Chromium-(II) and -(III) Complexes containing Hydrazines or Hydrazinecarboxylates as Ligands†

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The complexes $[\{CrX_2(R^2R^1NNH_2)_2\}_n]$ (X = Cl, R^1 = H, Me or Ph, R^2 = H; $R^1 = R^2$ = Me; X = Br, R^1 = H or Ph, R^2 = H) have been prepared and spectroscopic data acquired which suggest that the monomethylhydrazine complex is analogous to the well known hydrazine complexes with bridging NH_2NHR (R = H or Me) ligands and terminal halide ligands, whereas the *N,N*-dimethyl- and phenylhydrazine complexes involve unidentate hydrazine and bridging halide ligands. The quadruple metal–metal bonded complexes $[\{Cr_2(O_2CMe)_4(\mu\text{-}R^2R^1NNH_2)\}_n]$ (R^1 = H or Me, R^2 = H; $R^1 = R^2$ = Me) containing bridging $NH_2NR^1R^2$ ligands and $[Cr_2(O_2CMe)_4(PhNHNH_2)_2]$ containing unidentate NH_2NHPh ligands have also been prepared and characterised. Chromium(II) hydrazinecarboxylate, $[\{Cr(O_2CNHNH_2)_2(H_2O)\}_n]$ has been prepared by either cleavage of the metal–metal bonds of $[Cr_2(O_2CMe)_4L_2]$ (L = H_2O or $\tfrac{1}{2}N_2H_4$) or ligand-displacement reactions of mononuclear chromium(II) complexes. Its infrared spectrum and that of the fully deuteriated analogue have been recorded and vibrational assignments proposed. Oxidation of $[\{Cr(O_2CNHNH_2)_2(H_2O)\}_n]$ or other chromium(II) species in aqueous $[N_2H_5][O_2CNHNH_2]$ leads to the chromium(III) complex $[Cr(O_2CNHNH_2)_3]\cdot 2H_2O$. The substituted hydrazinecarboxylates $[Cr\{O_2CN(Me)NH_2\}_3]\cdot H_2O$ and $[Cr_2(O_2CNHNHPh)_4(MeOH)_2]$ have also been isolated, the latter probably containing carboxylate-*O,O′* groups bridging a metal–metal bonded Cr_2 unit in the manner well established for other carboxylate anions.

Anhydrous hydrazine, monomethylhydrazine and *N,N*-dimethylhydrazine have been used as propellants and fuels in, for example, launch vehicles for spacecraft and the in-orbit control of satellites. A problem related to this application is the increased rate of propellant decomposition in metal storage tanks brought about by carbon dioxide contamination.[1] In the case of hydrazine, this enhanced decomposition has been traced in part to a reaction producing hydrazinecarboxylic acid,[2] NH_2NHCO_2H, which exists in excess of hydrazine as $[N_2H_5][O_2CNHNH_2]$. In contact with steels, for example, metal ions are leached from the surfaces into the bulk propellant, the resulting metal complexes (most likely hydrazinecarboxylates) acting as homogeneous catalysts for hydrazine decomposition. Recent work[3] has shown chromium to be an active metal in this regard and so we have carried out some studies aimed at establishing the nature of the species formed in several hydrazines.

The reported chemistry of hydrazine complexes of chromium is not extensive. The only well characterised complexes are $[\{CrX_2(\mu\text{-}N_2H_4)_2\}_n]$ (X = Cl, Br or I),[4,5] an unstable, impure, fluoro-analogue also having been reported.[6] Several chromium(III) complexes *e.g.* $[CrCl_3(N_2H_4)_3]\cdot 2H_2O$,[7] $[Cr_2(C_2O_4)_3]\cdot xN_2H_4\cdot yH_2O$ (x = 2 or 6, y = 0; $x = y$ = 4; x = 7, y = 1)[8] and $[Cr(N_2H_4)_2(ClO_4)_2]ClO_4$[9] are mentioned in the literature, but the authenticity of these complexes may be in doubt having been prepared using hydrazine hydrate which acts as a strong base producing hydroxochromium(III) species. Indeed, the removal of chromate from waste waters as 'chromium(III) hydroxide' is achieved commercially using aqueous hydrazine. The complexes $[CrF_3(N_2H_4)_3]$[6] and $[CrCl_3(MeHNNHMe)_3]$[10] are less open to doubt, having been obtained from reactions employing anhydrous hydrazines.

We report here some of our studies on the chemistry of chromium-(II) and -(III) with the hydrazines $NH_2NR^1R^2$ (R^1 = H, Me or Ph, R^2 = H; $R^1 = R^2$ = Me) and with hydrazine-, monomethylhydrazine- and phenylhydrazine-carboxylic acids. A preliminary account of some chromium(II)–hydrazine reactions has been published.[11]

Experimental

Starting Materials.—The chromium(II) compounds $CrCl_2\cdot 4H_2O$,[12] $CrBr_2\cdot 6H_2O$,[12] $[Cr_2(O_2CMe)_4(H_2O)_2]$[13] and $[\{CrCl_2(NCMe)_2\}_n]$[14] were prepared by literature methods. Anhydrous $[Cr_2(O_2CMe)_4]$ was prepared by thermal dehydration of the hydrate *in vacuo*. Anhydrous hydrazine was provided by Royal Ordnance plc, Westcott and conformed to the US monopropellant specification (1% H_2O maximum, 0.003% CO_2 maximum). If necessary, it was distilled from calcium hydride under nitrogen before use. Monomethyl- and *N,N*-dimethyl-hydrazines were distilled from potassium hydroxide under nitrogen before use.

$[^2H_6]$Hydrazine hydrate (minimum 98% D) was a commercial product (MSD isotopes). Hydrazinecarboxylic acid was prepared by slowly passing CO_2 gas through an aqueous solution (30 cm³) of hydrazine (30 cm³) at 0 °C for 12 h. The colourless solid was filtered off under N_2 and purified by stirring in anhydrous methanol, followed by filtration under nitrogen, washing with diethyl ether and drying *in vacuo*. Yield 92% (Found: C, 15.6; H, 5.40; N, 36.7. Calc. for $CH_4N_2O_2$: C, 15.8; H, 5.30; N, 36.8%). $[^2H_4]$Hydrazinecarboxylic acid was obtained by saturating a solution of $N_2D_4\cdot D_2O$ (1.00 cm³) in D_2O (1.00 cm³) with CO_2 until a colourless precipitate began to form. $[^2H_4]$Methanol (4.00 cm³) was layered on to this solution and after 72 h the solid that had formed was filtered off, washed with diethyl ether and dried *in vacuo*. Yield 1.31 g, 91.0%. Methylhydrazinecarboxylic acid was prepared in a similar manner,[15] CO_2 being passed through a solution of $MeNHNH_2$ (2.30 g, 50 mmol) in ethanol (50 cm³) for 3 h. The colourless, highly hygroscopic, solid was filtered off under nitrogen and dried *in vacuo* (Found: C, 26.1; H, 6.70; N, 30.9.

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† *Non-SI unit employed:* eV ≈ 1.60×10^{-19} J.

Calc. for $C_2H_6N_2O_2$: C 26.7; H, 6.70; N, 31.1%). Phenylhydrazinecarboxylic acid was prepared as $PhNHNHCO_2H{\cdot}PhNHNH_2$[16] (or $[PhNHNH_3][PhNHNHCO_2]$), by passing CO_2 through a solution of $PhNHNH_2$ (10 cm^3, 102 mmol) in methanol (150 cm^3) for 2 h. The colourless precipitate was filtered off, washed with diethyl ether and dried *in vacuo* (Found: C, 60.5; H, 6.30; N, 21.9. Calc. for $C_{13}H_{16}N_4O_2$: C, 60.0; H, 6.20; N, 21.5%).

Solvents were thoroughly dried by standard methods (MeOH and EtOH, reflux over Mg under N_2; MeCN, reflux over P_2O_5 under N_2) and purged with N_2 before use.

