylaromatics by chromyl(VI)acetate in acetic anhydride [11].

Deep red crystals of a *t*-butylimido complex are formed [12] in the reaction.



A rapid and sensitive method has been developed [13] for the determination of trace amounts of Cr(VI). It is based on the pre-concentration of Cr(VI), as the diphenylcarbazide complex on a mixed resin prepared from finely divided anion and cation exchangers, and the subsequent measurement of absorbance of the resin phase after collection on a filter paper as a uniform thin layer. It is a hundred times more sensitive than the ordinary solution method with a 1 cm cell.

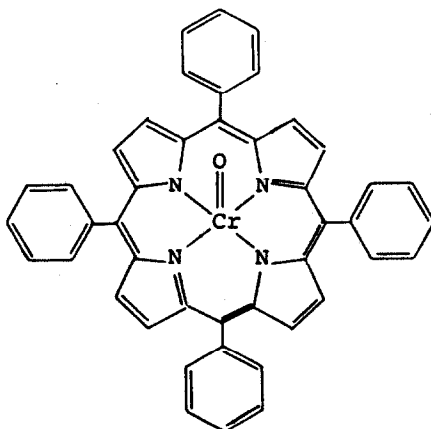
An X-ray spectroscopic study of compounds of chromium {in oxidation states (VI), (IV) and (II)}, nickel, and molybdenum has shown that the chemical shifts  $\Delta E$  of the K-absorption edges follow the expression  $\Delta E = aq + bq^2$ , where  $q$  is the effective charge of the absorbing metal ion and  $a$  and  $b$  are constants [14].  $\Delta E$  generally increases with oxidation state, but an exact relation could not be found because compounds in the same oxidation state show a wide range of  $\Delta E$ 's as  $\Delta E$  is determined by effective charge rather than oxidation state. In agreement, the  $\Delta E$  values vary linearly with metal  $2p_{3/2}$  binding energy data from XPES.

## 6.2 CHROMIUM(V)

The known neutral compounds of chromium(V),  $\text{CrF}_5$ ,  $\text{CrOF}_3$  and  $\text{CrOCl}_3$ , are poorly characterised. The last has been prepared [15] by a known method - reaction of  $\text{CrO}_2\text{Cl}_2$  and  $\text{BCl}_3$  - and found to be stable indefinitely in dry glass ampoules at *ca.* 263 K, although it slowly decomposes to  $\text{CrO}_2\text{Cl}_2$  at room temperature. The mass spectrum of the vapour above the samples at 283 K contained the molecular ion  $[\text{CrOCl}_3]^+$ , and the  $g$  value of 1.989 for solutions in  $\text{CCl}_3\text{F}$  is comparable with values for  $[\text{CrOCl}_4]^-$  and  $[\text{CrOCl}_5]^{2-}$ . The IR spectrum of  $\text{CrOCl}_3$  in an inert gas matrix at 12 K has been assigned on the basis of  $C_{3v}$  symmetry, and the  $\text{ClCrCl}$  bond angle is estimated to be  $105 \pm 5^\circ$ . However, the solid (at 250 K) is thought to be a polymer because of its low volatility and the presence of an additional  $\nu(\text{Cr}-\text{Cl})$  band in the IR spectrum. Decomposition to  $\text{CrO}_2\text{Cl}_2$  prevented the determination of the solution spectrum but the electronic spectrum in an argon matrix correlated well with that of  $\text{VOCl}_3$ .

The order of predominantly metal  $d$ -orbitals in  $[\text{CrOCl}_4]^-$ ,  $[\text{MoOCl}_4]^-$  and  $[\text{MoOBr}_4]^-$  has been determined from molecular orbital calculations to be  $d_{xy} < d_{xz,yz} < d_{x^2-y^2} < d_{z^2}$  [16]. The lowest energy absorption is due mainly to the  $d_{xy} \rightarrow d_{xz,yz}$  transition, and the second absorption and the two higher energy bands are predicted to arise from halogen-to-metal charge transfer transitions which obscure the symmetry forbidden  $d-d$  excitations. Further calculations of the ionisation energies of  $\text{CrOCl}_3$  [17] and investigations of the EPR spectra of  $[\text{CrO}_4]^{3-}$  in  $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$  and  $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$  [18,19] have been carried out.

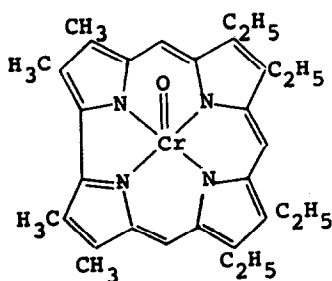
In the presence of chlorotetraphenylporphinatochromium(III),  $\text{Cr}^{\text{III}}(\text{TPP})\text{Cl}$ , iodosylbenzene will oxidise simple unsaturated hydrocarbons to alcohols and epoxides, and alcohols to ketones or aldehydes [20]. This is due to the formation of the oxoporphinatochromium(V) complex (1) which can also be



(1)

prepared by reaction of  $m$ -chloroperoxybenzoic acid with  $\text{Cr}(\text{TPP})\text{Cl}$ . The IR spectrum of (1) showed a strong peak at  $1026\text{ cm}^{-1}$  which shifted on  $^{18}\text{O}$  substitution and is assigned to the  $\text{Cr}=\text{O}$  stretch. Its magnetic moment of  $2.05\ \mu_{\text{B}}$  (Evans method) is consistent with the  $(\text{Cr}^{\text{V}}=\text{O})$  formulation, and the oxo ligand exchanges with  $\text{H}_2\ ^{18}\text{O}$ . The reactions resemble those of cytochrome P-450 and provide some evidence that  $(\text{Fe}=\text{O})^{3+}$  intermediates may be involved in the cytochrome oxidations.

Another oxochromium(V) complex (2), this time of a corrole (2,3,17,18-tetramethyl-7.8.12,13-tetraethylcorrole,  $\text{H}_3\text{MEC}$ ) has been described [21]. This compound was prepared by aerial oxidation of the chromium(II) species which was not isolated. A band at  $964\text{ cm}^{-1}$  was assigned to the  $\text{Cr}=\text{O}$  stretch and the magnetic moment of the solid was  $1.71\ \mu_{\text{B}}$  at room temperature; the ESR spectrum



(2)

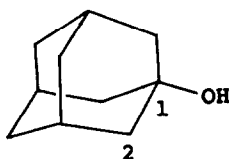
was consistent with a  $(d_{xy})^1$  configuration. The binding energies (XPES) of the core electrons of the metal in  $[\text{CrO}(\text{MEC})]$  were greater than in  $[\text{Cr}^{\text{III}}(\text{TPP})\text{OMe}]$ , indicating a higher oxidation state for the metal in the former.

### 6.3 CHROMIUM(IV)

In order to prevent an artificial separation of complexes of the same ligand, some chromium(III) and chromium(IV) complexes are considered together in this section.

Nitrosonium hexafluorochromate(IV),  $[\text{NO}]_2[\text{CrF}_6]$ , has been prepared by reaction of nitrosyl fluoride with  $\text{CrF}_5$  and characterised by Raman spectroscopy [22]. The structures of the new complex fluorides  $\text{A}_3[\text{CrF}_7]$ , where A is Rb or Cs, have been solved [23] by assuming that they are isotypic with  $\text{K}_3[\text{SiF}_7]$ . Ferromagnetic  $\text{CrO}_2$  has been prepared by a new method [24] and ESCA spectra are said to show that  $\text{CrO}_2$  and  $\text{TbCrO}_4$  can be considered to be  $\text{Cr}_2\text{O}_3$ ,  $\text{CrO}_3$  and  $3\text{Tb}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3 \cdot 4\text{CrO}_3$ , respectively [25].

The adamantoxo complex  $[\text{Cr}(\text{1-ado})_3]$  has been obtained [26] from  $\text{Cr}[\text{N}(\text{i-Pr})_2]_3$  and 1-adamantanol (3; 1-adoH). On oxidation with  $\text{CuCl}$ ,  $[\text{Cr}(\text{1-ado})_4]$  is formed

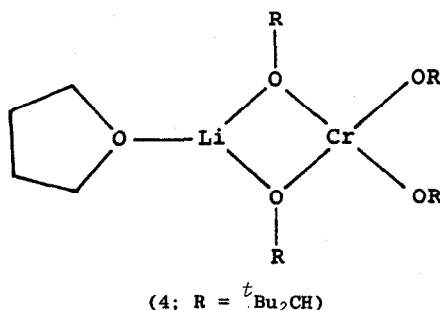


(3)

and this can also be prepared from  $\text{Cr}(\text{NEt}_2)_4$  by alcoholysis, or by oxidation with  $\text{CuCl}$  of the solid crystallised from  $[\text{CrCl}_3(\text{thf})_3]$  and  $\text{Na}(\text{1-ado})$  in  $\text{thf}$ . The chromium(IV) complex is air-stable and, because it does not undergo redox or disproportionation reactions, is a convenient starting material for the

preparation of tetraalkyls, *e.g.*  $\text{Cr}(\text{CH}_2\text{SiMe}_3)_4$ .  $[\text{Cr}(\text{l-ado})_3]$  reacts with nitric oxide to give  $[\text{Cr}(\text{l-ado})_3\text{NO}]$   $\{\nu(\text{NO}) = 1715 \text{ cm}^{-1}\}$ , and it is believed to be polymeric like  $[\text{Cr}(\text{OEt})_3]_n$ . There is a molecular ion in the mass spectrum of  $[\text{Cr}(\text{l-ado})_4]$  ( $\mu_{\text{eff}} = 2.68 \mu_B$  at room temperature), and the IR spectrum indicates a monomer. Its stability arises because the small covalent radius of Cr(IV) allows close packing of the adamantyl groups which protect against encroaching ligands.

Many alkoxo-complexes can be obtained as above by alcoholysis of the corresponding metal dialkylamide, but  $\text{Cr}\{\text{N}(\text{SiMe}_3)_2\}_3$  and  $\text{Cr}(\text{NEt}_2)_4$  do not react with the sterically demanding bis(*t*-butyl)methanol. The chromium(III) complexes  $\text{Cr}\{\text{OCH}(\text{}^t\text{Bu})_2\}_3\cdot\text{thf}$  and  $\text{LiCr}\{\text{OCH}(\text{}^t\text{Bu})_2\}_4\cdot\text{thf}$  have, however, been prepared from ethereal  $[\text{CrCl}_3(\text{thf})_3]$  and  $\text{Li}[\text{OCH}(\text{}^t\text{Bu})_2]$ , and the chromium(IV) complex  $\text{Cr}\{\text{OCH}(\text{}^t\text{Bu})_2\}_4$  by oxidation of  $\text{LiCr}\{\text{OCH}(\text{}^t\text{Bu})_2\}_4\cdot\text{thf}$  with CuCl or aerial oxidation of a mixture of anhydrous  $\text{CrCl}_3$  and  $\text{Li}[\text{OCH}(\text{}^t\text{Bu})_2]$  [27]. Related complexes with Mn(II), Fe(III), Co(II) and Cu(II) have also been isolated. All are very soluble in non polar solvents and  $\text{Cr}\{\text{OCH}(\text{}^t\text{Bu})_2\}_3$  is a monomer in benzene, but the solid has a low moment ( $\mu_{\text{eff}} = 3.2 \mu_B$  at  $23^\circ\text{C}$ ) and the broad IR band,  $\nu(\text{Cr-O})$ , at  $555 \text{ cm}^{-1}$  also suggests that it is a dimer. The absence of strong bands between  $450$  and  $750 \text{ cm}^{-1}$  suggests that  $\text{Cr}\{\text{OCH}(\text{}^t\text{Bu})_2\}_4$  is a monomer  $\{\nu(\text{M-O}) = 718 \text{ cm}^{-1}\}$ , and this has been confirmed by an X-ray investigation. The O-Cr-O angles are close to tetrahedral ( $108.8\text{--}112.4^\circ$ ), and the crowding in the molecule prevents coordination oligomerisation. The short Cr-O bond lengths ( $1.771$  and  $1.774 \text{ \AA}$ ) indicate  $\text{O} \rightarrow \text{Cr } p\pi\text{--}d\pi$  bonding, which may account for the rather large Cr-O-C bond angles ( $140.5, 141.1^\circ$ ). Steric effects rather than a non-spherical  $d^2$  shell may be responsible for slight flattening of the coordination tetrahedron. In  $\text{LiCr}\{\text{OCH}(\text{}^t\text{Bu})_2\}_4\cdot\text{thf}$  (4) the tetracoordination of the  $\text{Cr}^{3+}$  is severely



distorted by the formation of a  $\text{CrO}_2\text{Li}$  ring, in which  $\text{Li}^+$  forms two short Li-O bonds ( $1.832$  and  $1.861 \text{ \AA}$ ) and is three coordinate as it is also bonded to the thf molecule ( $\text{Li-O} = 1.943 \text{ \AA}$ ). Previously known chromium(III) alkoxides differ in that they are polymers probably containing  $\text{CrO}_6$  octahedra.

The stable alkyls  $\text{Cr}(2\text{-ad})_4$  and  $\text{Cr}(\text{adme})_4$  (where 2-ad and adme are the 2-adamantyl and 1-adamantylmethyl groups, respectively) have been prepared from  $\text{Cr}(\text{O}^t\text{Bu})_4$  and  $\text{Mg}(2\text{-ad})_2$  or  $\text{Li}(1\text{-adme})$  in light petroleum [28]. Helium(I) UVPES have been reported for  $\text{Cr}(\text{N}^t\text{Pr}_2)_3$  and  $\text{Cr}(\text{NEt}_2)_4$ , and the interpretation of the spectrum of the former was aided by calculations on the model compound  $\text{Cr}(\text{NH}_2)_3$ . Ionisations from the metal molecular orbitals of  $\text{Cr}(\text{N}^t\text{Pr}_2)_3$  are detectable, unlike with  $\text{Cr}\{\text{N}(\text{SiMe}_3)_2\}_3$  [29].

## 6.4 CHROMIUM(III)

### 6.4.1 Complexes of simple ligands

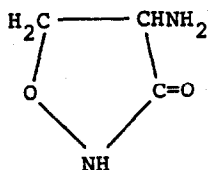
The ammonium salt  $[\text{NH}_4]\text{CrF}_4$ , prepared [30] by hydrothermal high pressure techniques, is antiferromagnetic ( $T_N = 34\text{ K}$ ), and has a structure related to that of  $\text{TiAlF}_4$ . It decomposes thermally to  $\text{CrF}_3$  at  $400^\circ\text{C}$  and  $\text{Cr}_2\text{F}_5$  at  $1000^\circ\text{C}$ . One dimensional magnetic behaviour is exhibited by  $\text{CaCrF}_5$  [31]; the nitrosonium salt  $[\text{NO}]_3[\text{CrF}_6]$  has been characterised by its Raman spectrum [22]; crystals of  $\text{NaCrF}_4$ ,  $\text{Na}_2\text{ZnCrF}_7$ , and  $\text{Rb}_2\text{Cr}_5\text{F}_{17}$  have been flux-grown [32]. Reflectance spectra show [33] that  $[\text{CrF}_3(\text{OH}_2)_3]$  is as written and not as  $[\text{Cr}(\text{OH}_2)_6][\text{CrF}_6]$ . A clear assignment of the two IR active metal-ligand vibrations in  $[\text{M}^{\text{III}}(\text{OH}_2)_6]^{3+}$  has come from comparisons among the mull IR spectra of the caesium alums  $\text{CsM}^{\text{III}}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  ( $\text{M}^{\text{III}} = \text{Al, Ti, V, Cr or Fe}$ ), and other alums [34]. A strongly metal-dependent band found in the region  $500$  to  $600\text{ cm}^{-1}$  was assigned to the antisymmetric  $\text{M}^{\text{III}}\text{-OH}_2$  stretch  $\nu_3$ , and a weakly metal-dependent band in the region  $300$  to  $360\text{ cm}^{-1}$  to the antisymmetric  $\text{M}^{\text{III}}\text{-OH}_2$  bend  $\nu_4$ . These assignments were confirmed by the study of chromium alums enriched in  $^{50}\text{Cr}$  or  $^{53}\text{Cr}$ : only  $\nu_3$  ( $5\text{ cm}^{-1}$ ) and  $\nu_4$  ( $1\text{ cm}^{-1}$ ) were shifted.

The crystal field absorption spectra of metamagnetic  $\text{CrCl}_3$  and ferromagnetic  $\text{CrBr}_3$  have been analysed [35]. X-ray diffraction studies [36] of concentrated chromium(III) solutions in equilibrium conditions give average values of  $1.97$  and  $2.31\text{ \AA}$  for the  $\text{Cr-OH}_2$  and  $\text{Cr-Cl}$  bond distances, respectively, similar to the values from solid state measurements. The free chloride ions are hexahydrated and there is a well defined second coordination sphere around the metal ions.

