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Linear chain complexes linked by hydrogen bonded $O_2H_3^-$ and $O_3H_5^-$ units: structural and magnetic comparison of *trans*-dihydroxo-, -diaqua-, and -aquahydroxo-chromium(III) complexes

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The syntheses and characterization of a series of chromium(III) complexes of the general types *trans*-$[(A)_4Cr(OH)(H_2O)]^{2+}$, *trans*-$[(A)_4Cr(OH)_2]^+$, and *trans*-$[(A)_4Cr(H_2O)_2]^{3+}$ are described. The ligands $(A)_4$ used include the tetradentate ligand 1,4,8,11-tetraazacyclotetradecane (cyclam), its hexamethylated derivative *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (cyca), and the bidentate ligand 2-aminomethylpyridine (pico). The cobalt(III) aquahydroxo complexes with cyclam and cyca are also reported. The *trans*-diaqua and *trans*-dihydroxo complexes are monomeric, but the *trans*-aquahydroxo complexes form linear chains. The complexes *trans*-$[Cr(cyclam)(OH)(H_2O)](CF_3SO_3)_2$ **1** and *trans*- $[Co(cyclam)(OH)(H_2O)](CF_3SO_3)_2$ **3** and their corresponding perchlorates (**2** and **4**, respectively) have been isolated and the structures of the chromium triflate salt **1** and the cobalt perchlorate salt **4** have been determined. Both of these complexes **1** and **4** form infinite chains in the solid state, adjacent metal centers being bridged by hydrogen bonds between hydroxo and aqua ligands. The Cr · · · Cr separation in **1** is 6.085 Å whereas the Co · · · Co separation in **4** is 6.078 Å. The complex *trans*-$[(pico)_2Cr(OH_2)_2](NO_3)_3\cdot H_2O$ **8** (where pico is picolylamine, 2-aminomethylpyridine) crystallizes with only one monomeric formula in a unit cell. In contrast to the structures of **1** and **4** (and, presumably, of **2** and **3** also), the two complexes *trans*-$[Cr(cyclam)(OH)_2]ClO_4\cdot H_2O$ **5** and **8** are monomeric in the solid state. The chromium complex *trans*-$[Cr(cyca)(OH)(H_2O)](ClO_4)_2\cdot H_2O$ **6** crystallizes with two monomeric formula units in a unit cell and the cobalt analogue **7** is isomorphous with the chromium complex. The structures of these complexes are also linear chains, but in this case there is an intervening water molecule between the aqua and hydroxo ligands on adjacent chromium centers. EPR spectroscopy of the chromium complex **1** doped in the diamagnetic cobalt host **3** reveals the presence of weak magnetic interactions.

Introduction

In a recent publication[1] we discussed the solid state structures of compounds of the general formula *cis*-$[CCrA_4(H_2O)(OH)]^{2+}$ [where $(A)_4$ represents the four nitrogen ligators from an appropriate number of monodentate or polydentate ligands], noting that they invariably have either a dimeric or a polymeric structure where adjacent chromium centers are bound together by hydrogen bonded $O_2H_3^-$ units. We also demonstrated that these hydrogen bonds are able to transmit an antiferromagnetic interaction between the chromium(III) ions, and that EPR spectroscopy provides an excellent method to distinguish between chain and dimeric structures both in the solid state and in frozen solutions. Other workers have made similar observations in related complexes, again finding both chain[2] and dimeric[3] structures. Numerous other forms of aggregation through hydrogen bonds are very common.[3,4]

We now turn our attention to the analogous *trans*-complexes. Other workers have suggested[5] that all such complexes will exhibit a μ-$(O_2H_3^-)$ chain structure, and indeed this has been confirmed by crystallographic studies of a number of complexes.[5–7] In the case of the *cis*-complexes, the dihydroxo and diaqua complexes do not generally give rise to these hydrogen bonded interactions. A logical extension of this observation would suggest that the *trans*-dihydroxo and *trans*-diaqua complexes should not exhibit this chain structure, although in principle hydrogen bonds could be formed between two hydroxo or two aqua ligands.

Here, we examine the structural and other physical properties of chromium(III) complexes of these general types in an attempt to deduce the structural patterns that are obtained. The specific systems used for our investigation were salts of *trans*-$[Cr(cyclam)(OH)(H_2O)]^{2+}$, *trans*-$[Co(cyclam)(OH)(H_2O)]^{2+}$, *trans*-$[Cr(cyca)(OH)(H_2O)]^{2+}$, *trans*-$[Co(cyca)(OH)(H_2O)]^{2+}$, *trans*-$[Cr(cyclam)(OH)_2]^+$, and *trans*-$[Cr(pico)(H_2O)_2]^{3+}$, where cyclam is 1,4,8,11-tetraazacyclotetradecane, cyca is *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, and pico is 2-aminomethylpyridine.