Physical Measurements.—Infrared spectra of Nujol mulls were recorded over the range 4000–200 cm^{-1} using a Perkin-Elmer 597 spectrophotometer. Magnetic moment determinations were carried out at room temperature by the Gouy method using $[Ni(en)_3]S_2O_3$ (en = ethane-1,2-diamine) as calibrant.

Electronic spectra of mulls were recorded using a Perkin-Elmer 330 spectrophotometer fitted with a diffuse reflectance attachment. Differential thermal analysis (DTA) and thermal gravimetry (TG) experiments were carried out on a Stanton Redcroft STA 780 thermal analyser, the powdered samples being heated at 10 °C min^{-1} in air or in flowing argon, the reference being α-alumina. The X-ray photoelectron spectra were recorded using a VG spectrometer, samples being loaded as powders dusted on to double-sided adhesive tape. The Al-K$\alpha_{1,2}$ line was used as the excitation source and surface-charging effects reduced by use of an electron 'floodgun'.

Chromium(II)*-Hydrazine Complexes.*—(*a*) $[\{CrX_2(N_2H_4)_2\}_n]$ (X = Cl *or* Br). These established complexes were prepared by treating ethanol solutions of $CrCl_2{\cdot}4H_2O$ or $CrBr_2{\cdot}6H_2O$ with a solution of anhydrous hydrazine in ethanol. The pale lilac precipitates were filtered off under N_2, washed with ethanol and diethyl ether and dried in a stream of N_2. Their identity was confirmed by infrared spectroscopy.[4]

The chloride was also isolated from a reaction between a methanol solution of $[\{CrCl_2(NCMe)_2\}_n]$ (1.50 g, 7.3 mmol) and hydrazinecarboxylic acid (1.11 g, 14.6 mmol) under N_2. The bromide was also obtained when an ethanol solution of $CrBr_2{\cdot}6H_2O$ (1.44 g, 4.5 mmol) was added to hydrazinecarboxylic acid (3.04 g, 40.0 mmol) under N_2 at −10 °C. The mixture was stirred for 1 h and then warmed to room temperature.

(*b*) $[\{CrCl_2(MeNHNH_2)_2\}_n]$. A solution of $MeNHNH_2$ (0.53 cm^3, 10.01 mmol) in anhydrous MeCN (20 cm^3) was added under N_2 to a suspension of anhydrous $CrCl_2$ (0.59 g, 4.79 mmol) in anhydrous MeCN (25 cm^3). The light blue product which formed rapidly was filtered off under N_2, washed with MeCN and diethyl ether and dried in a stream of N_2 (Found: C, 10.9; H, 5.20; N, 25.5. Calc. for $C_2H_{12}Cl_2CrN_4$: C, 11.2; H, 5.65; N, 26.0%).

(*c*) $[\{CrCl_2(Me_2NNH_2)_2\}_n]$. This complex was prepared as a pale blue-green solid from acetonitrile solution using the method outlined in (*b*). The reactants were $CrCl_2$ (0.71 g, 5.74 mmol) and Me_2NNH_2 (0.92 cm^3, 12.03 mmol) (Found: C, 19.5; H, 6.85; N, 22.7. Calc. for $C_4H_{16}Cl_2CrN_4$: C, 19.8; H, 6.65; N, 23.0%).

(*d*) $[\{CrX_2(PhNHNH_2)_2\}_n]$ (X = Cl *or* Br). A methanol solution of $CrCl_2{\cdot}4H_2O$ (0.975 g, 5.0 mmol) or $CrBr_2{\cdot}6H_2O$ (1.60 g, 5.0 mmol) was added to a solution of $PhNHNH_2$ (1.02 cm^3, 10.4 mmol) in diethyl ether (30 cm^3). Pale blue products precipitated immediately and were filtered off under N_2, washed with diethyl ether and dried in a stream of N_2 (Found: C, 42.2; H, 4.85; N, 16.4. Calc. for $C_{12}H_{16}Cl_2CrN_4$: C, 42.5; H, 4.75; N, 16.5%).

(*e*) $[\{Cr_2(O_2CMe)_4(\mu\text{-}N_2H_4)\}_n]$. To a degassed solution of $[Cr_2(O_2CMe)_4(H_2O)_2]$ (2.04 g, 5.42 mmol) in methanol (30 cm^3) was added a degassed solution of anhydrous hydrazine (5.0 cm^3, 15.78 mmol) in methanol (10 cm^3) under N_2. After stirring under N_2 at room temperature for 12 h, the orange product was filtered off, washed with methanol and diethyl ether and dried in a stream of N_2 (Found: C, 25.3; H, 4.25; Cr, 27.6; N, 7.55. Calc. for $C_8H_{16}Cr_2N_2O_8$: C, 25.8; H, 4.35; Cr, 27.9; N, 7.55%). Selected IR bands (cm^{-1}): 1595vs (br), $\nu_{asym}(CO_2) + \delta(NH_2)$; 1453vs, $\nu_{sym}(CO_2)$; 1349m, $\omega(NH_2)$; 1125s, $\rho_t(NH_2)$; 1049s, 1032w, $\rho_r(CH_3)$; 961w, $\nu(NN)$; 926w, $\nu(CC)$; 679s, $\delta(CO_2)$; and 621m, $\pi(CO_2)$.

(*f*) $[\{Cr_2(O_2CMe)_4(\mu\text{-}MeNHNH_2)\}_n]$. A suspension of anhydrous $[Cr_2(O_2CMe)_4]$ (1.15 g, 3.37 mmol) in ethanol (25 cm^3) under N_2 was treated with a solution of $MeNHNH_2$ (0.54 cm^3, 10.2 mmol) in ethanol (15 cm^3). After stirring for 1 h at room temperature the red-orange product was filtered off under N_2, washed with diethyl ether and dried in a stream of N_2 (Found: C, 28.0; H, 4.95; N, 6.95. Calc. for $C_9H_{18}Cr_2N_2O_8$: C, 27.9; H, 4.70; N, 7.25%).

(*g*) $[\{Cr_2(O_2CMe)_4(\mu\text{-}Me_2NNH_2)\}_n]$. A suspension of anhydrous $[Cr_2(O_2CMe)_4]$ (1.18 g, 3.45 mmol) in ethanol (25 cm^3) under N_2 was treated with a solution of Me_2NNH_2 (0.84 cm^3, 11.0 mmol) in ethanol (10 cm^3). The product was filtered off under N_2, washed with diethyl ether and dried in a stream of N_2 (Found: C, 30.0; H, 5.60; N, 7.35. Calc. for $C_{10}H_{20}Cr_2N_2O_8$: C, 30.0; H, 5.05; N, 7.00%).

(*h*) $[Cr_2(O_2CMe)_4(PhNHNH_2)_2]$. To a suspension of $[Cr_2(O_2CMe)_4(H_2O)_2]$ (1.20 g, 3.20 mmol) in ethanol (20 cm^3) was added a solution of $PhNHNH_2$ (0.94 cm^3, 9.6 mmol) in ethanol (10 cm^3). The mixture was stirred under N_2 at room temperature for 3 h before filtration of the pale orange product which was then washed with ethanol and diethyl ether before drying in a stream of N_2 (Found: C, 43.1; H, 5.35; N, 10.3. Calc. for $C_{20}H_{28}Cr_2N_4O_8$: C, 43.2; H, 5.05; N, 10.1%).

Chromium–Hydrazinecarboxylate Complexes.—(*a*) *Bis*(*hydrazinecarboxylato*)*chromium*(II) *monohydrate*. This compound can be prepared by treating a variety of chromium(II) sources *e.g.* $[Cr_2(O_2CMe)_4(H_2O)_2]$, $[\{Cr_2(O_2CMe)_4(\mu\text{-}N_2H_4)\}_n]$, $CrCl_2{\cdot}4H_2O$, $CrBr_2{\cdot}6H_2O$ and $[\{CrX_2(\mu\text{-}N_2H_4)_2\}_n]$ (X = Cl or Br) with either hydrazinecarboxylic acid or hydrazinium hydrazinecarboxylate. Two typical preparations are given below.