Anhydrous  $\text{Cr}[\text{ClO}_4]_3$  has been prepared by reaction of perchloric acid with anhydrous  $\text{CrCl}_3$  at  $10^\circ\text{C}$  [6]. Its IR spectrum indicates the presence of bidentate perchlorate groups which may arise from a monomeric structure or a three-dimensional structure with weakly bonded  $[\text{ClO}_4]^-$ . The perchlorate complex  $[\text{ClO}_2]_2[\text{Cr}^{\text{III}}(\text{ClO}_4)_5]$  was also prepared (see p.106). Hydrated and anhydrous chromium(III) perrhenates [37], and the phosphites  $\text{H}_3[\text{Cr}(\text{HPO}_3)_3]$  and  $\text{Cr}_2(\text{HPO}_3)_3 \cdot 7\text{H}_2\text{O}$  [38] have been isolated. The ion  $[\text{Cr}(\text{NH}_3)_5\text{OH}]^{2+}$  reacts rapidly

with dissolved sulphur dioxide in aqueous solution to form the unstable O-bonded sulphito species  $[\text{Cr}(\text{NH}_3)_5\text{OSO}_2]^+$  which has been characterised by its visible absorption spectrum [39].

Some complexes of monodentate O-donor ligands have been isolated including the following:  $[\text{CrL}_6][\text{BF}_4]_3$ , (L = 2,6-lutidine N-oxide) [40],  $[\text{CrL}_4(\text{OCIO}_3)_2][\text{ClO}_4]$ , (L = methyl methylphenylphosphinate,  $\text{MePh}(\text{MeO})\text{PO}$ ) [41], the *fac*- and *mer*-isomers of  $[\text{CrCl}_3\text{L}_3]$ , (L = hexamethylphosphoramide) [42] and  $[\text{Cr}(\text{ccs})_6]\text{X}_3$  and  $[\text{Cr}(\text{ccs})_3\text{Y}_3]$  (where ccs is the broad spectrum antibiotic cycloserine (5) and



(5)

$\text{X} = \text{Cl}, \text{Br}, \text{I}$  and  $\text{Y} = \text{Br}, \text{I}$ ) [43]. The cycloserine is monodentate, through carbonyl oxygen in the first group of compounds and NH of the aminoketo form in the second group, which from the far IR spectra contain coordinated halide and are the meridional isomers.

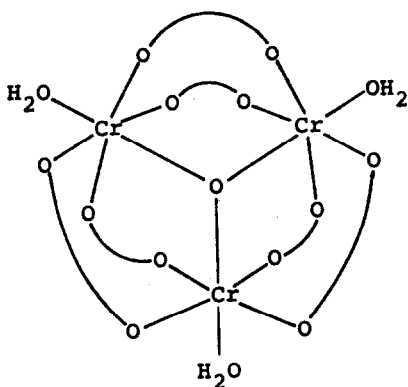
In  $[\text{Cr}(\text{urea})_6][\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]_3 \cdot 3\text{H}_2\text{O}$  the chromium atoms are coordinated to six urea molecules, but the crystal lattice contains two non-crystallographically equivalent chromium complexes [44].

The reaction of  $\text{CrCl}_3$  with anhydrous formic acid gives [45] the basic trinuclear formate  $[\text{Cr}_3\text{O}(\text{O}_2\text{CH})_6(\text{CH}_2)_2(\text{HCO}_2\text{H})](\text{HCO}_2)\cdot\text{HCO}_2\text{H}$ , and not  $[\text{Cr}(\text{O}_2\text{CH})_3]$  as suggested earlier. With bases (L), the compounds  $[\text{Cr}_3\text{O}(\text{O}_2\text{CH})_6(\text{L})_3](\text{O}_2\text{CH})$  are obtained. With carboxylic acids generally in rigorously anhydrous conditions,  $\text{CrCl}_3$  produces the basic trinuclear carboxylates  $[\text{Cr}_3\text{O}(\text{O}_2\text{CR})_6]\text{Cl}$  [46]. Since they have low magnetic moments ( $\sim 2.8 \mu_B$  at room temperature), they are thought to be analogous to the known [47] acetate (6), but it is not obvious which ligand would occupy the apical positions in these carboxylates. However, ammonia adducts can be obtained although their magnetic moments were not given. The reaction of  $\text{CrCl}_3$  with glacial acetic acid was said [48] to give  $[\text{Cr}_3(\text{OH})(\text{O}_2\text{CCH}_3)_8]$ , and this is thought to be because the acid contained some water. The exchange parameters in the trinuclear carboxylates  $[\text{Cr}_3\text{O}(\text{O}_2\text{CR})_6(\text{CH}_2)_3]\text{Cl} \cdot 6\text{H}_2\text{O}$  and  $\text{NO}_3 \cdot \text{CH}_3\text{COOH}$  ( $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$ ) have been determined from their  $\text{N}_2$  laser-excited luminescence spectra [49].

The thermogravimetric behaviour of  $\text{CrCl}_2(\text{O}_2\text{CR}) \cdot \text{thf}$ ,  $\text{CrCl}(\text{O}_2\text{CR})_2$ , and  $\text{Cr}(\text{O}_2\text{CR})_3$  (where  $\text{R} = \text{C}_{11}\text{H}_{23}, \text{C}_{15}\text{H}_{31}, \text{C}_{17}\text{H}_{35}$  or  $\text{C}_{21}\text{H}_{43}$ ) has been analysed [50].

Temperatures below 1 K have become more readily accessible because of the advent of the  $^3\text{He}$ - $^4\text{He}$  dilution refrigerator, and measurements of the magnetic





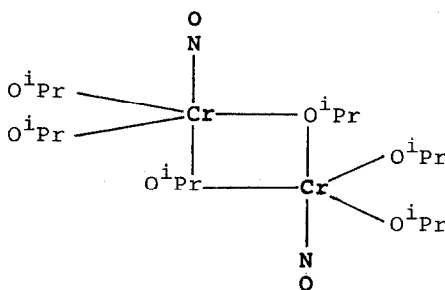
(6)

susceptibilities of single crystals of the new compound  $[\text{Cr}(\text{NH}_3)_6][\text{ClO}_4]_2\text{Br}\cdot\text{CsBr}$  have been used to calculate precisely the zero field splitting [51].

On heating  $[\text{Cr}(\text{urea})_6]\text{Cl}_3$  in the presence of ammonia the isocyanato complex  $[\text{Cr}(\text{NH}_3)_5\text{NCO}]\text{Cl}_2$  can be obtained [52]. The methylamine complex  $[\text{Cr}(\text{NH}_2\text{Me})_5(\text{OH}_2)][\text{NO}_3]_3$  has been isolated but it polymerises in air at room temperature with loss of nitric acid [53]. The hydroxylamine complexes  $[\text{Cr}(\text{NH}_2\text{OH})_3(\text{OH}_2)_2\text{Cl}](\text{OH})_2\cdot\text{EtOH}$ ,  $[\text{Cr}(\text{NH}_2\text{OH})_5\text{OH}]\text{Cl}_2$ ,  $[\text{Cr}(\text{NH}_2\text{OH})_3(\text{OH}_2)(\text{OH})_2]\text{OH}\cdot 1.5\text{H}_2\text{O}$  and  $[\text{Cr}(\text{NH}_2\text{OH})_4(\text{SO}_4\text{Cl})\cdot 2\text{H}_2\text{O}]$  have been reported [54]. Electronic spectroscopy shows that the isothiocyanato-species  $[\text{Cr}(\text{NCS})_6]^{3-}$  is formed from  $\text{Cr}^{\text{III}}$  in a potassium thiocyanate melt [55]. The thermal decomposition of  $[\text{Co}(\text{OH}_2)(\text{NH}_3)_5][\text{Cr}(\text{NCS})_6]$  first produces  $[(\text{H}_3\text{N})_5\text{Co}(\text{SCN})_3\text{Cr}(\text{NCS})_3]$  and then amide and imide bridged linear polymers [56]. Some cyano-bridged compounds  $\text{A}[\text{cis}-(\text{en})_2\text{FCrN}(\text{M}(\text{III}))(\text{CN})_5]\text{aq}$ . (where  $\text{A} = \text{Na}, \text{K}, \text{NH}_4$  and  $\text{M}(\text{III}) = \text{Co}, \text{Cr}$ ) have been prepared [57] from  $\text{trans}-[\text{CrF}(\text{OH}_2)(\text{en})_2]^{2+}$  and  $[\text{M}(\text{CN})_6]^{3-}$ . When  $\text{M}(\text{III}) = \text{Cr}$ , the compounds are antiferromagnetic. Some monoamino acid complexes have been prepared by substitution of the chloro-ligand in  $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  [58].

Chromium(III) differs from molybdenum(III) in not forming dinuclear alkoxides of the type  $\text{M}_2(\text{OR})_6$  containing metal-metal triple bonds, but it does form [59] related nitrosyls  $\text{Cr}_2(\text{O}^i\text{Pr})_6(\text{NO})_2$  and, in solution,  $\text{Cr}(\text{O}^i\text{Pr})_3(\text{NO})\text{L}$  (where  $\text{L} = \text{NH}_3$ , pyridine, or 2,4-lutidine). With the bulky *tert*-butoxy ligand, a monomer  $\text{Cr}(\text{O}^t\text{Bu})_3\text{NO}$  has been isolated. Dinuclear molybdenum nitrosyls  $\text{Mo}_2(\text{OR})_6(\text{NO})_2$  are obtained by reaction of  $\text{Mo}_2(\text{OR})_6$  with nitric oxide, but  $\text{Cr}_2(\text{O}^i\text{Pr})_6(\text{NO})_2$  was obtained from  $\text{Cr}(\text{N}^i\text{Pr}_2)_3$  by reaction with nitric oxide to give  $\text{Cr}(\text{N}^i\text{Pr}_2)_3\text{NO}$ , which was then heated with isopropyl alcohol. The air sensitive dinitrosyl compound is diamagnetic, from cryoscopy is dimeric in solution, and there is a weak molecular ion  $[\text{Cr}_2(\text{O}^i\text{Pr})_6(\text{NO})_2]^+$  in its mass

spectrum. A complete structural determination was not possible because the brick red crystals soon decomposed in the X-ray beam, but as the crystal data were similar to those for  $\text{Mo}_2(\text{O}^i\text{Pr})_6(\text{NO})_2$  the same structure (7) has been

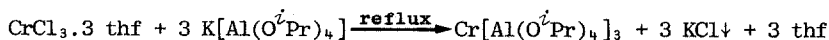


(7)

assigned in which each chromium atom is in a trigonal bipyramidal environment.

The values of  $\nu(\text{NO})$  for  $\text{Cr}(\text{N}^i\text{Pr}_2)_3\text{NO}$ ,  $\text{Cr}(\text{O}^t\text{Bu})_3\text{NO}$  and  $\text{Cr}_2(\text{O}^i\text{Pr})_6(\text{NO})_2$  are respectively 1641, 1707 and  $1720\text{ cm}^{-1}$ . In these and the related molybdenum and tungsten compounds, all of which have the formal oxidation state II, the M-N-O groups are linear, and the degree of back bonding increases as the electronegativity decreases and the  $\pi$ -donor ability increases from OR to  $\text{NR}_2$ . The degree of back bonding also increases down the group  $\text{Cr} < \text{Mo} < \text{W}$ . The low temperature limiting  $^1\text{H}$  NMR spectrum of  $\text{Cr}_2(\text{O}^i\text{Pr})_6(\text{NO})_2$  is consistent with structure (7) in solution. Above  $80^\circ\text{C}$  there is rapid exchange on the NMR time scale between the bridging and terminal isopropoxy ligands, as found for  $\text{Mo}_2(\text{O}^i\text{Pr})_6(\text{NO})_2$ . The bridge  $\rightleftharpoons$  terminal exchange is believed to be intramolecular, the first step being the formation of a monobridged dimer with one four coordinate chromium atom through separation of the  $\text{O}^i\text{Pr}$  group *trans* to the NO group.  $^1\text{H}$  NMR studies show that in toluene the mixed metal dimer  $\text{CrMo}(\text{O}^i\text{Pr})_6(\text{NO})_2$  forms in equilibrium from equimolar amounts of the homonuclear dimers. These studies also demonstrate the equilibrium formation of the base adducts  $\text{Cr}(\text{O}^i\text{Pr})_3(\text{NO})\text{L}$ , but solids could not be isolated because L is lost and  $\text{Cr}_2(\text{O}^i\text{Pr})_6(\text{NO})_2$  reformed on removal of the solvent.

The double isopropoxide  $\text{Cr}[\text{Al}(\text{O}^i\text{Pr})_4]_3$  is a green liquid which, unlike simple isopropoxides, is soluble in organic liquids and can be distilled in vacuum [60]. The  $[\text{Al}(\text{O}^i\text{Pr})_4]^-$  ions act as bidentate ligands and the complex is prepared as follows:-



The alkoxy  $\beta$ -diketonate complexes  $[\text{Cr}(\text{OEt})_2\text{L}]$  and  $[\text{Cr}(\text{OEt})\text{L}_2]$  (where

HL = acetylacetone, benzoylacetone or thenoyltrifluoroacetone), and  $[\text{Cr}(\text{OMe})(\text{acac})_2]$  have been characterised [61].

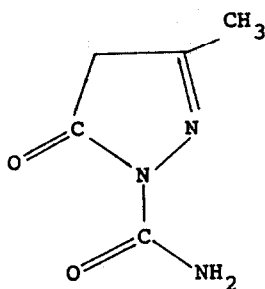
#### 6.4.2 Complexes of bidentate ligands

The electronic absorption spectra of  $\text{CrL}_3$  (HL = pentane-2,4-dionato or other  $\beta$ -diketones) in the gas phase are identical [62] with those in solution. The pairs of chromium atoms in di- $\mu$ -diphenylphosphinatotetrakis(pentane-2,4-dionato)dichromium(III) are held by two  $-\text{O}-\text{PPh}_2-\text{O}-$  bridges forming a puckered, eight-membered ring [63]. Mass spectra at normal and elevated pressures of  $[\text{Cr}(\text{dpm})_3]$  {dpmH = dipivaloylmethane (2,2,6,6-tetramethyl-3,5-heptanedione)} show that, as with similar transition metal complexes, at higher pressures the primary positive fragment ions, e.g.  $[\text{Cr}(\text{dpm})_3]^+$ , formed at low pressure, undergo bimolecular reaction with the neutral mononuclear complex to form heavier polynuclear ions (mainly  $\text{Cr}_2\text{L}_4^+$  and  $\text{Cr}_2\text{L}_5^+$  for  $\text{CrL}_3$ ) with unfragmented ligands [64]. This behaviour is like that observed for chelates of less hindered  $\beta$ -diketonate ligands. The *t*-butyl groups hinder but do not prevent gaseous ion/neutral molecule association of octahedral (and tetrahedral) complexes, and do not affect the association of planar species. Charge transfer between fragment ions and the neutral complex, producing  $[\text{Cr}(\text{dpm})_3]^+$ , competes with association. This has not been observed with  $[\text{Cr}(\text{acac})_3]$ . Ligand field parameters have been reported [65] for a number of  $\beta$ -diketonate complexes.

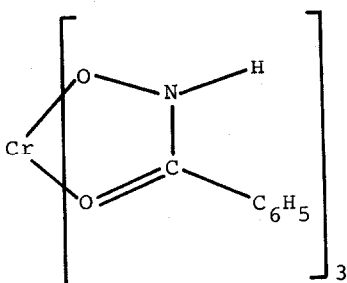
Thermal decomposition of  $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$  takes place in five steps, involving the formation of carbonato-complexes and finally the mixed oxides [66]. Other dicarboxylates have also been investigated by thermal analysis [67]. The disappearance of the  $-\text{CH}_2-$  wagging and bending bands on reaction of bromine in diethyl ether or of *N*-bromosuccinimide in chloroform with the tris(malonato)chromate(III) ion, shows that  $[\text{Cr}\{(\text{O}_2\text{C})_2\text{CHBr}\}_3]^{3-}$  is obtained [68]. The same product is obtained by reaction of monobromomalonic acid with potassium dichromate. The magnetic and spectroscopic properties of  $\text{Cr}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cr}_2(\text{C}_2\text{O}_4)_3 \cdot 4\text{N}_2\text{H}_4 \cdot 4\text{H}_2\text{O}$  and  $\text{Cr}_2(\text{C}_2\text{O}_4)_3 \cdot 7\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  have been discussed [69].

The complex  $[\text{CrL}_3] \cdot 4\text{H}_2\text{O}$  (where LH = 1-carbamido-3-methylpyrazol-5-one (8)) has been prepared by reaction of NaL with  $[\text{Cr}(\text{urea})_6]\text{Cl}_3 \cdot 6\text{H}_2\text{O}$  [70].