Experimental

Physical measurements

Electronic absorption spectra in the visible region were recorded on a Perkin-Elmer Lambda 17 spectrophotometer. The spectra are characterized by their maxima $(\varepsilon, \lambda)_{max}$, where the molar absorption coefficient ε is in units of l mol^{-1} cm^{-1} and λ is in nm. The compounds were dissolved in water (*ca.* 3×10^{-3} M) and their spectra measured immediately afterwards. The magnetic susceptibilities of powdered samples were measured by the Faraday method in the temperature range 2–300 K at a field strength of 1.3 T. The susceptibility data were

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corrected for diamagnetism by Pascal's constants. The magnetic field was calibrated with Hg[Co(NCS)$_4$].[8] A more detailed description of the equipment is published elsewhere.[9] EPR spectra were recorded on a Bruker ESP-300 spectrometer equipped with an Oxford ESR-9 gas-flow cryostat. X-Ray powder patterns were recorded on a Guinier camera using Cu Kα radiation. The metal analyses were performed on a Perkin-Elmer 403 atomic absorption spectrometer. The microanalytical laboratory of the H. C. Ørsted Institute carried out analyses for carbon, nitrogen, hydrogen, halogen and sulfur by standard methods.

Syntheses

CAUTION. Some of the compounds described were isolated as perchlorate salts and should be handled as potentially explosive compounds. Mother liquors containing even small amounts of perchloric acid should never be mixed with washing liquors containing ethanol.

Ligands. 1,4,8,11-Tetraazacyclotetradecane (cyclam) and 2-methylpridine (pico) were purchased from Fluka. *C-meso*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane (cyca) was prepared according to a method described in the literature.[10]

Complexes. The following compounds were synthesized by methods described in the literature: *trans*-[Cr(cyclam)Cl$_2$]Cl,[11] *trans*-[Co(cyclam)Cl$_2$]Cl,[12] *trans*-[Cr(pico)$_2$(H$_2$O)$_2$](NO$_3$)$_3$·H$_2$O,[13] *trans*-[Cr(cyca)(H$_2$O)$_2$](ClO$_4$)$_3$[14] and *trans*-[Co(cyca)(H$_2$O)$_2$](ClO$_4$)$_3$.[15]

***trans*-[Cr(cyclam)(OH)(H$_2$O)](CF$_3$SO$_3$)$_2$ 1.** *trans*-[Cr(cyclam)Cl$_2$]Cl (0.360 g, 1.00 mmol) was dissolved in water (1.5 ml). A solution of sodium hydroxide (0.5 ml, 4 M) was added, and the solution was heated to 60 °C for 3–4 min. After filtering, the pH of the solution was adjusted to 5 with triflic acid. Sodium triflate (0.5 g) was added, and the solution was cooled on ice for 30 min. By then a crop of orange-red crystals had separated. The crystals were filtered and washed with a small amount of ice-cooled ethanol (99%) and with diethyl ether. Yield 0.43 g (73%). The compound was recrystallized from boiling water with a loss of 41%. Anal. calc. for [Cr(C$_{10}$H$_{24}$N$_4$)(OH)(H$_2$O)](CF$_3$SO$_3$)$_2$: Cr, 8.88; C, 24.62; N, 9.57; H, 4.65. Found: Cr, 9.49; C, 24.44; N, 9.59; H, 4.54%. $(\varepsilon, \lambda)_{max}$ = (29.0, 495), (60.1, 386).

***trans*-[Cr(cyclam)(OH)(H$_2$O)](ClO$_4$)$_2$ 2.** Was obtained by the same procedure as used for the triflate salt, but triflic acid and sodium triflate were replaced by perchloric acid (1 M) and sodium perchlorate, respectively. The compound was washed with a solution of sodium perchlorate (2 M) and with ethanol (99%). From *trans*-[Cr(cyclam)Cl$_2$]Cl (0.360 g, 1.00 mmol) a yield of 0.375 g (77%) was obtained. The compound was recrystallized by dissolving in boiling water and reprecipitated with a saturated solution of sodium perchlorate. Anal. calc. for [Cr(C$_{10}$H$_{24}$N$_4$)(OH)(H$_2$O)](ClO$_4$)$_2$: Cr, 10.65. Found: Cr, 10.69%. The analyses for C, N, H and Cl were not carried out because of the danger of explosion. $(\varepsilon, \lambda)_{max}$ = (27.2, 497), (57.4, 386).