(*i*) Passage of CO_2 through an aqueous solution (5.0 cm^3) of $N_2H_4{\cdot}H_2O$ (0.78 cm^3, 16.0 mmol) for 2 h generated a solution containing $[N_2H_5][O_2CNHNH_2]$ (8.0 mmol). Addition of an aqueous solution (1.50 cm^3) of $CrCl_2$ (0.139 g, 1.13 mmol) under N_2 caused rapid precipitation of a lilac product which was stirred under N_2 for 15 min before filtration, washing successively with water, methanol and diethyl ether and drying under N_2. Yield: 0.152 g (61.0%, based on $CrCl_2$ used) (Found: C, 11.2; H, 3.45; Cr, 23.8; N, 25.8. Calc. for $C_2H_8CrN_4O_5$: C, 10.9; H, 3.65; Cr, 23.6; N, 25.5%).

(*ii*) A mixture of $[Cr_2(O_2CMe)_4(H_2O)_2]$ (1.00 g, 2.7 mmol) and hydrazinecarboxylic acid (1.50 g, 19.8 mmol) was heated in refluxing methanol (50 cm^3) under N_2 for 2 h. After cooling, the lilac product was filtered off under N_2, washed with methanol and diethyl ether and dried in a stream of N_2. This reaction must be carried out at reflux temperature as it was found to be extremely slow at lower temperatures. Thus, largely unreacted hydrazinecarboxylic acid was recovered after 4 weeks at room temperature.

Fully deuteriated $[Cr(O_2CNHNH_2)_2(H_2O)]$ was prepared by method (*i*) above using $N_2D_4{\cdot}D_2O$ (0.78 cm^3, 16.0 mmol) in D_2O (3.5 cm^3) to generate $[N_2D_5][O_2CNDND_2]$ before reaction with $CrCl_2$ in D_2O. After filtration, the pale lilac product was washed with D_2O, CH_3OD and diethyl ether. Yield: 0.13 g (55.2%, based on $CrCl_2$ used).

(*b*) *Tris*(*hydrazinecarboxylato*)*chromium*(III) *dihydrate*. Although this complex can be prepared by oxidation of $[Cr(O_2CNHNH_2)_2(H_2O)]$, $CrCl_2{\cdot}4H_2O$, $CrBr_2{\cdot}6H_2O$ or $[\{CrX_2(\mu\text{-}N_2H_4)_2\}_n]$ (X = Cl or Br) in the presence of $[N_2H_5][O_2CNHNH_2]$, it is most easily prepared from $[CrCl_2(H_2O)_4]Cl{\cdot}2H_2O$.

Table 1 Magnetic and spectroscopic data for $[\{CrCl_2(R^2R^1NNH_2)_2\}_n]$ and related complexes

			IR/cm^{-1}		
Complex	μ_{eff}, r.t.	Reflectance spectrum, λ/nm[a]	ν(CrN)	ν(CrX)	Ref.
$[\{CrCl_2(\mu\text{-}N_2H_4)_2\}_n]$	4.85	570	427m, 346m	*b*	*c*
$[\{CrBr_2(\mu\text{-}N_2H_4)_2\}_n]$	4.80	570	420m, 338m	*b*	*c*
$[\{CrCl_2(\mu\text{-}MeNHNH_2)_2\}_n]$	4.59	594	426w, 359w	*b*	*c*
$[\{Cr(\mu\text{-}Cl)_2(Me_2NNH_2)_2\}_n]$	4.85	662	441 (sh), 434s	302s	*c*
$[\{Cr(\mu\text{-}Cl)_2(PhNHNH_2)_2\}_n]$	4.59	704	390w	323s	*c*
$[\{Cr(\mu\text{-}Br)_2(PhNHNH_2)_2\}_n]$	4.61	*d*	393w	*b*	*c*
$[\{Cr(\mu\text{-}Cl)_2(NCMe)_2\}_n]$	4.79	752		320vs	14
$[\{Cr(\mu\text{-}Cl)_2(C_5H_5N)_2\}_n]$	4.84	685	219m	303s	17
$[\{Cr(\mu\text{-}Cl)_2(NH_3)_2\}_n]$	4.57	714			18

[a] Broad band assigned to overlapping $^5B_{1g} \longrightarrow {}^5B_{2g}$, ^5E_g. [b] Not observed above 200 cm^{-1}. [c] This work. [d] Spectrum could not be recorded reproducibly because of rapid surface oxidation.

A solution of anhydrous hydrazine (17.0 cm^3, 531 mmol) in water (75 cm^3) was saturated with CO_2 for 1 h while being heated to 80 °C. Then with the CO_2 flow being maintained, a solution of $[CrCl_2(H_2O)_4]Cl{\cdot}2H_2O$ (1.60 g, 6.0 mmol) in water (5 cm^3) was added dropwise. The red solution was kept at 80 °C for 24 h and then cooled to produce a pink microcrystalline precipitate. This was filtered off, washed with water, ethanol and diethyl ether and dried *in vacuo*. Yield: 1.02 g, 54% based on Cr (Found: C, 11.7; H, 4.20; Cr, 16.3; N, 26.8. Calc. for $C_3H_{13}CrN_6O_8$: C, 11.5; H, 4.20; Cr, 16.6; N, 26.8%).

(*c*) *Tris(methylhydrazinecarboxylato)chromium*(III) *hydrate*. (*i*) A solution of $MeNHNH_2$ (2.30 g, 50 mmol) in ethanol (90 cm^3) was treated with CO_2 for 2 h whilst kept at 60 °C. A solution of $[CrCl_2(H_2O)_4]Cl{\cdot}2H_2O$ (1.33 g, 5.0 mmol) in ethanol (40 cm^3) was then added dropwise. The resulting pink microcrystalline product was filtered off, washed with ethanol and diethyl ether and dried *in vacuo* (Found: C, 21.0; H, 4.65; Cr, 15.3; N, 24.3. Calc. for $C_6H_{12}CrN_6O_7$: C, 21.4; H, 5.10; Cr, 15.4; N, 24.9%).

(*ii*) This complex could also be prepared by oxidation of chromium(II). A solution of $MeNHNH_2$ (1.15 g, 25 mmol) in methanol (30 cm^3) was treated with CO_2 for 2 h and then cooled under N_2 to −10 °C. A solution of $CrCl_2{\cdot}4H_2O$ (0.195 g, 1.0 mmol) in methanol (15 cm^3) was added dropwise initially to give a purple solution which on standing slowly produced a pink precipitate of $[Cr\{O_2CN(Me)NH_2\}_3]{\cdot}H_2O$.

(*d*) *Bis(methanol)tetrakis(phenylhydrazinecarboxylato)dichromium*(II). A solution of $CrCl_2{\cdot}4H_2O$ (0.975 g, 5.0 mmol) in methanol (15 cm^3) was added under N_2 to a suspension of $PhNHNHCO_2H{\cdot}PhNHNH_2$[16] (3.0 g, 11.5 mmol) in methanol (30 cm^3). A salmon-pink product precipitated rapidly, was filtered off under N_2, washed with methanol and diethyl ether and dried in a stream of N_2 (Found: C, 46.5; H, 4.70; N, 14.8. Calc. for $C_{30}H_{36}Cr_2N_8O_{10}$: C, 46.6; H, 4.70; N, 14.5%).