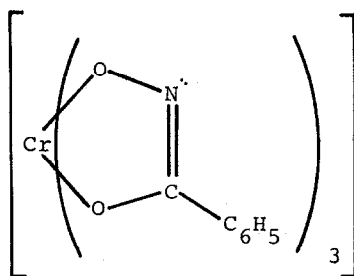
*N*-Unsubstituted tris(hydroxamato)metal complexes, for example (9), can be deprotonated in strong acid to give the anionic tris(hydroximato)metal complexes (10). The *cis*-tris(benzohydroximato)chromate(III) salt  $\text{Na}_3[\text{Cr}(\text{C}_7\text{H}_5\text{NO}_2)_3] \cdot \text{NaI} \cdot \text{NaOH} \cdot 9\text{H}_2\text{O} \cdot 3\text{CH}_3\text{OH} \cdot \text{C}_2\text{H}_5\text{OH}$  and the *trans* salt  $\text{Na}_3[\text{Cr}(\text{C}_7\text{H}_5\text{NO}_2)_3] \cdot 8\text{H}_2\text{O} \cdot \text{C}_2\text{H}_5\text{OH}$  have been obtained in this way, but from the hydroxamato-complexes of the opposite geometry [71]. Small changes in bond



(8)



(9)



(10)

lengths occur on the loss of the proton and these are rigid, octahedral complexes, in which the hydroximate ligand has substantial negative charge on both oxygen atoms and nearly full formation of a C=N double bond in the ring.

The formulation of neutral tris(*o*-quinone) complexes of chromium(III) is uncertain (see 1979 review). It has been confirmed [72] that  $[\text{Cr}(3,5\text{-di-tert-butyl-1,2-benzoquinone})]$  is diamagnetic in  $\text{CH}_2\text{Cl}_2$ , and the IR spectrum is compatible with the presence of coordinated *o*-semiquinone (sq) rather than *o*-quinone or catecholate, so it appears that it is  $[\text{Cr}^{\text{III}}(\text{sq})_3]$  with strong coupling between the metal and semiquinone electrons. Four new complexes of 2,2'-bipyridine-*N,N'*-dioxide (bpdo) and 3,3'-dimethyl-2,2'-bipyridine-*N,N'*-dioxide (dmbpdo), which form skew seven-membered rings on coordination, have been prepared [73]. These contain mixed ligands, and are the perchlorates of  $[\text{Cr}(\text{L})_2(\text{bpdo})]^{3+}$  and  $[\text{Cr}(\text{L})_2(\text{dmbpdo})]^{3+}$  {L = bipy or phen}. Each complex gave only one (resolved chromatographically) of two possible pairs of enantiomers. From the CD spectra, molecular models, and the recovery of optically active free dmbpdo ligand, it was decided that the enantiomeric pairs consist of  $\Delta(\delta)$  and  $\Lambda(\lambda)$  isomers, with the skew dioxide chelates in the *ob* configuration. Steric interactions between the hydrogen atoms of the

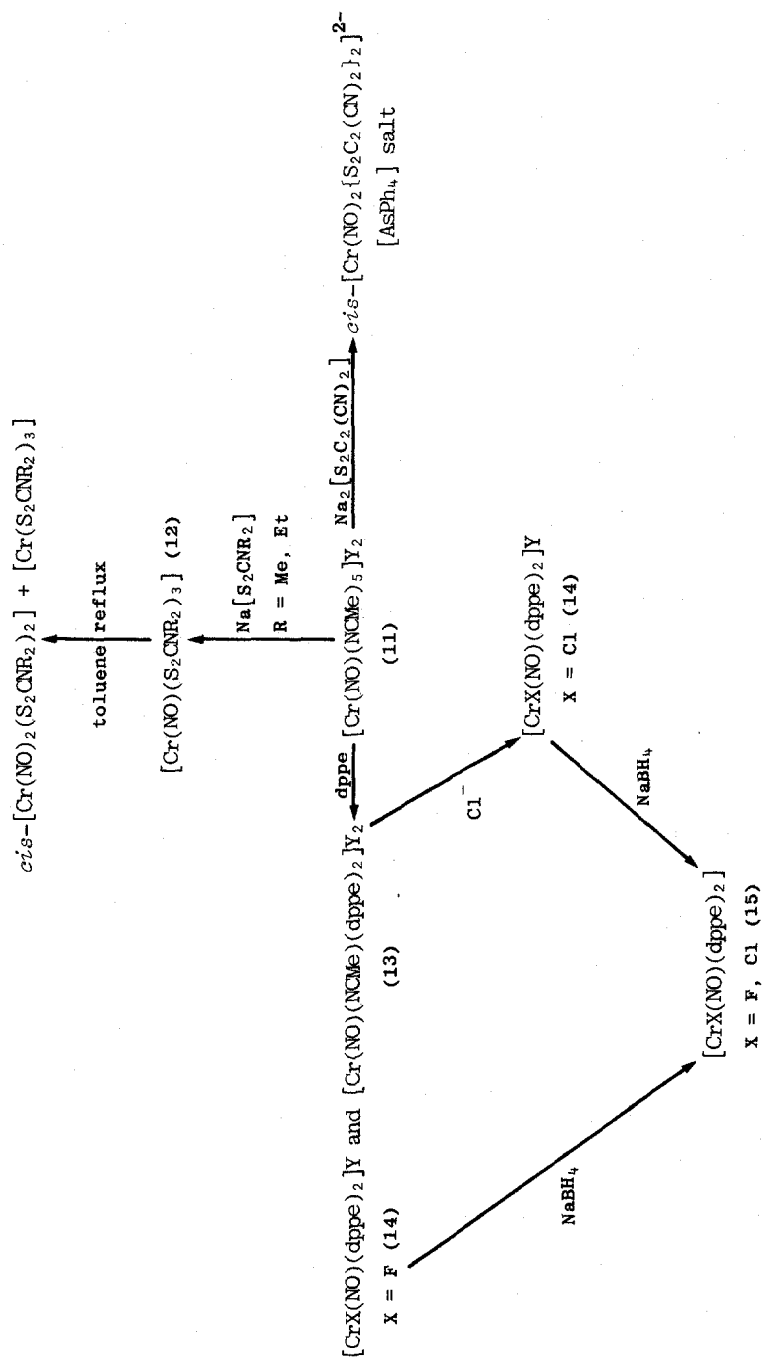
dioxide and  $\alpha$ -diimine ligands seem to prevent the formation of *lel* enantiomers.

When diisopropyl methylphosphonate  $\{(O^iPr)_2CH_3PO = \text{dimp}\}$  is refluxed in di-*n*-butylether with  $Cr(CO)_6$ , aerial oxidation produces the previously characterised polymeric chromium(III) complex of isopropyl methylphosphinate (imp),  $[Cr\{OP(CH_3)(O^iPr)O\}_3]_n$  [74]. Reaction of  $Cr(CO)_6$  with a large excess of dimp under dinitrogen, however, affords the polymer  $[Cr(\text{imp})(\text{mp})]_n$  (mp = methylphosphate) which has a subnormal magnetic moment of  $3.34 \mu_B$  at room temperature.

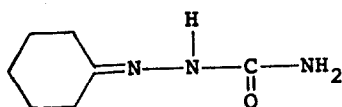
Chromium (and molybdenum) hexacarbonyls in ethanenitrile react with nitrosonium salts  $NOY$   $\{Y = BF_4 \text{ or } PF_6\}$  to give the paramagnetic complexes  $[M(NO)(NOMe)_5]Y_2$  (11), which readily undergo nitrile substitution reactions with anionic and neutral ligands [75]. The reactions of the air sensitive chromium complex are summarised in Scheme I. The redox properties of complexes (11) to (15) have also been studied by cyclic voltammetry, and the mutually *trans* positions of dppe in (13) to (15) have been verified by  $^{31}P$  NMR and ESR spectroscopy and, in the case of (15;  $X = F$ ), by X-ray crystallography also. Compound (12),  $R = Me$ , is seven coordinate, which is rare in chromium chemistry, with a pentagonal bipyramidal structure and a linear nitrosyl ligand in the axial position. The fluoro ligands in  $[CrF(NO)(dppe)_2]Y$  and  $[CrF(NO)(dppe)_2]$  must arise from decomposition of the anions (see also p. 121).

The UVES spectrum of  $Cr(S_2PET_2)_3$  has been assigned [76] in the low energy region, and the electrochemical behaviour of the dithiobenzoates,  $[Cr(S_2CC_6H_4R)_3]$  ( $R = H, Me, MeO, Me_2N$ , or  $Et_2N$ ), has been studied [77]. Published data on the volatility of complexes of the transition metals including chromium with bidentate sulphur donor and sulphur-oxygen donor ligands have been summarised [78]. Some complexes of alkynyl dithiophosphinic acids have been obtained, *e.g.*  $[Cr(S_2PCH_3(C\equiv CCH_3))_3]$  [79]. The replacement of water by thiourea derivatives in solutions of dithiocarbamate complexes of the type  $Cr[NO(\text{dtc})_2(OH_2)]$  has been followed by EPR measurements [80]. It appears that the thiourea derivatives arise from decomposition of the dithiocarbamate ligands.

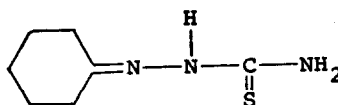
The addition of an excess of monoethanolamine (L) or diethanolamine (L') to solutions of  $CrCl_3 \cdot 6H_2O$  and an amino acid in dmf gave [81]  $[CrALCl(OH)]_2L$  ( $HA = \alpha$ - or  $\beta$ -alanine),  $[CrA'L_2Cl(OH)_2]_2 \cdot 2L$  ( $HA' = \alpha$ -amino-octanoic acid), and  $[CrAL'Cl(OH)]_2$  ( $HA = \alpha$ -alanine). Pyridine-2-aldoxime (pax) forms [82] the complexes  $[Cr(\text{pax})_3]Cl_3 \cdot 3H_2O$ ,  $[Cr(\text{pax})_2X_2][ClO_4]$  ( $X = F, Cl$ , or  $Br$ ) and  $[Cr(\text{pax})_2(OH_2)_3]Br_2 \cdot H_2O$ . IR spectra show that the neutral ligand is present, and 6-methylpyridine-2-aldoxime gives [83] compounds analogous to the last two types which have *trans*-structures. Cyclohexanone semicarbazone (16) and cyclohexanone thiosemicarbazone (17) bond through the hydrazinic *N* and *O(S)* atoms in  $[Cr(\text{ligand})_2X_2]X$ , where  $X = Cl$  or  $NO_3$  [84]. A series of octahedral



SCHEME I: Reactions of  $[Cr(NO)(NCMe)_5]Y_2$  ( $Y = BF_4$  or  $PF_6$ ) [75].

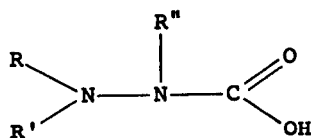


(16)



(17)

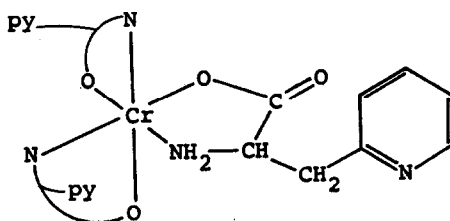
complexes typical of chromium(III),  $[\text{Cr}(\text{Cz})_3]$ , has been obtained from *N*-substituted carbazic acids (18). N(3) and O are coordinated except perhaps



(18)

when  $R = \text{Ph}$  [85]. The stability constants for complexation of 2-pyridyl-methanamine in dilute aqueous solution at  $25^\circ\text{C}$  are  $\log K_1$ , 5.65,  $\log K_2$  3.16,  $\log K_3$  2.21 [86]. Tris(diallylisocyanurato)chromium(III) is reported [87] to have a magnetic moment of  $3.05 \mu_B$ .

Investigations into the stereoselective chelation of  $\beta$ -(2-pyridyl)- $\alpha$ -alanine (pyalaH) to transition metal ions have been extended to chromium(III) [88]. From aqueous solutions of  $\text{Cr}^{3+}$  and D-pyalaH to which  $[\text{NBu}_4]\text{OH}$  has been added, pink crystals of *A-fac*- $[\text{Cr}(\text{D-pyala})_3] \cdot \text{H}_2\text{O}$  (19) have been isolated. The



(19)

structural assignment is based on IR, visible, and CD spectra. It appears to be in equilibrium with purple  $[\text{Cr}(\text{D-pyala})_2]^+$  in aqueous solution, but separates preferentially because of lower solubility. The cation  $[\text{Cr}(\text{D-pyala})_2]^+$  was separated by column chromatography, but salts could not be isolated. Its properties are as expected for a *trans*- $\text{CrN}_2\text{O}_2$  chromophore. The configurations of the complex ions in  $(+)-[\text{Cr}(\text{en})_3]\text{Br}_3 \cdot 0.6\text{H}_2\text{O}$  are  $\Lambda(\delta\delta\lambda)$  and it is not isostructural with  $(+)-[\text{Cr}(\text{en})_3]\text{Cl}_3$  [89]. The structure of the orthorhombic form of  $[(+)\text{Co}(\text{en})_3(-)\text{Cr}(\text{en})_3][\text{SCN}]_6$  has been published [90], and the 25 known

tris(ethylenediamine) complexes  $[M(en)_3]X_3$ , in which  $M = Cr(III)$ ,  $Co(III)$  or  $Rh(III)$ , and  $X = Cl^-$ ,  $Br^-$ ,  $\frac{1}{3}[Ni(CN)_5]^{3-}$  etc., have structures which can be described in terms of the packing of the complex cations taken as spheres of radius  $4 \text{ \AA}$  [91].

Some new geometrical isomers of bis(1,3-diaminopropane)chromium(III) complexes have been prepared [92] from the appropriate dichloro or diaqua complexes. These include *cis*- and *trans*- $[Cr(ONO)_2(1,3-pn)_2][ClO_4]$  and *cis*- and *trans*- $[Cr(N_3)_2(1,3-pn)_2][ClO_4]$ . The *cis*-nitrito complex could not be resolved, but  $(+)\text{-}_{\text{meso-cis}}-[Cr(N_3)_2(1,3-pn)_2][ClO_4]$  has been assigned the  $\Delta$  configuration, as have the known complexes  $(+)\text{-}_{\text{meso-cis}}-[Cr(NCS)_2(1,3-pn)_2][SCN]$  and  $(-)\text{-}_{\text{meso-cis}}-[Cr(N_3)_2(en)_2][ClO_4]$ . IR evidence supports the isothiocyanato- and nitrito- formulations, but earlier IR criteria for distinguishing *cis*- and *trans*- isomers do not work well. From CD spectra in the region of an intraligand absorption band localised on the nitrito ligands of  $\Lambda\text{-cis}$ - $[Cr(ONO)_2(en)_2][ClO_4]$ , *trans*- $[Cr(ONO)_2(R\text{-}1,2\text{-}pn)_2][ClO_4]$  and *trans*- $[Cr(ONO)_2(R,R\text{-}ptn)_2][ClO_4]$  (where  $R\text{-}1,2\text{-}pn$  and  $R,R\text{-}ptn$  are  $(R)\text{-}1,2$ -diaminopropane and  $(R,R)\text{-}2,4$ -pentanediamine, respectively), the chirality due to the rotational isomerism of the unidentate nitrito ligands has been substantiated [93]. The CD spectra of single crystals of  $(-)\text{-}_D-[Cr(en)_3]Cl_3 \cdot 2H_2O$  and  $[(+)\text{-}_D-Cr(en)_3-(+)\text{-}_D-Rh(en)_3]Cl_6 \cdot 6H_2O$  have been analysed [94].

The isocyano compound  $[Cr(en)_2(NC)_2Ag][ClO_4]_2$  has been obtained from *cis*- $[Cr(en)_2(CN)_2][ClO_4]$  [95] by reaction with silver nitrate, followed by the addition of sodium perchlorate.

The new complexes  $[Cr(en)_2(SCH_2CH_2CO_2)][ClO_4]$  and  $[Cr(en)_2(SC(CH_3)_2CO_2)][ClO_4]$  have been synthesised [96] by the reduction of the appropriate disulphide with chromium(II)-ethylenediamine perchlorate. Oxidation of these and other thiolatochromium(III) cations, with hydrogen peroxide in dilute perchloric acid, cleaves the Cr-S bond and produces a variety of incompletely characterised products, some containing metal and some not. The corresponding cobalt(III) complexes undergo 2-equivalent oxidation to isolable S-bonded sulphenato  $(Co-S(O)R)$ , and then sulphinato  $(Co-S(O)_2R)$  complexes; it is assumed that the chromium(III)-sulphenato intermediates are unstable through weaker  $\pi$ -bonding to sulphur than in the cobalt(III) complexes. The kinetic evidence suggests that thiols coordinated to cobalt(III) are slightly better nucleophiles than those coordinated to chromium(III).