***trans*-[Co(cyclam)(OH)(H$_2$O)](CF$_3$SO$_3$)$_2$ 3.** *trans*-[Co(cyclam)Cl$_2$]Cl (0.365 g, 1.00 mmol) was suspended in moist silver oxide, obtained from silver nitrate (0.8 g) and a solution of sodium hydroxide (5 ml, 2 M) and purified by decantation with water. After 3 min of careful stirring, the suspension was filtered, cooled on ice and the pH of the solution was adjusted to 4–5 with a solution of triflic acid (5 M). Sodium triflate (0.7 g) was added, and the reaction mixture was left for 30 min before filtering. The needle-shaped dark-violet crystals were then filtered and washed with ethanol (96%). Yield: 0.161 g (33%). The compound was recrystallized from boiling water. Anal. calc. for [Co(C$_{10}$H$_{24}$N$_4$)(OH)(H$_2$O)](CF$_3$SO$_3$)$_2$: Co, 9.95; C, 24.33; N, 9.46; H, 4.59; S, 10.82. Found: Co, 10.27; C, 24.19; N, 9.57; H, 4.71; S, 10.85%. $(\varepsilon, \lambda)_{max}$ = (46.3, 543), (39.4, 450sh), (100, 371).

***trans*-[Co(cyclam)(OH)(H$_2$O)](ClO$_4$)$_2$ 4.** Was prepared by the same procedure as described for the triflate salt, but triflic acid and sodium triflate were replaced by perchloric acid (4 M) and sodium perchlorate (0.7 g), respectively. The crystals were washed with a solution of sodium perchlorate (2 M) and with ethanol (96%). From *trans*-[Co(cyclam)Cl$_2$]Cl (0.365 g, 1 mmol) an amount of 0.161 g (33%) was obtained. Large, violet-black needles suitable for X-ray structure determination separated when the compound was recrystallized from boiling water. Anal. calc. for [Co(C$_{10}$H$_{24}$N$_4$)(OH)(H$_2$O)](ClO$_4$)$_2$·H$_2$O: Co, 11.95; C, 24.35; N, 11.36; H, 5.51. Found: Co, 11.92; C, 24.18; N, 11.43; H, 5.52%. $(\varepsilon, \lambda)_{max}$ = (45.0, 543), (38.0, 450sh), (96.5, 372).

***trans*-[Cr(cyclam)(OH)$_2$]ClO$_4$·H$_2$O 5.** Was obtained when a concentrated solution of *trans*-[Cr(cyclam)(OH)(H$_2$O)](ClO$_4$)$_2$ (0.080 g, 0.16 mmol) in water (2 ml) was added to a few drops of a solution of sodium hydroxide (2 M) and the resulting solution was allowed to evaporate at room temperature to approximately half of its original volume while a steady stream of nitrogen was bubbled through it. Small, well-shaped yellow-orange crystals separated. They were filtered and washed with ethanol (96%). Yield: 0.041 g (63%). Anal. calc. for [Cr(C$_{10}$H$_{24}$N$_4$)(OH)$_2$](ClO$_4$)·H$_2$O: C, 29.74; N, 13.88; H, 6.99. Found: C, 29.68; N, 13.60; H, 6.95%.

***trans*-[Cr(cyca)(OH)(H$_2$O)](ClO$_4$)$_2$·H$_2$O 6.** Was obtained by the same procedure as used for **2**. From *trans*-[Cr(cyca)Cl$_2$]Cl (2.02 g, 4.56 mmol) a yield of 1.99 g (72%) was obtained. Anal. calc. for [Cr(C$_{16}$H$_{36}$N$_4$)(OH)(H$_2$O)](ClO$_4$)$_2$·H$_2$O: C, 32.66; N, 9.52; H, 7.02; Cl, 12.05. Found: C, 32.72; N, 9.37; H, 7.25; Cl, 12.02%. $(\varepsilon, \lambda)_{max}$ = (28.3, 502), (65.7, 401).

***trans*-[Co(cyca)(OH)(H$_2$O)](ClO$_4$)$_2$·H$_2$O 7.** Was prepared by dissolving *trans*-[Co(cyca)(H$_2$O)$_2$](ClO$_4$)$_3$·H$_2$O (0.98 g, 1.41 mmol) in hot water followed by the addition of a solution of sodium hydroxide (14 ml, 0.1 M). The solution was cooled on ice for 30 min. The crystals were then filtered and washed with ice-cold water and ethanol (96%). Yield: 0.65 g (75%). Anal. calc. for [Co(C$_{16}$H$_{36}$N$_4$)(OH)(H$_2$O)](ClO$_4$)$_2$·H$_2$O: C, 32.28; N, 9.41; H, 6.94; Cl, 11.91. Found: C, 31.67; N, 9.24; H, 7.17; Cl, 11.91%. $(\varepsilon, \lambda)_{max}$ = (38.1, 549), (41.3, 480sh), (117, 380).