Results and Discussion

(*a*) *Complexes of Chromium*(II) *Halides with Hydrazines*.— The insoluble, polymeric, complexes $[\{CrX_2(R^2R^1NNH_2)_2\}_n]$ (X = Cl, R^1 = H, Me or Ph, R^2 = H; $R^1 = R^2$ = Me; X = Br, R^1 = H or Ph, R^2 = H) have been prepared and characterised by solid-state methods (Table 1). The substituted hydrazine complexes are especially air-sensitive. The results obtained suggest that two structural types are formed dependent on the nature of the hydrazine ligands. The previously reported[4] complexes $[\{CrX_2(\mu\text{-}N_2H_4)_2\}_n]$ (X = Cl or Br) have been prepared by both established and new routes, *e.g.* displacement of the acetonitrile ligands of $[\{Cr(\mu\text{-}Cl)_2(NCMe)_2\}_n]$[14] by hydrazine or reaction of anhydrous $CrCl_2$ with anhydrous hydrazine in methanol. Infrared and visible spectroscopic data[4] indicate the complexes to be octahedral with bridging hydrazine ligands and terminal axial, halides as established crystallographically[19] for $[\{MCl_2(\mu\text{-}N_2H_4)_2\}_n]$ (M = Mn or Zn). The spectroscopic results obtained in this work, which confirm earlier results,[4] support the formation of tetragonally distorted octahedral, magnetically dilute, high-spin chromium(II) complexes. The infrared spectra contain two bands in the 430–330 cm^{-1} region, assignable to ν(Cr–N) modes ($2e_u$ assuming CrN_4X_2 units of D_{4h} symmetry), but no ν(Cr–X) stretches have been found, the weakness of the axial Cr–X bonds probably resulting in such modes appearing below 200 cm^{-1}. These results are in line with infrared and Raman data reported[20] for $[\{MX_2(\mu\text{-}N_2H_4)_2\}_n]$ (M = Mn, Co or Zn; X = Cl or Br) which show that bands with high ν(MN) character are found in the 400–340 cm^{-1} region whereas bands with high ν(MX) character appear at exceptionally low frequencies for terminal metal–halide stretches *e.g.* ν(ZnCl) at 285 and 149 cm^{-1}. Additional Jahn–Teller-induced distortion can weaken the chromium–halide interactions still further. Other infrared bands *e.g.* ν(NN) at *ca.* 965 cm^{-1} are in the range suggested for bridging hydrazine ligands.[4,20,21]

No reactions of chromium-(II) or -(III) compounds with $MeNHNH_2$, Me_2NNH_2 or $PhNHNH_2$ appear to have been reported previously. Reactions of hydrated chromium(II) chloride or bromide with methanol solutions of $MeNHNH_2$ afforded only impure products containing hydroxo groups. However, reaction of $[\{CrCl_2(NCMe)_2\}_n]$ with $MeNHNH_2$ in anhydrous acetonitrile produced $[\{CrCl_2(MeNHNH_2)_2\}_n]$. The reflectance spectrum, magnetic moment and infrared ν(Cr–N) stretching frequencies (Table 1) are all very similar to those of $[\{CrCl_2(\mu\text{-}N_2H_4)_2\}_n]$, so a structure involving bridging $MeNHNH_2$ ligands and weak, axial, Cr–Cl bonds is proposed. This structural type has been suggested[22] for analogues of Fe^{II}, Co^{II} and Ni^{II}.

For Me_2NNH_2 the inductive effect of the methyl groups will enhance the basicity of the adjacent nitrogen atom, so electronic considerations favour $M{\leftarrow}NMe_2NH_2$ co-ordination. However, steric interactions involving the methyl groups may result in the NH_2 nitrogen being the favoured donor site, as in $[RuH(\eta^4\text{-cod})(Me_2NNH_2)_3][PF_6]$[23] (cod = cycloocta-1,5-diene) and the boroxin $[(EtBO)_3(Me_2NNH_2)]$.[24] Bridging co-ordination has also been established[25] as in $[\{RuCl(H)(\eta^4\text{-cod})\}_2(\mu\text{-}Me_2NNH_2)]$.

As for $MeNHNH_2$, the reactions of hydrated chromium(II) chloride or bromide with Me_2NNH_2 in ethanol resulted in hydroxide formation, however $[\{CrCl_2(Me_2NNH_2)_2\}_n]$ could be obtained from $[\{CrCl_2(NCMe)_2\}_n]$ in anhydrous acetonitrile. The room-temperature magnetic moment is similar to others listed in Table 1 but the maximum of the broad peak in the visible reflectance spectrum is shifted to lower energy by nearly 100 nm relative to that of $[\{CrCl_2(\mu\text{-}N_2H_4)_2\}_n]$, being closer to those of $[\{Cr(\mu\text{-}Cl)_2L_2\}_n]$ species (L = NH_3, C_5H_5N or MeCN) which possess $CrCl_4N_2$, rather than $CrCl_2N_4$, tetragonally distorted octahedral arrangements. Again, unlike

Table 2 Magnetic and spectroscopic data for $Cr_2(O_2CMe)_4$ products

Complex (X = O_2CMe)	μ_{eff}, r.t.	Reflectance spectrum, λ/nm	IR/cm^{-1}	
			ν(CrN)	ν(CrO)
$[\{Cr_2(\mu\text{-}X)_4(\mu\text{-}N_2H_4)\}_n]$	0.57	478s (br), 360s (sh), 333vs	469m	402s, 384m (sh)
$[Cr_2(\mu\text{-}X)_4(NH_3)_2]$[a]	0.6	513s (br), 361s (br), 350s (br), 336s (br)	475	
$[\{Cr_2(\mu\text{-}X)_4(\mu\text{-}MeNHNH_2)\}_n]$	0.49	476m (br), 349m (sh), 331s	475w	398s
$[Cr_2(\mu\text{-}X)_4(PhNHNH_2)_2]$	0.39	476m (br), 346m (sh), 324vs,[b] 265vs (br)	427w	401ms
$[\{Cr_2(\mu\text{-}X)_4(\mu\text{-}Me_2NNH_2)\}_n]$	0.59	478m (br), 360s (sh), 333vs		408s
$[Cr_2(\mu\text{-}X)_4(H_2O)_2]$	0.5	486s (br), 347s (sh), 326vs		407m, 384m

[a] Ref. 29. [b] Spectrum of solution in MeOH.

$[\{CrCl_2(\mu\text{-}RNHNH_2)_2\}_n]$ (R = H or Me), the infrared spectrum of $[\{CrCl_2(Me_2NNH_2)_2\}_n]$ contains a strong band assignable to a ν(CrCl) stretch at a very similar frequency to those of $[\{Cr(\mu\text{-}Cl)_2L_2\}_n]$ (L = C_5H_5N or MeCN). Therefore, it is proposed that in $[\{CrCl_2(Me_2NNH_2)_2\}_n]$ the Me_2NNH_2 ligands are unidentate and most likely bonded to the metal *via* the NH_2-nitrogen atoms. Octahedral $[\{MX_2(Me_2NNH_2)_2\}_n]$ (M = Fe, X = Cl or Br;[22] M = Ni, X = Cl[26]) complexes are known but the nature of the bonding of the halide and Me_2NNH_2 ligands was not resolved.

Phenylhydrazine also reacts with first-row transition-metal halides producing $[\{MX_2(PhNHNH_2)_2\}_n]$ complexes (M = Mn, Fe, Co, Ni or Zn; X = Cl or Br),[27] but the bonding modes of the ligands remain unestablished. The hydrazine ligand is unidentate in both $[V(salen)(PhNHNH_2)]I$ [H_2salen = *N,N'*-ethylenebis(salicylideneimine)] and $[\{Mo(N_2Ph)_2(OMe)_2(PhNHNH_2)\}_2]$, bonding *via* the more basic NH_2-nitrogen atom.[28] Reactions of $[Cr(H_2O)_4Cl_2]$ and $[Cr(H_2O)_6]Br_2$ with $PhNHNH_2$ in ethanol–diethyl ether afford the very air-sensitive complexes $[\{CrX_2(PhNHNH_2)_2\}_n]$ (X = Cl or Br). The severe air-sensitivity of the bromide did not allow reproducible analyses or good reflectance spectra to be obtained. The magnetic moment values, although somewhat reduced from the spin-only value, are indicative of high-spin mononuclear chromium(II), the actual values obtained perhaps resulting from a little oxidation on handling rather than additional electronic interactions through bridging groups as in $[\{Cr(\mu\text{-}Cl)_2(NH_3)_2\}_n]$.[18] The similarity of the reflectance spectrum and the infrared ν(CrCl) frequency of $[\{CrCl_2(PhNHNH_2)_2\}_n]$ to those of $[\{Cr(\mu\text{-}Cl)_2L_2\}_n]$ (L = MeCN, C_5H_5N or NH_3) suggests that the chloride ligands are bridging and the phenylhydrazine ligands are unidentate. The infrared spectra of the chloride and bromide complexes are virtually identical between 3500 and 400 cm^{-1} suggesting an analogous structure for the bromide.