It is known that the thermal deamination of  $[Cr(en)_3][NCS]_3$  gives *trans*- $[Cr(en)_2(NCS)_2][NCS]$  and that this is catalysed by  $[NH_4][SCN]$ , although with a relatively large amount of catalyst the product is the *cis*-isomer. Both  $\Delta H$  and activation energy have now been found [97] to change in a continuous way with amount of catalyst, when this is from 2 to 8 mole percent of the amount of complex, suggesting that a mixture of *cis*- and *trans*-isomers results.  $[NH_4]Cl$



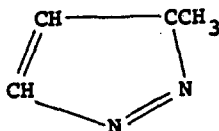
catalyses the deamination of  $[\text{Cr}(\text{en})_3]\text{Cl}_3$ , but this yields *cis*- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ . The amount of  $[\text{NH}_4]\text{Cl}$  does not alter the nature of the product, and it is a less effective catalyst than  $[\text{NH}_4][\text{SCN}]$  [98], possibly because SCN bridges more readily.

The thermal *trans* to *cis* isomerisation of *trans*- $[\text{Cr}(\text{en})_2\text{Br}_2]\text{Br}\cdot\text{H}_2\text{O}$  (I) and *cis* to *trans* isomerisation of *cis*- $[\text{Cr}(1,3\text{-pn})_2\text{Br}_2]\text{Br}\cdot 2\text{H}_2\text{O}$  (II) have been studied [99] by derivatographic and isothermal methods. In both cases isomerisation (activation energies I, 420, and II, 275  $\text{kJ mol}^{-1}$ ) took place after dehydration (I, 61, and II, 38  $\text{kJ mol}^{-1}$ ).

#### 6.4.3 Complexes containing amine and fluoride ligands

A rapid synthesis of  $[\text{Cr}(\text{en})\text{F}_2(\text{OH}_2)_2]\text{Cl}$ , starting from  $\text{CrF}_3\cdot 3.5\text{H}_2\text{O}$  and ethylenediamine *via* the easily prepared compound  $[\text{Cr}(\text{en})_2\text{F}_2][\text{Cr}(\text{en})\text{F}_4]$ , has been devised [100] and a short review of the reactivity and methods of preparation of fluoro-containing complexes of chromium(III) has appeared [101]. Most of the complexes discussed were *cis*- or *trans*-difluoro compounds, with two molecules of a bidentate amine such as ethylenediamine, 1,2-propanediamine or 2,2'-bipyridyl. Besides  $\text{CrF}_3\cdot 3.5\text{H}_2\text{O}$ ,  $\text{CrF}_2$  suspended in dry ethereal HF,  $\text{CrCl}_3\cdot 6\text{H}_2\text{O}$  in 48% HF, and *trans*- $[\text{Cr}(\text{py})_4\text{F}_2]^+$  were used in reactions with various amines. Other methods described included, the reaction of  $[\text{Cr}(\text{bipy})_2(\text{C}_2\text{O}_4)]\text{Cl}$  with liquid HF to give *cis*- $[\text{Cr}(\text{bipy})_2\text{F}_2]^+$ , chloride abstraction from *cis*- $[\text{Cr}(\text{AA})_2\text{Cl}_2]^+$  with  $\text{HgF}_2$  in liquid HF, and thermal deamination of  $[\text{Cr}(\text{AA})_3]\text{X}_3$  in an  $[\text{NH}_4]$  matrix. Fluoroaqua complexes of the type  $[\text{Cr}(\text{en})_2\text{F}(\text{OH}_2)]\text{X}_2$ , made by acid hydrolysis of the difluoro compounds, can be used in a variety of syntheses, for example *cis*- $[\text{Cr}(\text{en})_2\text{FX}]\text{X}$  (X = Cl, Br, I or SCN) have been prepared from *trans*- $[\text{Cr}(\text{en})_2\text{F}(\text{OH}_2)]\text{X}_2$  by thermal dehydration. The preparations of complexes containing mixed amines, and anionic complexes, are also discussed, and the results of kinetic studies and IR and electronic spectroscopy summarised.

The use of tetrafluoroborate can lead to the unexpected production of fluoro-complexes. For example, on treatment of  $\text{Cr}^{\text{II}}(\text{BF}_4)_2$  with 3(5)-methylpyrazole (5Mepz) (20) the chromium(III) compound  $[\text{Cr}(\text{5Mepz})_4\text{F}_2][\text{BF}_4]$  was



(20)

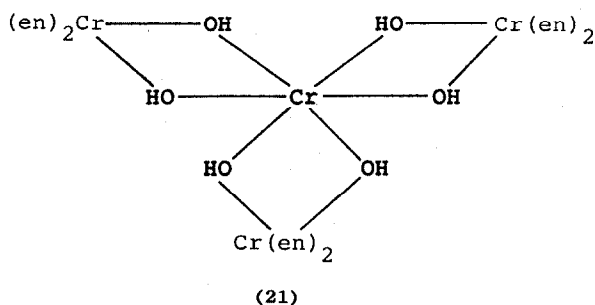
produced [102] (see also p.117). This contains *trans*-octahedral cations in

which the Cr-F bond distance is 1.960 Å.

#### 6.4.4 Hydroxo-bridged complexes

In *cis*-[(NH<sub>3</sub>)<sub>5</sub>Cr(OH)Cr(NH<sub>3</sub>)<sub>4</sub>(OH)][S<sub>2</sub>O<sub>6</sub>]<sub>2</sub>·3H<sub>2</sub>O, the geometry around each chromium atom in the dimeric cation is approximately octahedral and the Cr-OH-Cr bridging angle is 142.8°. The complex is antiferromagnetic, and the magnetic data (4.290 K) fit reasonably the Van Vleck model with a triplet energy of ~21 cm<sup>-1</sup> and *g* close to 2 [103]. Similar results were obtained for the chloride dihydrate, although there are slight differences from earlier values (19 to 25 cm<sup>-1</sup>). More elaborate models did not improve the fits significantly. The bridging angle is considerably smaller than the various values (154 to 166°) reported for [(NH<sub>3</sub>)<sub>5</sub>Cr(OH)Cr(NH<sub>3</sub>)<sub>5</sub>]Cl<sub>5</sub>.aq, which shows greater magnetic interaction, emphasising the angular dependence. Earlier preparative procedures were modified to prevent the production of monomeric impurities which could affect the magnetic data.

The ageing of aqueous solutions of the sulphamate [Cr(en)<sub>3</sub>][SO<sub>3</sub>NH<sub>2</sub>]<sub>3</sub> produces the hydroxo-bridged species [Cr<sub>2</sub>(OH)<sub>3</sub>(en)<sub>3</sub>][SO<sub>3</sub>NH<sub>2</sub>]<sub>3</sub>·3H<sub>2</sub>O [104], and the two complexes are in equilibrium in aqueous solution. The unusual tri-μ-hydroxo formulation was based mainly on IR evidence. The new *racemic* binuclear cations Δ,Δ-Λ,Λ-[(en)<sub>2</sub>Cr(OH)<sub>2</sub>Cr(en)<sub>2</sub>]<sup>4+</sup> and Λ,Λ-Δ,Δ-[(H<sub>2</sub>O)(en)<sub>2</sub>Cr(OH)Cr(en)<sub>2</sub>(OH)]<sup>4+</sup> have been prepared from the *meso* isomer Δ,Λ-[(en)<sub>2</sub>Cr(OH)<sub>2</sub>Cr(en)<sub>2</sub>]<sup>4+</sup> as the bromide or perchlorate salt [105]. The rapid equilibration between the two cations has been studied and, on heating, the solid bromides form the *meso* diol. The complex salt [Cr{(OH)<sub>2</sub>Cr(en)<sub>2</sub>}]<sub>3</sub>[S<sub>2</sub>O<sub>6</sub>]<sub>3</sub>·8H<sub>2</sub>O has a monoclinic unit cell almost identical with that of the corresponding cobalt(III) complex in which (21) the four metal atoms lie in a plane, and the apical atoms are equidistant



from the central one [106]. The dominating antiferromagnetic interaction (*J* = 16.2 cm<sup>-1</sup>) is between the central and each of the peripheral chromium atoms, and an *S* = 3 level lies lowest. If the bond distances are the same as in the cobalt(III) compound, the Cr-Cr bond distance and Cr-O-Cr bond angle are

smaller than in any dihydroxo-bridged dinuclear  $\text{Cr}^{\text{III}}$  complex, except the new complex  $[\text{Cr}(\text{EDDA})(\text{OH})_2 \cdot 4\text{H}_2\text{O}]$  mentioned below, but it was not possible to decide whether direct exchange or superexchange was dominant. The dimer, di- $\mu$ -hydroxo-bis[(ethylenediamine)malonatochromium(III)], has a structure similar to those of related complexes, although it contains a slightly shorter Cr-Cr bond, 3.003 Å, than the bis(malonato), 3.05 Å, and bis(ethylenediamine), 3.03 Å, complexes [107].

When an alkaline solution of  $[\text{Cr}_2\text{L}_2(\text{OH})_2(\text{OH})_2][\text{ClO}_4]_4$  (where L = 1,4,7-triazacyclononane) is exposed to  $\text{CO}_2$ , a  $\mu$ -carbonato-complex is formed slowly and the salts  $[\text{Cr}_2\text{L}_2(\text{OH})_2(\text{CO}_3)][\text{ClO}_4]_2 \cdot 3\text{H}_2\text{O}$  and  $[\text{Cr}_2\text{L}_2(\text{OH})_2(\text{CO}_3)]\text{I}_2 \cdot 3\text{H}_2\text{O}$  have been isolated [108]. The carbonato-complexes can be obtained more rapidly by the use of aqueous sodium carbonate at 70 °C. The iodide loses two water molecules easily and the  $\mu$ -carbonato-di- $\mu$ -hydroxo structure of the monohydrate has been confirmed crystallographically. Well-defined carbonato-complexes of chromium(III) have not been described previously.

Ethylenediamine-*N,N'*-diacetic acid ( $\text{EDDAH}_2$ ) forms the dimer  $[\text{Cr}(\text{EDDA})(\text{OH})]_2 \cdot 4\text{H}_2\text{O}$  [109]. The geometry around each metal atom is roughly octahedral, with the tetradentate EDDA assuming an  $\alpha$ -*cis* configuration in which the complex possesses two out-of-plane glycinate (R) rings and the backbone ethylenediamine ring (E). The bridging unit is strictly planar, there is an inversion centre, and the Cr-Cr separation is 2.950 Å and the Cr-O-Cr bridging angle 97.6°.

#### 6.4.5 Photochemistry

Irradiation (at 254 nm) of the binuclear rhodo complex  $[\text{Cr}(\text{NH}_3)_5\text{OHCr}(\text{NH}_3)_5]\text{Cl}_5 \cdot n\text{H}_2\text{O}$  causes [110] excitation into the charge transfer region, which obscures the  ${}^4T_1(\text{P})$  level, and leads to bridge cleavage (quantum yield,  $\phi = 0.02$ ) to produce  $[\text{Cr}(\text{NH}_3)_5(\text{OH}_2)]^{3+}$ , accompanied by formation of the aqua-erythro- $[\text{Cr}(\text{NH}_3)_5\text{OHCr}(\text{NH}_3)_4(\text{OH}_2)]^{5+}$  ( $\phi = 0.179$ ) and chloro-erythro- $[\text{Cr}(\text{NH}_3)_5\text{OHCr}(\text{NH}_3)_4\text{Cl}]^{4+}$  ( $\phi = 0.087$ ) complexes. Thermal reaction of the binuclear rhodo complex in acid also cleaves the bridge, but photochemical excitation into the  ${}^4T_{2g}$  and  ${}^4T_{1g}(\text{F})$  levels does not. Thus, the thermal reaction mode becomes more prominent on excitation into the charge transfer region, as happens with other chromium(III) complexes.

There is much information on the photochemical behaviour of  $[\text{Cr}(\text{NH}_3)_5\text{X}]^{2+}$  species in which X (F, Cl, Br, NCS, CN or  $\text{O}_2\text{CR}$ ) is lower in the spectrochemical series than ammonia. The cyano species  $[\text{Cr}(\text{NH}_3)_5(\text{CN})]^{2+}$  has now [111] been synthesised by cyanide anation of  $[\text{Cr}(\text{NH}_3)_5(\text{Me}_2\text{SO})]^{3+}$  in dmsO, and isolated as the perchlorate salt. In the cyano-complex the stronger average ligand field lies along the  $z(\text{NH}_3 \dots \text{CN}^-)$  axis, so that the  ${}^4B_2$  level lies below the  ${}^4E$  level (both derived from  ${}^4T_2(\text{O}_h)$ ), the reverse ordering from that in the other

acido-complexes which leads to bond weakening in the  $z$  direction. Excitation to the  ${}^4B_2$  level introduces antibonding electron density into the  $d_{x^2-y^2}$  orbital, so that preferential bond weakening would now be expected in the equatorial plane, and it has been found [112] that ligand field (LF) irradiation of  $[\text{Cr}(\text{NH}_3)_5(\text{CN})]^{2+}$  in aqueous acid leads to exclusive aquation of  $\text{NH}_3$ , but only  $\text{CN}^-$  is released thermally primarily through an acid-catalysed pathway. The quantum yields ( $\phi = 0.33$ ) are wavelength independent throughout the LF region. The photo-product  $[\text{Cr}(\text{NH}_3)_4(\text{OH}_2)(\text{CN})]^{2+}$  consists of *cis* and *trans* isomers in 2:1 ratio and it is suggested that equatorial photoaquation occurs with partial stereochemical change. On charge transfer (CT) excitation also, ammonia loss is the only photoreaction with similar  $\phi$ 's and product distribution, indicating efficient conversion of CT (metal-to-ligand) states to LF ones.

The luminescence and  ${}^4A_2 \rightarrow {}^2E, {}^2T_1$  absorption spectra of  $[\text{Cr}(\text{urea})_6]\text{X}_3 \cdot 3\text{H}_2\text{O}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ),  $[\text{Cr}(\text{urea})_6][\text{NO}_3]_3$  [113],  $[\text{Cr}(\text{urea})_6]\text{I}_3$ , and  $[\text{Al}(\text{urea})_6]\text{I}_3$  doped with  $[\text{Cr}(\text{urea})_6]^{3+}$  [114], have been re-examined and a consistent interpretation presented.

Analysis of the 80 K absorption and emission spectra of *trans*- $[\text{Cr}(\text{en})_2\text{Cl}_2]^+$  and *trans*- $[\text{Cr}(1,3\text{-pn})_2\text{Cl}_2]^+$  in the 13000-16000  $\text{cm}^{-1}$  region indicates the presence of two electronic origins separated by 210 and 239  $\text{cm}^{-1}$ , respectively [115]. These are assigned as transitions from the  ${}^4A_{2g}(O_h)$  state to the components of the  ${}^2E_g(O_h)$  state, although the splitting is several times the calculated value. Investigations of the luminescence spectra of  $[\text{Ph}_4\text{P}][\text{Cr}(\text{CN})_6]$  at 15 K show [116] that the Cr-C bond is shortened by 0.02-0.03 Å in the first excited electronic state.

Through recent syntheses, *cis* and *trans*- $[\text{Cr}(\text{en})_2(\text{CN})_2][\text{ClO}_4]$  have become available and their photoaquation in aqueous acid has been investigated [117]. Both isomers aquate thermally at significant rates and corrections were made for this. Ligand field calculations of the energy levels of the split  ${}^4T_2$  excited state place  ${}^4B_2$  2500  $\text{cm}^{-1}$  below  ${}^4E$  for *trans*- $[\text{Cr}(\text{en})_2(\text{CN})_2]^+$ , and photochemical investigations of *trans*-acido chromium(III) complexes with this ordering have not previously been carried out. For *cis*- $[\text{Cr}(\text{en})_2(\text{CN})_2]^+$ ,  ${}^4E$  lies below  ${}^4B_2$ , with half the above separation, although there is no evidence of splitting in the absorption spectrum of either isomer. Photochemical aquation of the *trans* complex in aqueous acid takes place exclusively with proton uptake due to release and protonation of one end of an en ligand ( $\phi = 0.6$ ), as predicted by Adamson's rules and the Vanquickenborne-Ceulemans model [118]. As no  $\text{CN}^-$  labilisation was observed, photochemical reaction is entirely from the  ${}^4B_2$  level. *Cis*- $[\text{Cr}(\text{en})_2(\text{CN})_2]^+$  releases mainly en in a one-ended mode ( $\phi = 0.4$ ), as predicted, but appreciable cyanide loss was also observed ( $\phi = 0.1$ ). This may be due to reaction from the higher  ${}^4B_2$  state, formed directly by absorption before internal conversion, although it is possible that the quantum yield for

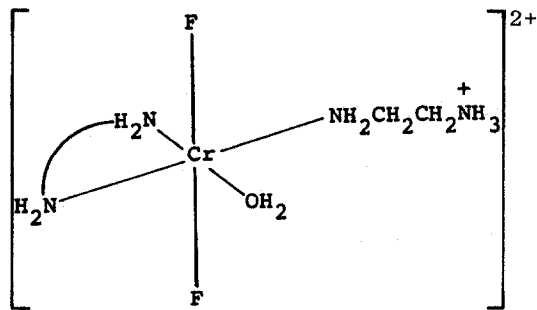
CN<sup>-</sup> release may be too high through experimental problems.

The effects of deuteration on the  $^2E$  solution [119] and solid state [120] lifetimes of chromium(III) complexes have been examined. The  $^2E$  lifetimes may be written as  $\tau = 1/(k_r + k)$  (where  $k_r$  is the radiative rate constant from  $^2E$  and  $k$  is the summed rate constant for all non-radiative processes from  $^2E$ , i.e.  $k = k_{cr} + k_{disc} + k_{nr}$ , where  $k_{cr}$ ,  $k_{disc}$ , and  $k_{nr}$  are the rate constants for direct chemical reaction from  $^2E$ , back intersystem crossing  $^2E \rightsquigarrow ^4T_2$ , and radiationless deactivation  $^2E \rightsquigarrow ^4A_2$ , respectively). Since  $k \gg k_r$ , the lifetime data reflect variations in the non-radiative rate constants. Deuteration had only a small effect on the lifetime of  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  and other complexes in solution at room temperature and back intersystem crossing or direct reaction could not be distinguished from the solution studies. No photodecomposition on ligand field excitation has been detected for  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  and  $[\text{Cr}(\text{en})_3]^{3+}$  in the solid state, provided only poorly coordinating counterions such as  $[\text{ClO}_4]^-$  are present. Therefore, non-radiative decay through chemical reaction from  $^2E$  does not occur in the solid, and investigations of solids have potential because  $k_{cr}$  is zero and only back intersystem crossing and non-radiative deactivation can occur. The room temperature lifetime for solid  $[\text{Cr}(\text{NH}_3)_6][\text{ClO}_4]_3$  is more than ten times longer than in solution and is temperature independent, and there is a strong deuteration effect, all of which eliminate back intersystem crossing as a significant pathway in the solid, and by inference in solution. Deactivation is principally by  $^2E \rightsquigarrow ^4A_2$  relaxation. The complex  $[\text{Cr}(\text{en})_3][\text{ClO}_4]_3$  behaves similarly in the solid, but as the lifetimes show significant temperature dependence and the deuteration effect is more modest, back intersystem crossing seems to make some contribution as well, possibly because of the lower symmetry of the cation.

As implied above, the role of the excited doublet ( $^2E$ ) in photochemical mechanisms is still uncertain, and there has been some dispute over the pathway of decay from this state in *trans*- $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$ ; some workers [121] believe that the  $^2E$  state disappears primarily through back intersystem crossing to the first quartet excited state  $^4T_2$ , but others [122] consider that direct chemical reaction is dominant. The latter pathway is apparently in agreement with rules [123] recently adduced for  $^2E$  emission lifetimes of chromium(III) complexes, and other evidence. The temperature dependences of the luminescence lifetimes of several Cr(III) complexes have been determined in a variety of media [124]. In most cases the luminescent rate constant,  $k_{lum}$ , fits an expression  $k_{TI} + A_{NR} \exp(-\Delta E_{NR}^*/RT)$ . The subscripts refer to temperature-independent and non-radiative (temperature-dependent) terms. The activation energy  $\Delta E_{NR}^*$  was found to be solvent dependent and only a fraction of the  $^4T_2$ - $^2E$  splitting, suggesting a chemical pathway for deactivation of the  $^2E$  state rather than back intersystem crossing.

Since photochemistry in aqueous solution is studied at or near room temperature, luminescence studies of a variety of chromium(III) ammine and ethylenediamine complexes have been carried out in aerated aqueous solution at 22 °C [125] to provide a basis for mechanistic comparisons. Most of the complexes surveyed display phosphorescence although some with fluoro ligands emit delayed fluorescence. The phosphorescence quantum yields ( $\phi_{phos}$ ) are small because non-radiative transitions determine the lifetime of the excited state, but they show a great variation with the type of ligand and the structure of the complex which is paralleled by variations in the excited state lifetimes  $\tau$ . There is no correlation of  $\phi_{phos}$  and  $\tau$  with ligand field strength, so it is unlikely that back intersystem crossing alone is responsible for these variations. The results are in some disagreement with the recent rules [123] governing emission lifetimes.

The major product of photolysis of  $trans-[Cr(en)_2F_2]^+$  was thought to be the isomer of  $[Cr(en)(enH)(OH_2)F_2]^{2+}$  produced from thermal aquation of  $trans-[Cr(en)_2F_2]^+$ , presumably (22). In a recent report [126] the photoproducts are



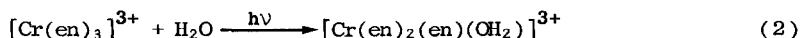
(22)

said to be substantially different from (22) and, as this also relates to theoretical treatments specifically relating to the role of  $F^-$  [118], the products have been re-investigated [127] by improved techniques. Three products have now been identified but (22) is still the dominant one.

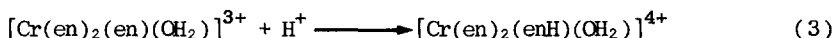
Differential quenching of two reaction modes of  $trans-[Cr(en)_2(NCS)F]^+$  has been observed [128]. This ion photoaquates thiocyanate and ethylenediamine (one end as in (22)) in a wavelength and temperature-dependent ratio [129]. It emits at 717 nm from aqueous solution and the emission is quenchable by  $[Cr(CN)_6]^{3-}$ . The thiocyanate mode is quenched independently of wavelength by  $[Cr(CN)_6]^{3-}$ , in parallel with the phosphorescence quenching. In contrast, the quenching of the ethylenediamine mode is smaller, especially on short wavelength excitation, showing that differential quenching occurs. The results have been explained by assuming that two quartet states participate, in addition to the

doublet, and a possible scheme has been given.

Irradiation of  $[\text{Cr}(\text{en})_3]^{3+}$  in the ligand field or charge transfer bands leads to the photoaquation (2), with a quantum yield of 0.4 independent of wavelength:



In acidic media, the protonation (3) of the monodentate ethylenediamine occurs:



In the first direct measurement [130] of the rate of primary photoproduct formation from a chromium(III) compound, the growth in optical absorption due to  $[\text{Cr}(\text{en})_2(\text{enH})(\text{OH}_2)]^{4+}$  was followed. The protonation (3) was too fast to be measured under the conditions used (pH 2). The product formation took place in two distinct stages; the lifetime of the slower was the same as that of phosphorescence from the  ${}^2E$  ( $D_1^0$ ) state and the faster was attributed to reaction from the  ${}^4T_2$  ( $Q_1^0$ ) state. The situation was complicated by the occurrence of excited state absorption from the relatively long lived doublet state. This problem has been overcome [131] by conductivity detection of the photoproduct, a method which may be of more general use. The earlier results have been confirmed and investigations extended to the processes following irradiation into the second quartet  ${}^4T_1$ . On pulse irradiation of  $[\text{Cr}(\text{en})_3]^{3+}$  solutions, the resultant conductivity decreased in short- and long-term stages which became better resolved as the pH decreased from 3.1 to 2.3. The short term change was ascribed to the presence of some  $[\text{Cr}(\text{en})_2(\text{en})(\text{OH}_2)]^{3+}$  at the end of the pulse and the occurrence of reaction (3). From the acid dependence of the short term rate, the proton transfer rate constant for (3) has been found to be  $3.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . Analysis of the results for the long term stage shows that the long term change is controlled by exiting from the  ${}^2E$  state. The fraction of photoproduct from the doublet state is the same ( $\sim 0.7$ ), as found by optical measurements [130], and is the same for irradiation of either of the  ${}^4T_2$  and  ${}^4T_1$  bands, so that the second excited state is chemically unreactive.

When a solution of  $[\text{Cr}(\text{en})_3]^{3+}$  is photolysed to a 10% yield of the dominant products, *i.e.* the two isomers of  $[\text{Cr}(\text{en})_2(\text{enH})(\text{OH}_2)]^{4+}$ , there is no detectable change in the molar rotation of the remaining  $[\text{Cr}(\text{en})_3]^{3+}$ . This means that photoracemisation ( $\Delta\text{-}[\text{Cr}(\text{en})_3]^{3+} \rightleftharpoons \Lambda\text{-}[\text{Cr}(\text{en})_3]^{3+}$ ) is inefficient compared to photoaquation, so that to determine the quantum yield ( $\phi_R$ ) for photoracemisation extensive photolysis and careful separation of  $[\text{Cr}(\text{en})_3]^{3+}$  from major amounts of photoproducts were necessary to obtain reasonable amounts of

inverted material [132]. At ambient temperature  $\phi_R$  was found to be 0.015, independent of hydrogen ion concentration (from 0.08 to 1.0 M). Photo-racemisation could occur through twisting of the octahedral complex about a three-fold axis, or by bond rupture, and the former was marginally preferred.

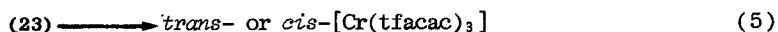
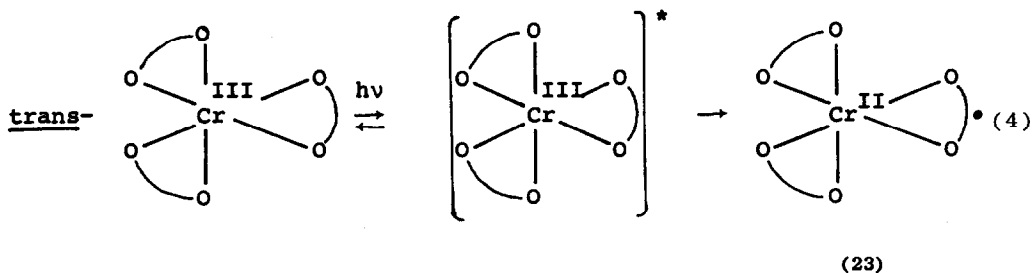
The solvent can exert a large influence on photolysis processes. The luminescence lifetime and quantum yield of  $[\text{Cr}(\text{bipy})_3]^{3+}$  irradiated in argon-saturated dmf are fifteen times smaller than in water, and in mixed solvent systems they vary monotonically with solvent composition [133]. The photochemical quantum yield for disappearance of  $[\text{Cr}(\text{bipy})_3]^{3+}$  [133] in dmf is greater than it is in water [134]. The data support the hypothesis that the kinetics of radiationless deactivation are solvent dependent and, in dmf, initial photoreduction to a kinetically labile chromium(II) bipyridine complex occurs. The Cr(II) intermediate acts as a chain carrier in an autocatalytic reaction, which does not take place in water because the intermediate decays by back electron transfer before it can undergo other reactions. When the solvent is changed from water to more viscous 80% glycerol, the intensity of emission from  $[\text{Cr}(\text{en})_3]^{3+}$  after irradiation shows decreased variation with wavelength [135]. It is believed that this is due to the effects of solvent relaxation on intersystem crossing ( ${}^4T_2 \rightsquigarrow {}^2E$ ) efficiency, and it is predicted that in a rigid glass medium the intersystem crossing efficiency will not be dependent on the excitation wavelength.

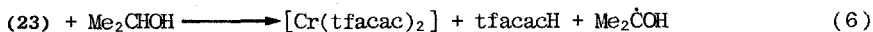
The photohydrolysis of  $[\text{Cr}(\text{bipy})_3]^{3+}$  in basic media to give  $[\text{Cr}(\text{bipy})_2(\text{OH})_2]^+$  is the only photosubstitution of a chromium(III) complex for which the  ${}^4T_{2g}$  excited state has been excluded as an origin of reactivity. This is because it has been shown [136] that the intersystem crossing yield ( $\phi_{ISC}$ ),  ${}^4T_{2g} \rightsquigarrow {}^2E$  is essentially unity and, therefore, reaction must be from  ${}^2E$ . The wavelength dependence of reaction (photohydrolysis) and luminescence (at 727 nm) quantum yields of  $[\text{Cr}(\text{bipy})_3]^{3+}$  have been studied [137]. The luminescence quantum yields represent variation of  $\phi_{ISC}$  and, since they decrease with increasing wavelength near 590 nm, there is a crossover point in this region where the quartet falls below the doublet. The reaction quantum yields decrease similarly, so that reaction has a  ${}^2E$  origin. The unit quantum yield for intersystem crossing [136] is valid only for quartet excitation well above the 0-0 band. In the long wavelength tail of the quartet band the main fate of quartets is relaxation to the ground state without intersystem crossing or reaction. It has been pointed out [137] that the similar species  $[\text{Cr}(\text{phen})_3]^{3+}$  apparently behaves differently, with  $\phi_{ISC}$  much smaller (ca. 0.2 in  $\text{H}_2\text{O}/\text{dmf}$ ) [136] and photoracemisation [138] taking place from the quartet state. However, photochemical behaviour can be dependent on the solvent [133], and the ground state quenching of the  ${}^2E$  excited state of  $[\text{Cr}(\text{bipy})_3]^{3+}$  and  $[\text{Cr}(\text{phen})_3]^{3+}$  can be dependent on the concentration of ground state substrates and anions such as chloride [139].



Thus,  $\phi_{ISC}$  must [140] be determined under the same conditions of solution medium in which the photochemistry is investigated. The photochemical quantum yields of  $[\text{Cr}(\text{bipy})_3]^{3+}$  and  $[\text{Cr}(\text{phen})_3]^{3+}$  in identical aqueous alkaline conditions, from direct irradiation into the  ${}^4T_2$  manifold, and into the  ${}^2T_1/{}^2E$  states, have been compared [140]. From the comparison it has been deduced that  $\phi_{ISC}$  for the phen complex is not, in fact, 0.2, but close to 1. Raman scattering from the  ${}^2E$  and  ${}^4T_2$  excited states of aqueous  $[\text{Cr}(\text{bipy})_3][\text{ClO}_4]_3$  has been achieved by the use of suitable laser radiation [141].

A full account of the photochemical behaviour of *trans*- $[\text{Cr}(\text{tfacac})_3]$  (*tfacacH* = 1,1,1-trifluoropentane-2,4-dione) in benzene, cyclohexane, ethanol, and 2-propanol has appeared [142]. Continuous photolysis and flash photolysis experiments show that the photoreactivity of this complex is more complicated than so far reported for chromium(III)  $\beta$ -diketonates, and is qualitatively similar to that of  $\beta$ -diketonates of other first row transition metals. *Trans* to *cis* isomerisation is the dominant process occurring in benzene and cyclohexane solution upon continuous photolysis at wavelengths  $\geq 366$  nm, but both isomerisation and decomposition occur in 2-propanol and ethanol at 366 nm. Photolysis at 254 nm results in isomerisation and redox decomposition, with the latter pathway being favoured in solvents of greater H-atom donor ability. The variation with excitation wavelength in the ratio of quantum yields for the two processes establishes the presence of two photoactive excited states; the lower energy state responsible for isomerisation at longer wavelengths is assigned as the ligand field quartet  ${}^4T_{2g}$ , whereas the higher lying state favouring decomposition at shorter wavelengths appears to contain considerable ligand to metal charge transfer character. Flash photolysis at  $\leq 330$  nm induces in alcohol/cyclohexane mixtures a metastable species which reacts rapidly with oxidants and is believed to be  $[\text{Cr}^{\text{II}}(\text{tfacac})_2]$ . It is produced in greater yield if the alcohol is 2-propanol which has the greatest hydrogen atom donor ability. Reactions (4)-(6) appear to account for the results. In poor hydrogen atom donor solvents the chromium(II)-radical species (23) decays *via* (5), explaining why no redox

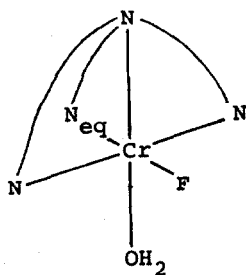




products were detected in hexane or aqueous mixtures.

As is clear from the above and other work, the nature of the intermediates in thermal and photochemical reactions of coordination compounds remains a matter for speculation. The intermediates cannot be studied in gas matrices because the parent complexes are involatile, but reactive species can be observed on UV irradiation of inorganic complex ions in alkali halide disc matrices at 77 K. On irradiation [143] of  $\text{K}_3[\text{Cr}(\text{CN})_6]$  in a KBr or KCl disc new IR bands appeared in the CN stretching region and the parent peak weakened as the photolysis proceeded. On warming to 293 K the new bands disappeared, and the original spectrum reappeared. The intermediates have not been identified although  $[\text{Cr}(\text{CN})_5]^{3-}$  may be one, suggestive of a dissociative pathway, and  $[\text{Cr}(\text{CN})_6]^{4-}$  was excluded.