In summary, it is suggested that, probably as a reflection of competition between steric and electronic influences, reactions with N_2H_4 or $MeNHNH_2$ give hydrazine-bridged complexes while use of $PhNHNH_2$ or Me_2NNH_2 results in halide-bridged complexes.

(*b*) *Complexes of Chromium*(II) *Acetate with Hydrazines*.—The co-ordination behaviour of N_2H_4, $MeNHNH_2$ and $PhNHNH_2$ in the complexes formed with dinuclear chromium(II) acetate parallels that found in the dichloride complexes. However, Me_2NNH_2 displays an alternative co-ordination mode.

Reaction of $[Cr_2(O_2CMe)_4(H_2O)_2]$ with anhydrous hydrazine in ethanol gives the sparingly soluble, air-sensitive $[\{Cr_2(O_2CMe)_4(\mu\text{-}N_2H_4)\}_n]$. The reflectance spectrum and the very weak paramagnetism of the product (Table 2) indicate retention of a quadruple metal–metal bonded structure, the axial aqua ligands being replaced by bridging hydrazine ligands to generate a polymer of alternating $Cr_2(O_2CMe)_4$ and N_2H_4 units, as in $[\{Cr_2(O_2CMe)_4(\mu\text{-}pyz)\}_n]$ (pyz = pyrazine).[30] The infrared spectrum (see Experimental section) contains bands assignable to both bridging acetate and bridging hydrazine ligands and a band at 469 cm^{-1} has been assigned to ν(CrN) in agreement with that at 475 cm^{-1} for $[Cr_2(O_2CMe)_4(NH_3)_2]$.[31]

Reaction of $[Cr_2(O_2CMe)_4(H_2O)_2]$ with $MeNHNH_2$ in ethanol gave an impure product which nevertheless analysed close to that required for $[\{Cr_2(O_2CMe)_4(\mu\text{-}MeNHNH_2)\}_n]$. However, replacing the hydrate by the bis(ethanol) adduct gave the pure product. The spectroscopic and magnetic properties, (Table 2) are closely similar to those of the hydrazine product.

The reaction between $[Cr_2(O_2CMe)_4(H_2O)_2]$ and $PhNHNH_2$ in ethanol gave air-sensitive $[Cr_2(O_2CMe)_4(PhNHNH_2)_2]$, the spectroscopic and magnetic properties of which strongly suggest retention of the metal–metal bonds with axial unidentate phenylhydrazine ligands. An additional band for this complex in the reflectance spectrum can be assigned to a $\pi \longrightarrow \pi^*$ transition of the ligated phenylhydrazine.

Finally, reaction of $[Cr_2(O_2CMe)_4(EtOH)_2]$ with Me_2NNH_2 in ethanol afforded $[\{Cr_2(O_2CMe)_4(\mu\text{-}Me_2NNH_2)\}_n]$, the stoichiometry implying the presence of bridging Me_2NNH_2 ligands, a different co-ordination mode to that suggested for $[\{Cr(\mu\text{-}Cl)_2(Me_2NNH_2)_2\}_n]$. There is some indication that the $Cr\text{–}NMe_2$ bond is easily cleaved. Thus, the UV/VIS solid-state and methanol solution spectra are rather different, the solution spectrum being closer to that of $[Cr_2(O_2CMe)_4(H_2O)_2]$, suggesting replacement of an axial nitrogen donor by an oxygen donor. Also, addition of ethanol to $[\{Cr_2(O_2CMe)_4(\mu\text{-}Me_2NNH_2)\}_n]$ gives a product which has an infrared spectrum containing bands assignable to both Me_2NNH_2 and ethanol ligands. No further characterisation of this product was attempted.

(*c*) *Chromium Hydrazinecarboxylate Complexes*.—(*i*) *Chromium*(II) *and* -(III) *hydrazinecarboxylates*. We have previously noted[11] that treatment of $[\{Cr_2(O_2CMe)_4(\mu\text{-}N_2H_4)\}_n]$ with hydrazinecarboxylic acid under nitrogen yields $[\{Cr(O_2CNHNH_2)_2(H_2O)\}_n]$. Subsequently, this complex was also isolated[32] from an aqueous chromium(II) chloride solution. Full details are now reported, including additional preparative routes.

Apart from the reactions mentioned above, chromium(II) hydrazinecarboxylate monohydrate also results from the reactions of $[Cr_2(O_2CMe)_4(H_2O)_2]$ with either hydrazinecarboxylic acid in aqueous hydrazine (essentially $[N_2H_5][O_2CNHNH_2]$), or hydrazine and carbon dioxide in refluxing methanol. These reactions are noteworthy in that the metal–metal bonds of the acetate are cleaved yielding a mononuclear chromium(II) product, the bridging hydrazine or unidentate aqua ligands and the bridging acetate ligands being replaced by hydrazinecarboxylate groups. In view of this metal–metal bond cleavage, it is not surprising that $[\{Cr(O_2CNHNH_2)_2(H_2O)\}_n]$ may also be prepared from a variety of mononuclear chromium(II) reactants. Thus, reactions of deoxygenated aqueous solutions of chromium(II) chloride or bromide, or suspensions of $[\{CrX_2(\mu\text{-}N_2H_4)_2\}_n]$ (X = Cl or Br), with aqueous $[N_2H_5][O_2CNHNH_2]$ (prepared by passage of CO_2 into an aqueous solution of hydrazine) all result in the formation of deep blue solutions from which good yields (> 60%) of the lilac product are precipitated. The product is insoluble in all common organic solvents and more stable in moist air than many mononuclear chromium(II) compounds, being only slowly subject to oxidation to chromium(III) as shown by reflectance spectrum changes or the generation of peaks in the X-ray photoelectron spectrum at similar binding energies to those of chromium(III) hydrazinecarboxylate dihydrate (oxidised $[\{Cr(O_2CNHNH_2)_2(H_2O)\}_n]$: 589.9, 579.3 and 46.1 eV, $[Cr(O_2CNHNH_2)_3]\cdot 2H_2O$: 589.1, 579.4 and 46.6 eV, relating to Cr $2p_{\frac{1}{2}}$, $2p_{\frac{3}{2}}$ and 3s, respectively). Prolonged contact of $[\{Cr(O_2CNHNH_2)_2(H_2O)\}_n]$ with an excess of aqueous $[N_2H_5][O_2CNHNH_2]$ results in dissolution and oxidation to a bright red solution from which $[Cr(O_2CNHNH_2)_3]\cdot 2H_2O$ can be isolated (see below). The rate of oxidation appears to increase with increasing concentration of $[N_2H_5][O_2CNHNH_2]$, the successful isolation of $[\{Cr(O_2CNHNH_2)_2(H_2O)\}_n]$ depending on its rapid precipitation and isolation from solution.

Analytical data would not distinguish between $[\{Cr(O_2CNHNH_2)_2(H_2O)\}_n]$ and the hydroxo-bridged chromium(III) species $[\{Cr(\mu\text{-}OH)(O_2CNHNH_2)_2\}_2]$. However, the latter can be rejected because decomposition of the product in HCl under nitrogen generated Cr^{2+}(aq) only and a redox titration showed that in basic solution 1 mol of the product consumed 9 mol of $[Fe(CN)_6]^{3-}$, in agreement with a one-electron change for chromium and two four-electron changes for the hydrazinecarboxylato-groups ($O_2CNHNH_2^- \longrightarrow N_2 + CO_2 + 3H^+ + 4e^-$).

Attempts to remove the water from $[\{Cr(O_2CNHNH_2)_2(H_2O)\}_n]$ using refluxing 2,2-dimethoxypropane or triethyl orthoformate were unsuccessful and DTA/TG results point to very strongly held water in the structure. Whereas DTA determinations on other hydrated metal hydrazinecarboxylates *e.g.* $[M(O_2CNHNH_2)_2]\cdot xH_2O$ (M = Mg, Ca or Mn) indicate water loss in the range 130–170 °C, the chromium(II) compound shows a major exothermic peak at 214 °C both in air and in argon relating to water loss as indicated by complementary TG data. A second exothermic DTA peak at 304 °C in argon represents carboxylate decomposition leading ultimately to Cr_2O_3 formation. These results differ markedly from those reported by Manoharan and Patil.[32] The intermediate $[Cr(O_2CNHNH_2)_2]$ was not isolable and we infer from this that the water ligand plays a crucial role in the stability of the hydrazinecarboxylate *via* extensive hydrogen bonding to the hydrazinecarboxylate groups in addition to co-ordination to the metal centre in a polymeric structure.