On ligand field photolysis in acidic solution,  $[\text{Cr}(\text{tren})\text{F}_2]^+$  releases  $\text{F}^-$  with a quantum yield of 0.21 [144]. From its electronic spectrum, the product is believed to be  $\alpha\text{-}[\text{Cr}(\text{tren})\text{F}(\text{OH}_2)]^{2+}$  (24), which is also the product of



(24)

thermal aquation. This is not consistent with the Vanquickenborne-Ceulemans model [118] which predicts labilisation of  $\text{N}_{eq}$ . Investigations of the luminescence spectra at 85 K of a series of *trans*-bis(*N*-alkyliminodiacetato)chromate(III) complexes,  $\text{K}[\text{CrL}_2]$  (where  $\text{H}_2\text{L} = \text{RN}(\text{CH}_2\text{CO}_2\text{H})_2$  and  $\text{R} = \text{Me}, \text{Et}, \text{Pr}, i\text{-Pr}, \text{Bu}$  or  $t\text{-Bu}$ ) confirm [145] earlier assignments.

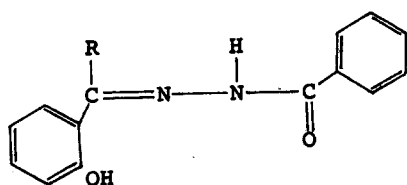
#### 6.4.6 Complexes of polydentate ligands

In  $\text{K}[\text{Cr}\{\text{HN}(\text{CH}_2\text{CO}_2)_2\}_2] \cdot 3\text{H}_2\text{O}$  the nitrogen atoms occupy *cis* positions [146a], but in  $\text{Na}[\text{Cr}\{(^i\text{Pr})\text{N}(\text{CH}_2\text{CO}_2)_2\}_2] \cdot 2\text{H}_2\text{O}$  the *iso*-propyl group causes the nitrogen atoms to take up *trans* positions in the distorted octahedron around the chromium atom [146b]. For  $[\text{Cr}(\text{EDDA})(\text{OH})_2]^+$ ,  $\log K = 12.45$  at room temperature [147]. The uncoordinated OH group of *N*-(hydroxyethyl)ethylenediamine-*N,N',N'*-

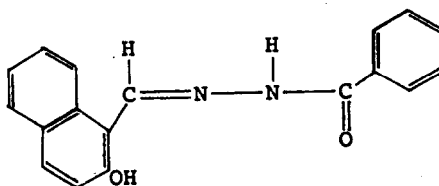
triacetic acid ( $H_3L$ ) in  $[CrL(OH_2)]$  is readily acetylated [148]. Ethylenediamine-*N,N'*-di(*o*-hydroxyphenylacetic acid) ( $H_4L'$ ) forms the complex  $[CrH_3L'Cl_2] \cdot 4\frac{1}{2}H_2O$ , which shows unionised  $CO_2H$  absorptions in its IR spectrum [149].

Some complexes containing tetradentate Schiff's bases have been reported:  $[Cr(sal_2en)(OH_2)(NCS)]$ ,  $[Cr(sal_2en)(OH_2)(N_3)]$  [150];  $[Cr(acac_2en)L_2][BPh_4]$ ,  $[Cr(acac_2en)ClL]$ ,  $[Cr(acac_2en)L(CNS)]$ ,  $[Cr(acac_2en)L_2][ClO_4]$ ,  $[Cr(acac_2en)(OH_2)_2][CNS]$ , in which  $L$  = pyridine or 4-methylpyridine [151]; and  $[Cr(sal_2en)L'] [BPh_4]$  ( $L'$  = bipy, phen, or en),  $[Cr(salphen)L'] [ClO_4]$ , and  $[Cr(sal_2en)(acac)]$  [152].

The tridentate ligands (25) and (26), derived from benzoylhydrazine and

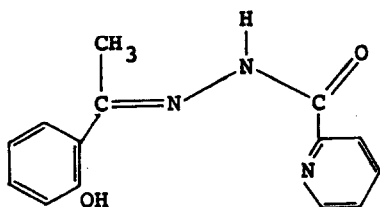


(25)

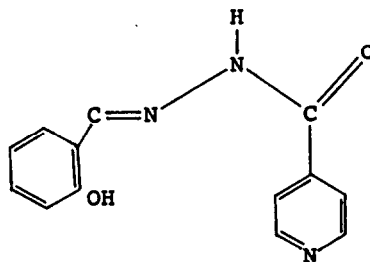


(26)

various *o*-hydroxyaldehydes, form typical six-coordinate complexes  $[Cr(L-H)_2]Cl$ , in which the ketone groups are thought to be *trans* [153]. The dimers  $[Cr(L-2H)X]_2$  (where  $X$  can be  $Cl$ ,  $Br$ , or  $NO_3$ ) are formed at higher pH. They are believed to contain five coordinate chromium atoms bridged by phenolic oxygen atoms. Condensation of *o*-hydroxyacetophenone with picoloylhydrazine and iso-nicotinoylhydrazine produces the ligands (27) and (28), respectively. These form the complexes  $[Cr(L-H)Cl_2]$  and, at higher pH,  $[Cr(L-2H)Cl]_2$  [154],



(27)



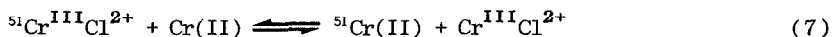
(28)

some of which seem to contain five coordinate chromium(III) although there is no crystallographic evidence.

Previous attempts to prepare *trans*- $[Cr(cyclam)Cl_2]^+$  (cyclam = 1,4,8,11-tetraazacyclotetradecane) in good yield have been unsuccessful, but it has now [155] been prepared by prolonged reflux of an aqueous solution of *cis*- $[Cr(cyclam)Cl_2]Cl$ , after the adjustment of pH to approximately 7 with

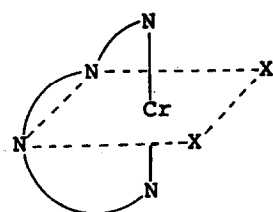
2,4,6-trimethylpyridine, followed by acidification with HCl, concentration, and extraction. The isomerisation of *cis*-[Cr(cyclam)Cl<sub>2</sub>]<sup>+</sup> is pH-dependent, being most efficient near pH 7 when the starting material is essentially *cis*-[Cr(cyclam)(OH)(OH<sub>2</sub>)]<sup>2+</sup>. Isomerisation in acid media is negligible and this is why the *trans* isomer could not be obtained earlier. The new *trans* complexes, *trans*-[Cr(cyclam)(NCS)<sub>2</sub>]X (X = NCS or ClO<sub>4</sub>) have also been obtained. The electronic spectra of *cis*- and *trans*-[Cr(cyclam)Cl<sub>2</sub>]<sup>+</sup> differ considerably in the usual way, but as *cis*- and *trans*-[Cr(cyclam)(NCS)<sub>2</sub>]<sup>2+</sup> have similar electronic spectra, the *trans* assignment was made from IR evidence. *Trans* complexes containing cyclam exhibit a doublet near 890 cm<sup>-1</sup> and a singlet near 810 cm<sup>-1</sup>, whereas the *cis* complexes show at least three bands in the range 840-890 cm<sup>-1</sup> and a doublet in the range 790-830 cm<sup>-1</sup>. The *trans* complexes also exhibited one ν(Cr-Cl) or one ν(Cr-NCS) absorption.

Chromium is believed to be an essential trace element, but dietary supplementation with simple Cr(III) salts is inefficient because insoluble hydrolysed products form at intestinal pH's. For investigations of dietary chromium, <sup>51</sup>Cr has been incorporated into chromium(III) porphyrin complexes [Cr<sup>III</sup>PCl] which should be stable at stomach and intestinal pH's [156]. The radiolabel is supplied as CrCl<sub>3</sub> in 0.1 M HCl and was first treated with a large excess of cold chromium(II) chloride solution. Chromium(III) is inert to substitution, but the electron exchange reaction (7) takes place rapidly, and as the equilibrium constant is 1, most of the <sup>51</sup>Cr is present in the +II



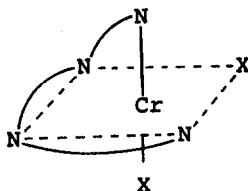
oxidation state at equilibrium, although its specific activity is reduced in proportion to the excess of CrCl<sub>2</sub> added. The solvent was then removed, dmf and the porphyrin in dmf added, and the mixture refluxed briefly to incorporate the Cr(II) before exposure to the air to produce the chromium(III) complex. This part of the procedure is based on an earlier method. The labelled complexes [<sup>51</sup>CrPCl] were separated chromatographically (H<sub>2</sub>P = mesoporphyrin dimethyl ester, deuteroporphyrin dimethyl ester, protoporphyrin IX dimethyl ester, haematoporphyrin dimethyl ester, or *meso*-tetraphenylporphyrin). Labelled Na<sub>3</sub>[Cr(TPPS)Cl], where H<sub>2</sub>TPPS is the tetrasulphonate of tetraphenylporphyrin, was also prepared. The formation constant of [Cr(TPPS)(OH<sub>2</sub>)(NCS)]<sup>4-</sup> (from [Cr(TPPS)(OH<sub>2</sub>)]<sup>3-</sup>) is much smaller (2.52 M<sup>-1</sup>) than in the cobalt case (2640 M<sup>-1</sup>) [157].

Three geometrical isomers, *cis*-α, *cis*-β and *trans* (29-31), are possible for octahedral complexes containing a linear tetradentate ligand such as *N,N'*-bis(2-pyridylmethyl)-1,2-diaminopropane (picpn), and two *cis*-α, and eight *cis*-β optical isomers. The Δ and Λ diastereoisomers of [CrX<sub>2</sub>(S-picpn)]<sup>+</sup> (X = Cl or Br)



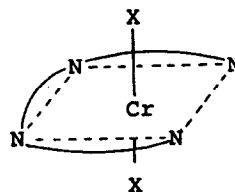
cis-α

(29)



cis-β

(30)



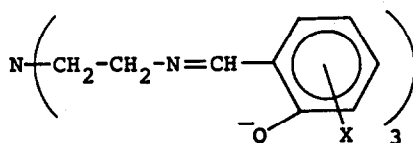
trans

(31)

of *cis*-α configuration have been isolated, and the configurations were assigned from their absorption and CD spectra [158]. The results have been confirmed and one *cis*-β isomer isolated [159].

The electrochemical behaviour [160] of two isomeric complexes (see 1979 review) of chromium(III) with thiobis(ethylenenitrilo)tetraacetic acid  $S[CH_2CH_2N(CH_2CO_2H)_2]_2$  has been reported.

In the chromium(III) complex of the potentially heptadentate ligand (32)



(32)

the apical nitrogen atom is not bonded. The Cr-O and Cr-N bonds are longer than usual and the ligand seems to fix a minimum sized "hole" into which the metal ion fits [161]. The Mn(III) and Fe(III) complexes are isomorphous with the Cr(III) complex. The chromium(III) complex of the 3,5-dichlorosalicylaldehyde derivative of (32) has been prepared [162].

## 6.5 CHROMIUM(II)

### 6.5.1 Complexes with simple chromium centres

The products of reactions of  $CrF_2$  with oxygen, nitric oxide, and sulphur at elevated temperatures [163], and its heat capacity from 10 to 300 K [164], have been reported. The gas phase He(I) and He(II) photoelectron spectra [165] of  $CrCl_2$  and some other divalent metal chlorides have been interpreted. Chromium(II) carbonate has been synthesised at high pressure and temperature from carbon dioxide and chromium hexacarbonyl [166].

The intensities of certain spin-forbidden, ligand field transitions in the solid state spectra of the recently obtained ferromagnetic tetrachlorochromates(II),  $A_2[CrCl_4]$ , are related to the magnetic order because they diminish rapidly below the Curie temperature. Quantitative investigations of intensity variation with temperature for single crystals of the tetrachlorochromates(II), with  $A = Rb$ ,  $CH_3NH_3$ , or  $C_2H_5NH_3$ , have been performed and the results compared with theoretical predictions [167].

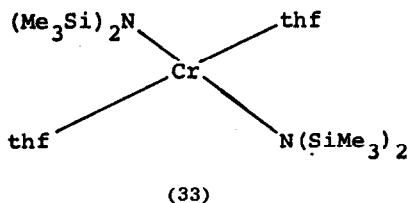
Some structural investigations of trihalochromates(II) have been carried out.  $\gamma$ - $RbCrCl_3$  undergoes [168] a transition to the known [169]  $\beta$ - $RbCrCl_3$  at 201 K. It has a slightly distorted hexagonal perovskite structure which is related to the  $\beta$ -phase and consists of chains of elongated face sharing octahedra. In  $\beta$ - $RbCrCl_3$  the chains contain alternating elongated and compressed face sharing octahedra. Below 170 K,  $CsCrCl_3$  is isomorphous with  $\beta$ - $RbCrCl_3$ . The iodide  $CsCrI_3$  has been found [170] to be isostructural with  $CsCrCl_3$  and  $CsCrBr_3$ . The iodide has also been investigated [171] by neutron powder diffraction at room temperature, 77 and 1.2 K. In the face sharing octahedra of the low temperature form,  $\beta$ - $CsCrI_3$  (orthorhombic), there are four short ( $\sim 2.8$  Å) and two long ( $\sim 3.05$  Å) Cr-I bonds. Its magnetic structure, at 1.2 K, consists of an anti-parallel sequence of ferromagnetic (001) planes with a magnetic moment of  $3.16 \mu_B$  in the (100) direction. At 150 K, it undergoes a phase transition to the  $\alpha$ -form (hexagonal), which is also Jahn-Teller distorted. Mössbauer spectra of  $CsCrI_3$  ( $^{129}I$ ) show magnetic ordering in the helium temperature range ( $T_N = 18 \pm 3$  K), and that there are two crystallographic sites for iodine [172]. The Mössbauer effect was too weak for measurements above 100 K and two sites are inconsistent with the known structure at room temperature. However, the crystal phase transition found by neutron diffraction [171] was confirmed by X-ray powder methods, although the transition temperature is given as 165 K. An analysis of the quadrupole interaction parameters of the two sites is in agreement with axial distortion of the  $CrI_6$  octahedra.

By heating stoichiometric amounts of  $TlI$  and  $CrI_2$  at  $600^\circ C$   $Tl_4CrI_6$  is obtained [173]. It contains isolated  $CrI_6$  octahedra in which, unusually, there are two short Cr-I bonds ( $2.738$  Å) and four long ones ( $3.046$  Å). Other investigations [174] indicate elongated octahedra, although this does not seem to be a clear-cut conclusion.

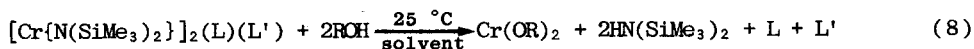
As part of a study of the electron transfer bands of the divalent 3d transition series ions in  $LiCl$ , the chloride has been doped with  $Cr^{2+}$  [175]. The  $^5E \rightarrow ^5T_2$  band appeared at  $10900$  and  $10200 \text{ cm}^{-1}$ , in very concentrated and dilute crystals, respectively. The difference was thought to be due to double salt formation ( $Li_4CrCl_6$  or  $Li_3CrCl_6$ , and a  $LiCl$  rich phase). Bands at  $49900$  and  $54700 \text{ cm}^{-1}$  were assigned to chloride-to-metal charge transfer. The ligand field splitting of  $Cr^{2+}$  substituted in tetrahedral sites in  $ZnS$  is approximately

4800  $\text{cm}^{-1}$  [176].

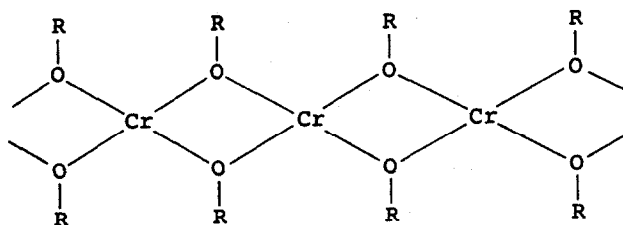
The chromium(II) silylamide  $\text{Cr}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{thf})_2$  has [177] the *trans* planar structure (33), and a number of derivatives have been prepared [178] in which



one or both molecules of thf have been replaced by other cyclic or aliphatic ethers, alkyl cyanides or aromatic tertiary amines to give complexes such as  $[\text{Cr}\{\text{N}(\text{SiMe}_3)_2\}_2].\text{thf}.\text{py}$  and  $[\text{Cr}\{\text{N}(\text{SiMe}_3)_2\}_2].\text{Et}_2\text{O}.\text{py}$ . In some cases, *e.g.*  $[\text{Cr}\{\text{N}(\text{SiMe}_3)_2\}_2].2\text{Et}_2\text{O}$ , the solids decomposed even in an inert atmosphere, but solutions in organic solvents were stable under dinitrogen for several weeks, and solutions of the dietherate especially were used in other reactions. The new compound  $[\text{ClCr}\{\text{N}(\text{SiMe}_3)_2\}](\text{thf})_n$ , where  $n \sim 2$ , has been isolated from the reaction between  $\text{Li}\{\text{N}(\text{SiMe}_3)_2\}$  and anhydrous  $\text{CrCl}_2$  in tetrahydrofuran. On further drying, substances with  $n \sim 1$  or 0 were obtained. Alcoholysis of  $[\text{ClCr}\{\text{N}(\text{SiMe}_3)_2\}](\text{thf})_2$  gave  $\text{ClCr}(\text{OR})$  (where  $\text{R} = \text{Me}, \text{Et}, \text{Pr}, {}^i\text{Pr}$  and  ${}^t\text{Bu}$ ); and reaction with  $\text{LiR}$  gave incompletely characterised products of the type  $\text{RCr}\{\text{N}(\text{SiMe}_3)_2\}.\text{thf}$ . On thermolysis of  $[\text{Cr}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{thf})_2$ , a mixture possibly containing  $[\text{Cr}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{thf})_2$  and  $[\text{Cr}\{\text{N}(\text{SiMe}_3)_2\}]_n$  was obtained. The compounds were characterised by analyses, including chromium as Cr(II), and reflectance spectra, and it was necessary to use carefully prepared anhydrous  $\text{CrCl}_2$  in their synthesis. Transition metal silylamides like (33) have been used to "silanize" a silica gel surface and impregnate it with metal ion for catalytic purposes. Many chromium(II) alkoxides have been prepared [179] by alcoholysis of  $[\text{Cr}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{thf})_2$  and similar compounds described above. The general reaction is (8), in which L and L' are  $\text{Et}_2\text{O}$ , thf, py, or  $t\text{-BuCN}$  or various



combinations of them, and ROH is a linear or branched chain alcohol or a phenol. The alkoxides are all sensitive to attack by dioxygen, and had to be carefully dried to obtain materials free from solvent. The alkoxides of higher molecular weight showed reasonable solubility in organic solvents. No structures were assigned, but they are certain to differ from the structures previously assigned to the low molecular weight compounds (34). Reflectance spectra were given but not interpreted. On addition to halogenated solvents the alkoxides gave intensely coloured solutions, stable to dioxygen and believed to contain  $\text{Cr}^{\text{III}}\text{-C}$



(34)

species.

From its IR and reflectance spectra, and its magnetically dilute behaviour, the thiocyanatochromate(II) salt,  $\text{Na}_3[\text{Cr}(\text{CNS})_5] \cdot 9\text{H}_2\text{O}$ , is believed [180] to contain a square-pyramidal arrangement of *N*-bonded thiocyanato-groups. Attempts to prepare similar salts of other metal cations were unsuccessful, and organic cations gave a new class of chromium(II) complexes, the tetrathiocyanates  $\text{A}_2[\text{Cr}(\text{CNS})_4]$ , where  $\text{A} = \text{NMe}_4$ ,  $\text{NEt}_4$ ,  $\text{NPr}_4$ ,  $\text{NBu}$ ,  $\text{Hmta}$ ,  $\text{Hpy}$ ,  $\frac{1}{2}\text{H}_2\text{en}$ , or  $\frac{1}{2}\text{H}_2\text{L}$  ( $\text{L} = 5,7,7,12,14,14$ -hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene). In general, these complexes show antiferromagnetic behaviour, and are thought to have thiocyanato-bridged structures. Monoethanol adducts of the  $[\text{NEt}_4]^+$  and  $[\text{NPr}_4]^+$  salts have been isolated and these are magnetically-dilute high spin complexes; the  $[\text{NBu}_4]^+$  salt has been isolated in two forms, one brown and magnetically dilute, and the other blue and antiferromagnetic. Structural studies are needed to explain how the different magnetic behaviour arises.

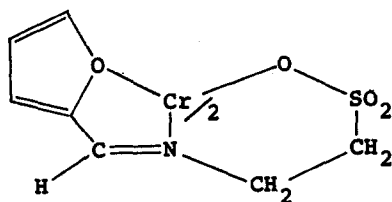
Chromium(II) is expected, from its position in the Periodic Table, to show predominantly Class A behaviour, and most known complexes are of *O*- and *N*-donor ligands. However, complexes of the *S*-donor ligands thiourea, *N,N'*-ethylene-thiourea (*etu*), and *N,N'*-dicyclohexylthiourea (*dctu*) with chromium(II) halides have been isolated [181] from a weakly-donating solvent mixture of acetone and small amounts of 2,2-dimethoxypropane and methanol. The complexes are  $\text{CrCl}_2 \cdot 2\text{tu}$  and its monoacetone adduct,  $\text{CrBr}_2 \cdot 4\text{tu}$ ,  $\text{CrI}_2 \cdot 6\text{tu}$ ,  $\text{CrCl}_2 \cdot 2\text{etu}$ ,  $\text{CrBr}_2 \cdot 5\text{etu}$ ,  $\text{CrI}_2 \cdot 4\text{etu}$ ,  $\text{CrCl}_2 \cdot \text{dctu}$  and  $\text{CrI}_2 \cdot 6\text{dctu}$ . The chlorides are antiferromagnetic and are believed to be linear polymers. The other complexes are high spin and magnetically-dilute.

Some chromium(II) complexes of 3(5)-methylpyrazole ( $5\text{Mepz}$ , (20)), 1-methylpyrazole ( $\text{NMepz}$ ), 2-methylimidazole ( $2\text{Meiz}$ ) and 1-ethylimidazole ( $\text{NEtiz}$ ) have been prepared [102]. Complexes  $\text{CrL}_4\text{X}_2$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$  or  $\text{I}$ ) were obtained with  $2\text{Meiz}$  and  $5\text{Mepz}$ ; from their electronic spectra the  $5\text{Mepz}$  complexes are assigned *trans*-octahedral structures, but the  $2\text{Meiz}$  complexes have different spectra and the chloride and bromide are isomorphous with analogous nickel(II) complexes which contain square pyramidal cations. Similarly, a tetraphenylborate salt is formulated as  $[\text{Cr}(2\text{Meiz})_5][\text{BPh}_4]_2$ , and in the antiferromagnetic compound



$[\text{Cr}(\text{2Meiz})_2(\text{NCS})_2]$  five coordination is believed to be achieved with bridging thiocyanate groups. Complexes  $\text{Cr}(\text{NETiz})_3\text{Cl}_2$  and  $\text{Cr}(\text{NETiz})_4\text{Br}_2$  are thought to have distorted octahedral structures from their reflectance spectra but structures could not be assigned to  $\text{Cr}(\text{NMepz})_2\text{Cl}_2$  and  $\text{Cr}(\text{NMepz})_3\text{Br}_2 \cdot \text{H}_2\text{O}$ . The chromium(III) complex  $[\text{Cr}(\text{5Mepz})_4\text{F}_2][\text{BF}_4]$  has been mentioned (p.121).

The chromium(II) complex (35) of the Schiff's base formed between furfuraldehyde



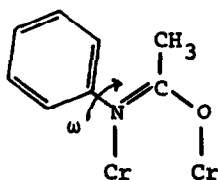
(35)

and 2-aminoethane sulphonic acid is said to be high spin, with  $\log \beta_2 = 6.77$  at  $25^\circ$  in  $0.1 \text{ M Na}[\text{ClO}_4]$  [182]. Complexes in which this sulphonic acid is replaced by *o*-aminobenzene sulphonic acid [183], *o*-aminobenzoic acid [184] and  $\beta$ -alanine have similar properties. There is no indication whether the complexes are air sensitive.

Chromocene reacts reversibly with the vapours of some primary aliphatic linear amines [185] to form aminates of the type  $\text{Cr}(\text{C}_5\text{H}_5)_2(\text{RNH}_2)_x$ . Since these are magnetically dilute, with magnetic moments ( $\sim 4.6 \mu_B$ ) corresponding to high spin chromium(II), the sandwich structure (chromocene is low spin) is destroyed on aminate formation. As  $x$  varies from 4.5 to 5.3, it is assumed that the aminates are  $\text{Cr}(\text{C}_5\text{H}_5)_2(\text{RNH}_2)_4$  with additional weakly associated amine.

#### 6.5.2 Complexes containing Cr-Cr quadruple bonds

Crystallographic investigations of the compounds (36) to (45) have emphasised how the length of the Cr-Cr quadruple bond,  $r(\text{Cr-Cr})$ , is primarily dependent

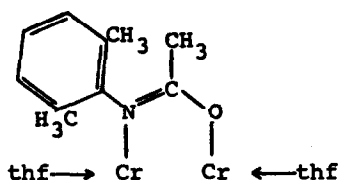


$$r(\text{Cr-Cr}) = 1.873 \text{ \AA}$$

$$\omega = 48^\circ$$

acetanilido

(36)

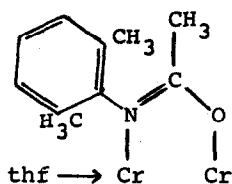


$$r(\text{Cr-Cr}) = 2.221 \text{ \AA}$$

$$\omega = 88^\circ$$

2,6-dimethylacetanilido

(37)

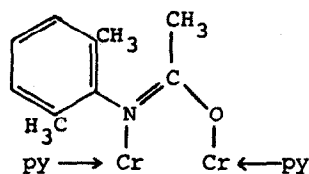


$$r(\text{Cr}-\text{Cr}) = 2.023 \text{ \AA}$$

$$\omega = 88.3^\circ$$

2,6-dimethylacetanilido

(38)

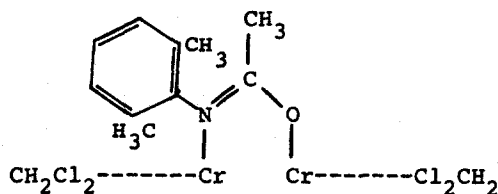


$$r(\text{Cr}-\text{Cr}) = 2.354 \text{ \AA}$$

$$\omega = 88^\circ$$

2,6-dimethylacetanilido

(39)



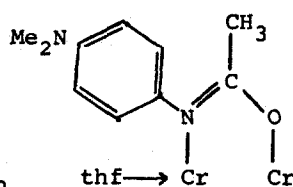
$$r(\text{Cr}-\text{Cr}) = 1.949 \text{ \AA}$$

$$\omega = 93.3^\circ$$

$$r(\text{Cr}-\text{Cl}) = 3.354 \text{ \AA} \text{ and } 3.58 \text{ \AA}$$

2,6-dimethylacetanilido

(40)

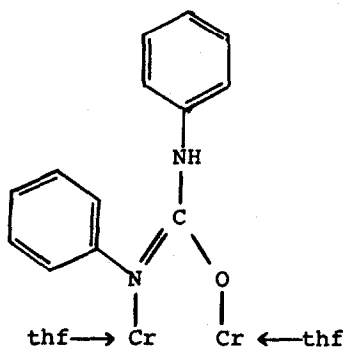


$$r(\text{Cr}-\text{Cr}) = 2.006 \text{ \AA}$$

$$\omega = 81.7^\circ$$

4-dimethylaminoacetanilido

(41)

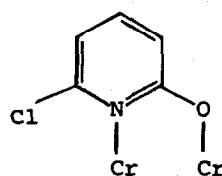


$$r(\text{Cr}-\text{Cr}) = 2.246 \text{ \AA}$$

$$\omega = 76.2^\circ$$

carbanilido

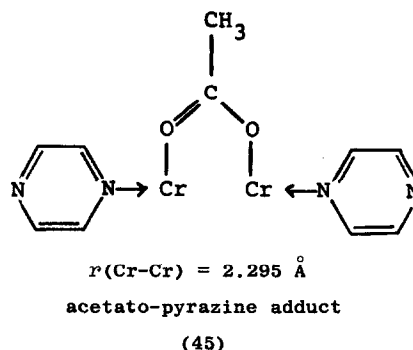
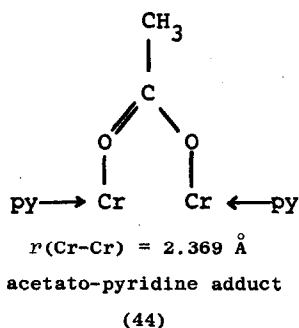
(42)



$$r(\text{Cr}-\text{Cr}) = 1.955 \text{ \AA}$$

6-chloro-2-oxypyridine

(43)

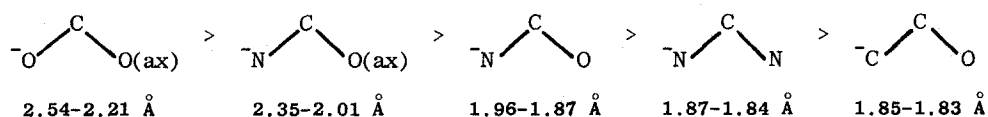


upon whether axial ligands are present and, if so, upon their nature and number. The compounds are of the type  $[\text{Cr}_2\text{L}_4]$ , and only one of the bridging, singly charged, anionic ligands L has been drawn, but any axial ligands have been shown. When L = acetanilido (36) the Cr-Cr bond length is  $1.873 \text{ \AA}$  [186], which is close to the shortest known value ( $1.828 \text{ \AA}$  in tetrakis(2-methoxy-5-methylphenyl)dichromium(II) [187]), and much shorter than in any carboxylato-complex. The most obvious difference between the acetanilido complex and a carboxylato complex is the steric hindrance to coordination of axial ligands presented by the NPh group. The axial positions are inaccessible because the acetanilido ligands are arranged with N *trans* to N and O *trans* to O, and the torsion angle  $\omega$  about the N-Ph bond is equal to  $48^\circ$ . Dichromium compounds (37) to (40), in which  $\omega$  has been increased to approximately  $90^\circ$  to open up the axial positions, have been obtained [188] by introducing methyl groups into the 2 and 6 positions of the phenyl rings. Steric effects then force the rings to lie perpendicular to the O-Cr<sub>2</sub>-N plane. Substitution of hydrogen in the 4 position by a dimethylamino group produces the same effect through electron donation by the NMe<sub>2</sub> group (41). Access by axial ligands can then occur in a series of complexes without fundamental change in the amido (N-C-O) bridging ligands or in the overall geometry of the complexes. Axial donation modifies the Cr-Cr bond distance as in the carboxylates, but with the carboxylates the bond separation without axial ligands is unknown because even in anhydrous  $[\text{Cr}_2(\text{O}_2\text{CCH}_3)_4]$  oxygen atoms of adjacent units occupy axial positions [189].

The Cr-Cr bond distance increases by approximately  $0.15 \text{ \AA}$  in each stage as first one and then two thf molecules are axially bonded (compounds 36, 38 and 37) but, for the same axial ligands, changes in substituent attached to the N-C-O bridge (compare (38) and (41), and (37) and (42)) have little effect on  $r(\text{Cr}-\text{Cr})$ . However, replacement of thf in (37) by the more basic pyridine in (39) clearly lengthens  $r(\text{Cr}-\text{Cr})$ , presumably by introducing greater electron density into the  $d_{z^2}-d_{z^2} \sigma^*$  orbital. A less marked effect is that coordination

of an axial ligand increases the lengths of bonds from the metal to the bridging ligands.

A tabulation of the Cr-Cr bond lengths in some thirty-five binuclear chromium(II) compounds of known structures [188] shows that the quadruple bonds (the ranges are given) shorten with type of bridging bidentate anion in the order:



The presence of axial ligands is signified by (ax), and the formally negatively charged atom is shown. However, with N-C-O bridges the formal charge is on N or O, according to whether the anion is derived from an amide, *e.g.* (36) or a hydroxypyridine, *e.g.* (43). It appears that the Cr-Cr bonds shorten as the donor strength (basicity) of the anions increases:  $\text{O}^- < \text{N}^- < \text{C}^-$ .

There is considerable variation of  $r(\text{Cr-Cr})$  within the O-C-O(ax) series according to the nature of the axial ligand, and this is also true of the new N-C-O(ax) substituted acetanilido series. The ranges of metal-metal bond lengths in these series overlap so that dichromium compounds no longer fall into two distinct classes - carboxylates, and others with much shorter metal-metal separations. It is predicted that isolated  $[\text{Cr}_2(\text{O}_2\text{CR})_4]$  units will have Cr-Cr separations between 1.90 Å and ~2.0 Å.

During attempts to crystallise unsolvated (37) from methylene chloride the disolvate (40) was obtained [190]. In this compound a chlorine atom of one methylene chloride molecule is 3.354 Å axially from one chromium atom, and a chlorine atom of the other methylene chloride molecule is 3.58 Å from the second chromium atom. The Cr-Cr separation is substantially longer (0.076 Å) than in the unsolvated molecule (36). It is suggested that, although the nearer chlorine atom would normally be considered too far away to be bonded to the chromium atom, the increased Cr-Cr separation shows that it is acting as a very weak Lewis base. This first example of such donation has been detected only because of the sensitivity of the Cr-Cr separation to axial  $\sigma$ -density. The corresponding molybdenum compound is isostructural but Mo-Mo quadruple bonds are not sensitive to axial donors, and there is no significant change from the unsolvated compound.