The magnetic moment of $[\{Cr(O_2CNHNH_2)_2(H_2O)\}_n]$ at 298 K (μ_{eff} = 4.73) confirms the presence of high-spin mononuclear chromium(II) centres but it is puzzling to note that Manoharan and Patil report[32] a value of 2.79, this reduced value being attributed to weak metal–metal bonding or strong magnetic exchange. We have found reproducible values in agreement with high-spin chromium(II) irrespective of the preparative method employed. The reflectance spectrum consists of a broad band with a maximum at 550 nm ($^5B_{1g} \longrightarrow {}^5B_{2g}, {}^5E_g$), rather similar to that of $[\{CrCl_2(\mu\text{-}N_2H_4)_2\}_n]$ but quite different to that of the glycinate[29] $[\{Cr(O_2CCH_2NH_2)_2(H_2O)\}_n]$ (614 nm) which would be expected to have the same donor atoms as the hydrazinecarboxylate.

Finally, we consider the infrared spectrum of the hydrazinecarboxylate. Although vibrational data of metal hydrazinecarboxylates have been reported, assignments have been based on comparisons with data from metal carboxylates and metal–hydrazine complexes, no consideration being given to skeletal vibrations of the OCNN core. In an attempt to propose firmer assignments, the infrared spectra of $[\{Cr(O_2CNHNH_2)_2(H_2O)\}_n]$ and its fully deuteriated analogue, prepared by reaction of anhydrous $CrCl_2$ with CO_2-saturated $N_2D_4\cdot D_2O$ in D_2O, have been recorded. The data presented in Table 3 show a division between bands with H:D ratios of 1.25–1.36:1 involving considerable NH character and those with H:D ratios of 1.00–1.03:1 in which the vibrations are essentially carboxylate or skeletal motions. Vibrations of the $NHNH_2$ groups are assigned by comparison with those of $MeNHNH_2$[33] and metal–hydrazine complexes[20] and will not be discussed further except to note that ν(OH) has not been assigned, perhaps being broad and weak as a result of hydrogen bonding. The separation between the ν_{asym} and ν_{sym} vibrations of the O_2CN moieties is 209 cm^{-1}, a low value for unidentate carboxylate, but acceptable for a structure involving five-membered $\overline{\mathrm{CrOC(O)NHN}}\mathrm{H_2}$ chelate rings particularly if bridging of a C=O oxygen to another chromium atom to generate an octahedral polymer, as in $[\{Cd(O_2CNHNH_2)_2(H_2O)\}_n]$,[34] occurs. Hydrogen bonding between the C=O and the water molecules present could also make the carboxylate bonds more equivalent than expected for unidentate carboxylate.

Assignment of bands at 604, 778 and 803 cm^{-1}, to carboxylate modes, leaves three bands that are only slightly deuteriation-sensitive. In agreement with data on metal–hydrazine complexes,[20] the band at 985 cm^{-1} is assigned to a skeletal vibration that is primarily ν(NN). The bands at 1215 and 1460 cm^{-1}, shifted to 1187 and 1424 cm^{-1} on deuteriation, must involve considerable ν(CO) and ν(CN) character. Deuteriation-insensitive bands at 417 and 369 cm^{-1} are likely to be ν(CrN) or ν(CrO) vibrations.

Chromium(III) hydrazinecarboxylate has been reported previously as a red, crystalline, dihydrate,[35] a green-violet or blue anhydrous salt,[36] or most recently as a red trihydrate.[32] We have found that the only product isolated from reactions carried out under conventional conditions is the dihydrate. Our interest in this complex arises from the observation that it can be isolated from reactions of various chromium(II) complexes with an excess of $[N_2H_5][O_2CNHNH_2]$ solution. Thus, when $[\{Cr(O_2CNHNH_2)_2(H_2O)\}_n]$ or precursors such as hydrated chromium(II) chloride or bromide, $[\{CrX_2(\mu\text{-}N_2H_4)_2\}_n]$ (X = Cl or Br) or anhydrous $CrCl_2$ are allowed prolonged contact with an excess of aqueous hydrazine and CO_2 is passed into the mixture a bright red colour develops in the solution and air-stable $[Cr(O_2CNHNH_2)_3]\cdot 2H_2O$ can be isolated. These oxidations proceed both in the presence and absence of air, suggesting that N_2H_4, $N_2H_5^+$ or $O_2CNHNH_2^-$ may be involved. Although N_2H_4 and $N_2H_5^+$ are usually regarded as reducing species, thermodynamic considerations indicate that they can behave as oxidants, being reduced to NH_3 or NH_4^+. A kinetic study[37] of the Cr^{2+}–N_2H_4 reaction in a perchlorate medium has been interpreted as producing Cr^{3+} and NH_3.

A more convenient route to $[Cr(O_2CNHNH_2)_3]\cdot 2H_2O$ is the reaction of $[CrCl_2(H_2O)_4]Cl\cdot 2H_2O$ with aqueous $[N_2H_5][O_2CNHNH_2]$. The complex normally precipitates as a pink finely divided solid but on increasing the $Cr^{3+}:O_2CNHNH_2^-$ ratio to 1:50 it is formed as red microcrystalline aggregates. Suitable crystals for a structure determination were not produced. The product is insoluble in all common solvents, but is soluble without change, as indicated by spectroscopy, in anhydrous N_2H_4 or concentrated $[N_2H_5][O_2CNHNH_2]$ solutions. The magnetic moment of 3.82 at 295 K is characteristic of octahedral chromium(III). The reflectance spectrum, (maxima at 698vw, 523s and 395m nm) and solution spectrum in anhydrous N_2H_4 [maxima at 700vw, 522s and 402s (br) nm] can be interpreted on the basis of three *N,O*-chelating hydrazinecarboxylate anions bonded to the metal (in O_h symmetry: $^4A_{2g} \longrightarrow {}^2E_g, \longrightarrow {}^4T_{2g}$ and $\longrightarrow {}^4T_{1g}$, respectively, with $10Dq$ = 19 100 cm^{-1}, B = 587 cm^{-1} and β = 0.64). These results can be compared with those for the glycinate[38] $[Cr(O_2CCH_2NH_2)_3]\cdot H_2O$ which has *N,O*-chelating amino acidate ligands (689vw, 503s and 384m nm; $10Dq$ = 19 900 cm^{-1}, B = 578 cm^{-1} and β = 0.63). The octahedral CrO_3N_3

Table 3 Infrared bands (cm^{-1}) of $[Cr(O_2CNHNH_2)_3]\cdot 2H_2O$, $[\{Cr(O_2CNHNH_2)_2(H_2O)\}_n]$ and its D_8-analogue