The Cr-Cr bond in the new compound  $[\text{Cr}_2(\text{chp})_4]$  (43) [191] is 0.066 Å longer than in  $[\text{Cr}_2(\text{mhp})_4]$  [192] (Hchp is 6-chloro-2-hydroxypyridine and Hmhp is 6-methyl-2-hydroxypyridine). Amongst previously known complexes without axial ligands, marked variations in the type of bridging ligand produced a range of

Cr-Cr distances spanning only 0.08 Å. Compared with this, replacement of CH<sub>3</sub> by Cl causes a significant increase in  $r(\text{Cr-Cr})$ . In the absence of axially bonded ligands in both molecules, it seems that the inductive effect of the chlorine substituent lowers the donor capacity of the bridging ligand and lengthens the metal-metal bond. However, as the Cr...Cl distances have an average value of 3.226 Å it is possible that weak axial interaction as in compound (40) may contribute to the lengthening because of the sensitivity of the Cr-Cr bond to axial interaction. It is intended to synthesise the 6-fluoro-substituted compound, in which electron withdrawal should be greater and direct interactions diminished; control by the inductive effect should produce a longer Cr-Cr bond. The analogous molybdenum and tungsten compounds have been structurally characterised but the metal-metal bond distances are much less sensitive to changes in bridging ligands or the presence of axial ligands.

Compounds (37), (41), (42) and (43) were prepared by reaction of anhydrous chromium(II) acetate with the lithium salt of the ligand in a mixture of hexane and thf. The number and type of axial ligand could be modified by heating and by recrystallisation from the appropriate solvent. Several compounds contain molecules of solvent in the lattice, but these have not been specified here.

The He(II) PE spectra of  $[\text{M}_2(\text{mhp})_4]$  {where M = Cr or Mo} show changes [193] in relative intensities compared with the earlier He(I) spectra and this, together with *ab initio* molecular orbital calculations on the enol form of 2-hydroxypyridine, have led to a full assignment of the spectra. The  $\delta$  and  $\pi(\text{E})$  ionisations are resolved, and the splitting in the chromium case has been found to be 1.4 eV, whereas it is less than 1 eV in the carboxylates because of their weaker metal-metal interaction. Another difference from the carboxylates is that the metal and ligand ionisations are not well separated, perhaps because of ligand ( $\pi$ ) to metal  $\delta^*(d_{xy})$  charge transfer which may be important in producing the shorter bond in  $[\text{Cr}_2(\text{mhp})_4]$  (1.889 Å) as compared with  $[\text{Cr}_2(\text{O}_2\text{CMe})_4]$  (2.288 Å).

Pyridine and pyrazine form 2:1 (44) and 1:1 (45) adducts with chromium(II) acetate, the structures of which have been determined [194]. The bifunctional pyrazine links the dichromium units into slightly zigzagging chains, and the Cr-Cr bond distance (2.295 Å) is considerably shorter than in the adducts formed by the more basic pyridine (2.369 Å) and piperidine (2.342 Å) [195]. The Cr-Cr bonds in the pyridine and piperidine adducts of  $[\text{Cr}_2(\text{O}_2\text{CCH}_3)_4]$  are very similar in length to that in (39).

In summary, the length of the Cr-Cr quadruple bond appears to depend primarily upon the extent of axial coordination and secondarily upon the donor strength of the bridging ligands. The latter may be more dependent upon substituent effects than earlier believed.

It is uncertain whether the weak paramagnetism of chromium(II) acetate is inherent and represents some slight population of the triplet state or arises from the presence of chromium(III) impurities. The ammine  $[\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{NH}_3)_2]$  has been prepared [196], by passing ammonia through a suspension of the hydrate in ethanol, and its small molar susceptibility is ascribed to temperature independent paramagnetism, so that population of the triplet state is insignificant. Liquid ammonia breaks the Cr-Cr bond and produces  $[\text{Cr}(\text{NH}_3)_4(\text{O}_2\text{CCH}_3)_2]$  ( $\mu_{\text{eff}} = 4.8 \mu_B$ , independent of temperature) which, unless in an ammonia atmosphere, reverts rapidly to the bridged ammine.

The Cr-Cr bond in  $[\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{OH}_2)_2]$  contracts from 2.362 Å at room temperature to 2.353 Å at 90 K, a value less than the interatomic distance in the metal [197]. This relatively large contraction agrees with the shallowness of the Cr-Cr potential calculated theoretically [198], and is in agreement with the increased sensitivity of the Cr-Cr bond to axial ligand interactions and ligand substitution as it becomes longer [188]. There is a broad region of excess electron density off the Cr-Cr bond axis and an electron-deficient area in the  $\sigma$ -bond region along the axis. This probably relates to the weakening of the Cr-Cr bond induced by interaction of the axial water molecules with the orbitals of the chromium. Theoretical electron density maps have been obtained from three different types of wavefunction and compared with the experimental data. The diamagnetic anisotropy of metal-metal multiple bonds has been briefly considered [199].

A detailed analysis of the low temperature (6 K) polarised single crystal spectra of  $[\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{OH}_2)_2]$  has been given [200]. The two most intense absorption bands at  $\sim 21000 \text{ cm}^{-1}$  (I) and  $\sim 30000 \text{ cm}^{-1}$  (II) have been assigned as  $^1A_{1g} \rightarrow ^1E_g$  and  $^1A_{1g} \rightarrow ^1E_u$  transitions, respectively, in  $D_{4h}$  symmetry. Band I corresponds to a  $\delta \rightarrow \pi^*$  transition within the metal orbitals of the Cr-Cr system, and band II to a transition from a carboxylate non-bonding  $p_\pi$  orbital to antibonding metal orbitals ( $np_\pi \rightarrow \pi^*$ ). A weak sharp band at  $\sim 16000 \text{ cm}^{-1}$  is thought to correspond to the  $\delta \rightarrow \delta^*$  transition ( $^1A_{1g} \rightarrow ^3A_{2u}$ ), and this assignment implies that the acetate should be essentially diamagnetic. The ground state Cr-Cr stretching frequency has been estimated to be in the  $150\text{--}250 \text{ cm}^{-1}$  range, from an analysis of the vibrational fine structure of the absorption bands. The energies of the bands I and II in a series of  $[\text{Cr}_2(\text{O}_2\text{CCH}_3)_4\text{L}_2]$  compounds decrease approximately linearly with Cr-Cr bond length.

## 6.6 MISCELLANEOUS CHEMISTRY OF LOWER OXIDATION STATES

In this section reductions by chromium(II) complexes,  $\sigma$ -bonded organo-chromium(III) complexes, electrochemical reductions and some thermal reactions of chromium(III) complexes, and a few zerovalent compounds not containing

chromium-carbon bonds are briefly and selectively reviewed.

Chromium(II) in acid solution reduces benzoquinone in good yield to hydroquinone [201]. Five chromium(III) products have been separated by cation exchange chromatography from the reaction mixture, and these include bi- and trinuclear intermediates containing hydroquinone which eventually hydrolyse to  $[\text{Cr}(\text{OH}_2)_6]^{3+}$ . Some aminopolycarboxylate complexes, *e.g.*  $[\text{Cr}(\text{O}_2\text{CCH}_2)_2\text{NH}(\text{OH}_2)_3]^+$ , have been obtained [202] in solution by reduction of related cobalt(III) complexes with  $\text{Cr}^{2+}(\text{aq})$ .

Chromium(II) acetate, in *dms*o containing butanethiol as H-donor, has been used for some time in the dehalogenation of certain  $\beta$ -hydroxyhalides, but the method fails for others [203]. Protection of the OH groups by ether formation and the use of the more powerfully reducing chromium(II)-ethylenediamine complex in *dmf* also containing butanethiol, have overcome the problems. The  $\text{Cr}^{2+}$  can be electrochemically regenerated and the method provides a convenient entry to deoxynucleosides.

Oxide dissolution is important in the extraction of metals from ores and in the de-scaling of high temperature water-cooled plants. At present strong acids or chelating agents are normally used, but investigations of the reactions of one-electron reducing agents with  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  and  $\text{NiFe}_2\text{O}_4$  have shown that  $\text{Cr}^{2+}$  in 0.1 M  $\text{Cl}^-$  and  $[\text{Cr}(\text{bipy})_3]^{2+}$  are among the most rapid reducing agents [204].

Intensely absorbing green 1:1 species  $[\text{Cr}(\text{pyzH})]^{3+}$  are formed when oxygen-free solutions of  $\text{Cr}^{2+}$  and pyrazine (pyz) are mixed at pH 1 to 2.  $[\text{Cr}(\text{pyzH})]^{3+}$  is a Cr(III)-pyrazine radical anion complex, stabilised by protonation of the remote nitrogen site [205].

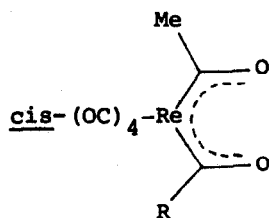
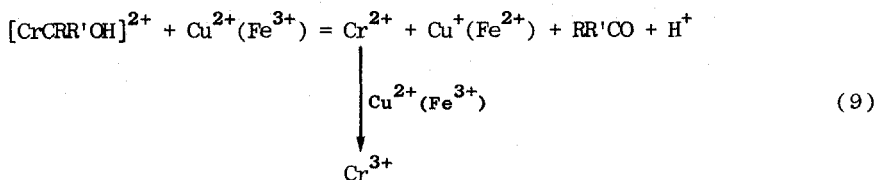
The electronic spectrum of  $\text{Cr}(\text{CCl}_3)_2^{2+}(\text{aq})$  has been reported [206]. It is formed in equal amounts with  $\text{CrCl}_2^{2+}(\text{aq})$ , on reduction of  $\text{CCl}_4$  by  $\text{Cr}^{2+}$  in acidic aqueous methanol. It is more labile than  $\text{Cr}(\text{CF}_3)_2^{2+}$  and aquates *via* a  $\text{CCl}_2$  intermediate to  $\text{CrCl}_2^{2+}(\text{aq})$ .

Chromium(II) reacts with 3-pyridineacrylic acid, 4-pyridineacrylic acid, maleic acid and fumaric acid, to give remarkably inert organochromium species [207], according to the general reaction:

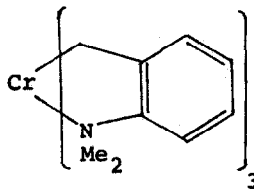


A number of new dimetallic bis(benzylchromium) cations have been obtained from the appropriate dibromides and chromium(II) [208] and the oxidative cleavage (9) of  $\alpha$ -hydroxyalkyl complexes such as  $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{OH}]^{2+}$  by  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$  has been investigated [209].

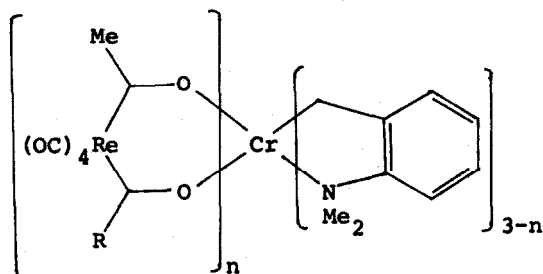
Mixed ligand, paramagnetic complexes containing the rhenaacetylacetonate and  $\sigma$ -bonded *N,N*-dimethyl-*o*-toluidyl ligands {see (46), (47) and (48)} have been prepared [210] according to reaction (10).



(46)



(47)



(49)



The polarographic behaviour of  $[\text{Cr}(\text{C}_6\text{H}_5)(\text{dpm})_2].\text{thf}$  has been investigated in anhydrous tetrahydrofuran [211]. The first step in the electrochemical reduction in dmsO of  $[\text{Cr}(\text{urea})_6]^{3+}$ ,  $[\text{Cr}(\text{dmsO})_6]^{3+}$ ,  $[\text{Cr}(\text{en})_3]^{3+}$ , and  $[\text{Cr}(\text{dien})_2]^{3+}$ , is reversible or quasi reversible, but is much more cathodic and irreversible for  $[\text{Cr}(\text{en})_2(\text{acac})]^{2+}$ ,  $[\text{Cr}(\text{en})(\text{acac})_2]^+$ , and  $[\text{Cr}(\text{acac})_3]$  [212]. On reduction in various supporting aqueous electrolyte solutions,  $[\text{Cr}(\text{urea})_6]^{3+}$  exhibits two irreversible polarographic waves [213]. These correspond to  $\text{Cr(III)} \longrightarrow \text{Cr(II)}$  and  $\text{Cr(II)} \longrightarrow \text{Cr(0)}$ .

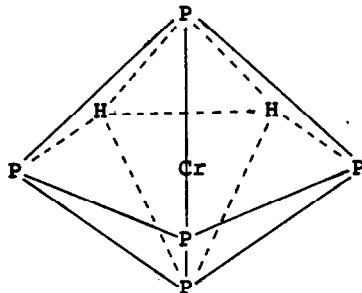
Polarographic and cyclic voltammetric studies show that the ions  $[\text{Cr}(\text{bipy})_3]^{3+}$ ,  $[\text{Cr}(\text{Ph}_2\text{bipy})_3]^{3+}$ , and  $[\text{Cr}(\text{Me}_2\text{bipy})_3]^{3+}$  undergo four reversible one electron reductions to the formal  $\text{Cr(-I)}$  oxidation state [214]. The *p*-phenyl substituent appears to stabilise both high and low oxidation states, relative to the unsubstituted complex. In the low valent compounds the redox changes take place



primarily on the ligands.

Recently, a new thermoanalytical instrument was developed (Q-derivatograph), in which thermal reactions can be studied in a quasi-closed system under quasi-isothermal and quasi-isobaric conditions instead of the more usual open, dynamic conditions (D-derivatograph). Its operation has been tested on the new hexaamminechromium(III) amino polycarboxylates:  $[\text{Cr}(\text{NH}_3)_6]\text{Na}(\text{edta}) \cdot 3\text{H}_2\text{O}$ ,  $[\text{Cr}(\text{NH}_3)_6]\text{Na}(\text{pdta}) \cdot 6\text{H}_2\text{O}$ ,  $[\text{Cr}(\text{NH}_3)_6]\text{HK}_3\text{Cl}(\text{nta})_2 \cdot 2\text{H}_2\text{O}$  and  $[\text{Cr}(\text{NH}_3)_6]\text{KCl}(\text{nta}) \cdot 2\text{H}_2\text{O}$ , where edta, pdta and nta, respectively, denote ethylenediaminetetraacetate, propylenediaminetetraacetate and nitrilotriacetate [215]. The reactions in the open system were too complicated to yield uniform intermediates but the reaction steps in the quasi-closed systems were definite and reproducible, with detectable plateaux and pure intermediates. A general mechanism has been proposed for thermal reactions in solid complexes including  $[\text{Cr}(\text{NH}_3)_5(\text{OH}_2)]\text{X}_3$ , the dehydration of which is consistent with the formation of a Frenkel type defect [216].

Co-condensation of Cr atoms with  $\text{P}(\text{OMe})_3$  onto a liquid nitrogen cooled surface produces  $\text{Cr}\{\text{P}(\text{OMe})_6\}$  which, in pentane under dihydrogen at one atmosphere, gives  $\text{Cr}\{\text{P}(\text{OMe})_3\}_5\text{H}_2$  almost quantitatively [217]. The hydride is fluxional on the NMR time scale and is the first of its type in which intramolecular exchange has been studied. The seven coordinate structure (49) is



(49)

considered most likely from an analysis of the  $^{31}\text{P}$  and  $^1\text{H}$  NMR spectra. Metal vapour synthesis has been used to prepare [218] complexes of zerovalent chromium and other metals with the  $\pi$ -acceptor aminodifluorophosphines,  $\text{Me}_2\text{NPF}_2$  and  $\text{MeN}(\text{PF}_2)_2$ . These ligands were selected because of their volatility and ease of preparation in the relatively large quantities required for metal vapour syntheses. The complex  $[\text{Cr}(\text{PF}_2\text{NMe}_2)_6]$  is appreciably less stable to oxidation and heat than  $\text{Cr}(\text{PF}_3)_6$  and  $\text{Cr}(\text{CO})_6$ , presumably due to the steric hindrance of its bulkier ligands. The metal vapour synthesis does not have any advantages over other methods in the preparation of  $[\text{Cr}\{(\text{PF}_2)_2\text{NMe}\}_3]$ , which was earlier

obtained from  $\text{Cr}(\text{CO})_6$ , but it has been useful for the preparation of  $[\text{Cr}(\text{PF}_2\text{NMe}_2)_4\{(\text{PF}_2)_2\text{NMe}\}]$  as major product by co-condensation of metal vapour with mixtures of the ligands. This complex is more stable than  $[\text{Cr}(\text{PF}_2\text{NMe}_2)_6]$  because of relief of steric strain on substitution by a bidentate ligand, and gives a molecular ion in its mass spectrum. The air-stable chromium(0) complex  $[\text{Cr}\{(\text{PF}_2)_2\text{NPh}\}_3]$  has been prepared from  $\text{Cr}(\text{CO})_6$  [219]. In the known complex tris[1,2-bis(dimethylphosphino)ethane]chromium(0), now prepared from the metal vapour [220], the chromium atom has a distorted octahedral environment.

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