$[Cr(O_2CNHNH_2)_3]\cdot 2H_2O$	$[\{Cr(O_2CNHNH_2)_2(H_2O)\}_n]$	$[\{Cr(O_2CNDND_2)_2(D_2O)\}_n]$	H/D	Assignment
3329s	3283s	2456s	1.34	$\nu(NH_2)$, $\nu(NH)$
3205s		2415ms (sh)		
3106ms (sh)		2385s		
3060ms	3155s	2327s	1.36	
1668vs	1627s	1219ms	1.34	$\delta(NH_2)$, $\delta(H_2O)$
1648s (sh)	1611s (sh)	1187m	1.36	
1615s (br)	1579vs	1572vs	1.00	$\nu_{asym}(CO_2)$
1570 (sh)		1556s (sh)		
1454vs	1460s	1424vs	1.03	Skeletal stretch
1367m (br)	1370s	1372vs (sh)	1.00	$\nu_{sym}(CO_2)$
1342m (br)				
1308w	1319mw	997m	1.32	NH_2 wag
1246m (sh)	1215m (sh)	1187m	1.02	Skeletal vib.
1226s (sh)	1194s	896m	1.33	NH_2 twist
1216s	1102m	879m	1.25	
983m	985w	989m	1.00	Skeletal vib.
783m	803m	802s	1.00	$\delta(OCO)$
	778mw	760mw	1.02	
710vw	693w (br)	538vw (br)	1.29	NH_2 rock, NH def.
	636m (br)	483m (br)	1.32	
619m	604s	598ms	1.01	$\pi(CO_2)$
488mw				$r(CO_2)$
408m	417m	415ms	1.01	$\nu(CrO)$ + $\nu(CrN)$
330m	369w	368mw	1.00	

unit could have the donor oxygen and nitrogen atoms co-ordinated in a *fac* or a *mer* arrangement. Both $[Cr(O_2CCH_2NH_2)_3]\cdot H_2O$[38] and $[N_2H_5][Ni(O_2CNHNH_2)_3]\cdot H_2O$[39] are *fac* isomers. A further similarity of $[Cr(O_2CNHNH_2)_3]\cdot 2H_2O$ with $[Cr(O_2CCH_2NH_2)_3]\cdot H_2O$ is the strong involvement of water in the crystal lattices. The glycinate is similarly insoluble in a wide range of solvents, the structure involving an extensive network of hydrogen bonding between the water of crystallisation and the amino and carboxylato groups. We have found that the water of the hydrazinecarboxylate cannot be removed by treatment with refluxing 2,2-dimethoxypropane or triethyl orthoformate and heating in air at 110 °C was ineffective (weight loss found 0.9%; calc. for loss of $2H_2O$, 11.5%). Endothermic peaks with maxima at 136 and 169 °C from DTA experiments carried out in air correspond to the stepwise loss of $2H_2O$ (TG supporting evidence), but pure samples of these intermediates could not be obtained, more extensive decomposition occurring. An exothermic DTA peak with a maximum at 222 °C relates to decomposition of the hydrazinecarboxylate groups with ultimate formation of Cr_2O_3. These results, which are rather different than those reported for the supposed trihydrate,[32] support extensive hydrogen bonding between the waters of crystallisation and the hydrazinecarboxylate ligands. Loss of the water molecules seems to induce collapse of the structure with concomitant decomposition of the hydrazinecarboxylate ligands. The report[36] of a proposed anhydrous chromium(III) hydrazinecarboxylate, prepared from an aqueous medium, therefore seems questionable. The infrared spectrum of the dihydrate is typical of an *O,N*-chelated hydrazinecarboxylate, bands being listed in Table 3. Overlying the $\nu(NH)$ bands is a very broad envelope associated with the hydrogen-bonded water molecules.

(*ii*) *Chromium*(III) *methylhydrazinecarboxylate*. Passage of CO_2 into a solution of $MeNHNH_2$ in ethanol gives a colourless, highly hygroscopic, precipitate of methylhydrazinecarboxylic acid.[15] The favoured site of CO_2 attack on $MeNHNH_2$ will probably be the more basic MeNH nitrogen, so the product is formulated as $H_2NN(Me)CO_2H$ rather than $MeNHNHCO_2H$.

Given the formation of $[\{Cr(O_2CNHNH_2)_2(H_2O)\}_n]$, isolation of a chromium(II) methylhydrazinecarboxylate was expected, for example, from a reaction of hydrated chromium(II) chloride with methylhydrazinecarboxylic acid in ethanol at 0 °C under nitrogen and carbon dioxide. The formation of an initial dark blue solution is observed, as in the hydrazinecarboxylate system, but rapid oxidation then ensues and the chromium(III) complex $[Cr\{O_2CN(Me)NH_2\}_3]\cdot H_2O$ is precipitated as a pink, microcrystalline, air-stable solid. A similar, but much slower, oxidation of $[\{Cr(O_2CNHNH_2)_2(H_2O)\}_n]$ to $[Cr(O_2CNHNH_2)_3]\cdot 2H_2O$ has already been discussed. It therefore seems that in the methylhydrazinecarboxylate system oxidation to chromium(III) occurs before a chromium(II) product can be precipitated.

The complex $[Cr\{O_2CN(Me)NH_2\}_3]\cdot H_2O$ is more conveniently prepared from $[CrCl_2(H_2O)_4]Cl\cdot 2H_2O$ and methylhydrazinecarboxylic acid in ethanol at 70 °C. The magnetic moment (3.84 at 292 K) and reflectance spectrum (517s and 384m nm, $^4A_{2g} \longrightarrow {}^4T_{2g}$ and $\longrightarrow {}^4T_{1g}$ respectively; $10Dq = 19\,300$ cm^{-1}, $B = 644$ cm^{-1}, $\beta = 0.70$) are consistent with chromium(III) octahedrally co-ordinated by three *O,N*-chelating anions. A report[36] that passage of CO_2 into an ethanol solution of $MeNHNH_2$ and chromium(III) chloride produced violet-blue anhydrous $[Cr\{O_2CN(Me)NH_2\}_3]$ could not be substantiated by us, the blue precipitate obtained always containing hydroxochromium(III) species. Indeed, DTA/TG evidence suggests that removal of water of crystallisation from the hydrate cannot be achieved without decomposition of the methylhydrazinecarboxylate groups. The decomposition pathway could not be elucidated, the TG trace not showing a specific step relating to water loss and the DTA showing five exothermic peaks with maxima at 195, 230, 255, 290 and 410 °C, the final product being Cr_2O_3. We conclude, as for the hydrazinecarboxylate, that hydrogen-bonded water molecules play a key role in the stability of the solid.

The infrared spectrum of the hydrate has been recorded but few useful comparisons are possible [major peaks at 3330m (vbr), $\nu(OH)$; 3182ms, 3041ms, $\nu(NH)$; 2930mw, $\nu(CH_3)$; 1635vs, 1580(sh), $\nu_{asym}(CO_2) + \delta(NH_2)$; 1432m, skeletal stretch; 1380ms, $\nu_{sym}(CO_2)$; 1266s, skeletal stretch, mainly $\nu(CN)$; 1008m, skeletal stretch, mainly $\nu(NN)$; 792ms, $\delta(OCO)$; 615m, $\pi(CO_2)$; 407s, 342w, 300w cm^{-1}, $\nu(CrO) + \nu(CrN)$].

(*iii*) *Chromium*(II) *phenylhydrazinecarboxylate*. Shortly after Fischer first reported the isolation of $PhNHNH_2$ in 1875, he described the preparation of $PhNHNH_2\cdot PhNHNHCO_2H$ by reaction with CO_2.[40] We have prepared this compound, probably better formulated as $[PhNHNH_3][O_2CNHNHPh]$, by precipitation from methanol. This formula implies CO_2 attack at the more basic NH_2 nitrogen of $PhNHNH_2$ and for electronic reasons it would be anticipated that the nitrogen lone pair adjacent to the phenyl ring in the anion might be less available for donation to metals than the O_2CNH nitrogen lone pair. However, *N,O* chelation would then involve a strained $\overline{MNCO}$ ring system, unlike the well established $\overline{MNNCO}$ ring systems found for many metal hydrazinecarboxylates. Alternative potential co-ordination modes for $PhNHNHCO_2^-$ in which it behaves as a functionally substituted carboxylate are therefore worthy of consideration *e.g.* (*i*) unidentate *O* bonding, (*ii*) *O,O′* chelation, as established crystallographically for $[\{Ba(O_2CNHNH_2)_2(N_2H_4)\}_n]$,[41] or (*iii*) *O,O′* bridging as found for binuclear chromium(II) carboxylates and the diethylcarbamate $[Cr_2(\mu\text{-}O_2CNEt_2)_4(NHEt_2)_2]$.[42]

Reaction of hydrated chromium(II) chloride with $[PhNHNH_3][O_2CNHNHPh]$ in methanol under a CO_2 atmosphere at 0 °C resulted in the precipitation of an extremely air-sensitive salmon-pink solid. It was almost diamagnetic ($\mu_{eff} = 0.56$ at 296 K) and the reflectance spectrum was characteristic of a binuclear chromium(II) compound [bands at 469m and 455m (br), $\delta \longrightarrow \pi^*$; 332s (sh) and 320vs nm, $p \longrightarrow \pi^*$]. The nature of this complex is clearly different to that of mononuclear chromium(II) hydrazinecarboxylate, analysis and the above results suggesting that it is $[Cr_2(O_2CNHNHPh)_4(MeOH)_2]$. The infrared spectrum indicates the presence of methanol and phenylhydrazinecarboxylate ligands although the carboxylate stretches appear in the same region of the spectrum as do strong phenyl vibrations (bands at 1599, 1563, 1483, 1460 and 1373 cm^{-1}). Tentatively, we suggest that $[Cr_2(O_2CNHNHPh)_4(MeOH)_2]$ has a metal–metal bonded structure akin to that of $[Cr_2(O_2CNEt_2)_4(NHEt_2)_2]$,[42] with a change of co-ordination mode from *N,O* chelation for the hydrazinecarboxylate to *O,O′* bridging for the phenylhydrazinecarboxylate, the methanol ligands being axial. Attempts to prepare chromium(III) phenylhydrazinecarboxylate, a compound previously reported,[36] have not been successful. Thus, reactions of $[CrCl_2(H_2O)_4]Cl{\cdot}2H_2O$ or $[CrCl_3(thf)_3]$ (thf = tetrahydrofuran) with $[PhNHNH_3][O_2CNHNHPh]$ did not lead to stoichiometric products.

References

1 J. M. Bellerby, *J. Hazard. Mater.*, 1983, **7**, 187 and refs therein.
2 R. Stollé and K. Hofmann, *Ber.*, 1904, **37**, 4523.
3 J. M. Bellerby, *J. Hazard. Mater.*, 1986, **13**, 57; J. M. Bellerby, D. A. Edwards and D. Thompsett, *Proceedings of the 3rd Conference on the Environmental Chemistry of Hydrazine Fuels*, eds. D. A. Stone and F. L. Wiseman, Air Force Engineering and Services Centre, Tyndall Air Force Base, FL, 1987, p. 86.
4 A. Earnshaw, L. F. Larkworthy and K. S. Patel, *Z. Anorg. Allg. Chem.*, 1964, **334**, 163 and refs. therein.
5 G. B. Kaufmann and N. Sugisaka, *Z. Anorg. Allg. Chem.*, 1966, **344**, 92.
6 P. Glavic, J. Slivnik and A. Bole, *Vestn. Slov. Kem. Drus.*, 1982, **29**, 227.
7 R. Y. Aliev, *J. Gen. Chem. USSR* (*Engl. Transl.*), 1972, **42**, 2365.
8 V. A. Sharov, N. V. Povarova, V. A. Perelyaev, E. I. Krylov and G. M. Adamova, *Koord. Khim.*, 1979, **5**, 537; V. A. Sharov, N. V. Povarova and E. I. Krylov, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1980, **25**, 1193.
9 K. C. Patil, K. C. Nesamani and V. R. Pai Verneker, *Chem. Ind.* (*London*), 1979, 901.
10 P. Barz and H. P. Fritz, *Z. Naturforsch., Teil B*, 1972, **27**, 1131.
11 J. M. Bellerby, D. A. Edwards and D. Thompsett, *Inorg. Chim. Acta*, 1986, **117**, L31.
12 A. Earnshaw, L. F. Larkworthy and K. S. Patel, *J. Chem. Soc.*, 1965, 3267.
13 J. C. Reeve, *J. Chem. Educ.*, 1985, **62**, 444.
14 D. M. Halepoto, L. F. Larkworthy, D. C. Povey, B. J. Tucker and G. W. Smith, *J. Chem. Soc., Dalton Trans.*, 1990, 699.
15 J. M. Bellerby and H. A. El-Magied, unpublished work.
16 A. Stern, *J. Prakt. Chem.*, 1899, **60**, 235.
17 D. G. Holah and J. P. Fackler, *Inorg. Chem.*, 1965, **4**, 1112; R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, 1965, **4**, 350.
18 L. F. Larkworthy and J. M. Tabatabai, *J. Chem. Soc., Dalton Trans.*, 1976, 814.
19 A. Ferrari, A. Braibanti and G. Bigliardi, *Acta Crystallogr.*, 1963, **16**, 498; A. Ferrari, A. Braibanti, G. Bigliardi and F. Dallevalle, *Z. Kristallogr.*, 1963, **119**, 284.
20 M. Goldstein and W. D. Unsworth, *Spectrochim. Acta, Part A*, 1972, **28**, 1297; W. Personette, J. Szczepanski, K. KuBulat and M. Vala, *J. Raman Spectrosc.*, 1989, **20**, 147.
21 L. Sacconi and A. Sabatini, *J. Inorg. Nucl. Chem.*, 1963, **25**, 1389.
22 A. Anagnostopoulos, D. Nicholls and J. Reed, *Inorg. Chim. Acta*, 1979, **32**, L17 and refs. therein.
23 T. V. Ashworth, M. J. Nolte and E. Singleton, *J. Chem. Soc., Dalton Trans.*, 1978, 1040.
24 M. K. Das, J. F. Mariategui and K. Niedenzu, *Inorg. Chem.*, 1987, **26**, 3114.
25 T. V. Ashworth, M. J. Nolte, R. H. Reimann and E. Singleton, *J. Chem. Soc., Dalton Trans.*, 1978, 1043.
26 D. Nicholls and R. Swindells, *J. Inorg. Nucl. Chem.*, 1968, **30**, 2211.
27 W. K. Glass and J. O. McBreen, *J. Inorg. Nucl. Chem.*, 1974, **36**, 747; M. S. Novakovskii, V. A. Starodub and E. V. Golovinova, *Zh. Neorg. Khim.*, 1974, **19**, 3288.
28 G. J. Leigh and J. R. Sanders, *Polyhedron*, 1989, **8**, 1782; V. Chilou, P. Gouzerh, Y. Jeannin, G. Olivares, F. Robert, T. C. Hsieh and J. Zubieta, *Polyhedron*, 1989, **8**, 29.
29 L. F. Larkworthy and J. M. Tabatabai, *Inorg. Chim. Acta*, 1977, **21**, 265.
30 F. A. Cotton and T. R. Felthouse, *Inorg. Chem.*, 1980, **19**, 328.
31 L. F. Larkworthy and J. M. Tabatabai, *Inorg. Nucl. Chem. Lett.*, 1980, **16**, 427.
32 S. S. Manoharan and K. C. Patil, *Proc. Indian Acad. Sci.*, (*Chem. Sci.*), 1989, **101**, 377.
33 D. P. Dowling and W. K. Glass, *Spectrochim. Acta, Part A*, 1988, **44**, 1351.
34 A. Braibanti, A. M. M. Lanfredi, A. Tiripicchio and F. Bigoli, *Acta Crystallogr., Sect. B*, 1969, **25**, 100.
35 H. Funk, A. Eichhoff and G. Giesder, *Omagiu Raluca Ripan, Edit. Acad. Rep. Soc. Romania*, 1966, 247 (*Chem. Abstr.*, 1967, **67**, 39661z).
36 A. K. Srivastava, *Croat. Chem. Acta*, 1979, **52**, 293.
37 C. F. Wells and M. A. Salam, *J. Chem. Soc. A*, 1968, 1568.
38 R. F. Bryan, P. T. Greene, P. F. Stokely and E. W. Wilson, *Inorg. Chem.*, 1971, **10**, 1468.
39 A. Braibanti, A. M. M. Lanfredi and A. Tiripicchio, *Z. Kristallogr.*, 1967, **124**, 335.
40 E. Fischer, *Liebigs Ann. Chem.*, 1878, **190**, 123.
41 D. A. Edwards, J. F. Keily, M. F. Mahon, K. C. Molloy and D. Thompsett, unpublished work.
42 M. H. Chisholm, F. A. Cotton, M. W. Extine and D. C. Rideout, *Inorg. Chem.*, 1978, **17**, 3536.

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