X-Ray structure determination

The structures of complexes **1**, **4**, **5**, **6**, and *trans*-[Cr(pico)$_2$(H$_2$O)$_2$](NO$_3$)$_3$·H$_2$O **8** were determined at room temperature (295 ± 1 K) on a Siemens P3 diffractometer equipped with a molybdenum tube [$\lambda(K\alpha_1) = 0.70926$ Å; $\lambda(K\alpha_2) = 0.71354$ Å] and a graphite monochromator. Crystal data and experimental parameters are presented in Table 1. The data were corrected for Lorentz-polarization effects and absorption. The structures were solved by direct methods and refined by least-squares techniques; the programs used were from the SHELXTL IRIS system.[16]

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***trans*-[Cr(cyclam)(OH)(H$_2$O)](CF$_3$SO$_3$)$_2$ 1.** The complex crystallizes in the centrosymmetric monoclinic space group *C*2/*c* with four mononuclear formula units in the unit cell. X-Ray powder diagrams demonstrate that the Co analogue **3** is isomorphous with this Cr complex. All hydrogen atoms were located in a difference Fourier map and were refined

Table 1 Crystallographic parameters for complexes **1**, **4**, **5**, **6** and **8**

Complex	**1**	**4**	**5**	**6**	**8**
Formula	$C_{12}H_{27}CrF_6N_4O_8S_2$	$C_{10}H_{25}Cl_2CoN_4O_{10}$	$C_{10}H_{28}Cl_2CrN_4O_7$	$C_{16}H_{41}Cl_2CrN_4O_{11}$	$C_{12}H_{22}CrN_7O_{12}$
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*C*2/*c*	$P\bar{1}$	$\mathrm{P}\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	17.144(3)	9.479(2)	9.506(2)	10.208(2)	7.058(2)
b/Å	11.063(2)	9.574(2)	9.576(2)	11.059(2)	7.672(2)
c/Å	12.170(2)	12.156(2)	11.452(2)	12.812(3)	10.248(2)
α/°	90	84.78(2)	95.76(3)	99.54(3)	70.73(3)
β/°	94.71(3)	76.34(2)	110.20(3)	95.63(3)	81.12(3)
γ/°	90	61.84(2)	113.32(3)	112.81(3)	84.38(3)
V/Å^3	2300.5(7)	944.9(3)	863.7(3)	1293.8(5)	517.2(2)
Z	4	2	2	2	1
D_c/mg m^{-3}	1.690	1.726	1.553	1.510	1.632
μ(Mo Kα)/mm^{-1}	0.773	1.249	0.856	0.708	0.630
Radiation (λ/Å)	0.71096	0.71096	0.71096	0.71096	0.71096
T/K	295	295	296	296	296
R^a	0.0461	0.0519	0.0541	0.0387	0.0335
$R_w{}^b$	0.0587	0.0701	0.0750	0.0520	0.0467

^{a} $R = \Sigma\left||F_o| - |F_c|\right|/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

isotropically; non-hydrogen atoms were refined anisotropically. The final values of the conventional R factors were $R = 0.0461$, $wR = 0.0587$, based on 2068 independent reflections with $I > 3\sigma(I)$.

***trans*-[Cr(cyclam)(OH)(H$_2$O)](ClO$_4$)$_2$ 4.** The complex crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with two mononuclear formula units in the cell. X-Ray powder diagrams demonstrate that the Cr analogue **2** is isomorphous with this Co complex. Hydrogen atoms associated with the nitrogen atoms and central H atom on the bridging O···H···O unit were located from a difference Fourier map and were refined isotropically, while hydrogen atoms bound to carbon atoms were placed in fixed calculated positions (C–H = 0.96 Å); the other hydrogen atoms associated with the $O_2H_3^-$ unit were not located. All non-hydrogen atoms were refined anisotropically. The final values of the conventional R factors were $R = 0.0519$, $wR = 0.0701$ based on 2805 independent reflections with $I > 3\sigma(I)$.

***trans*-[Cr(cyclam)(OH)$_2$]ClO$_4$·H$_2$O 5.** The complex crystallizes in the triclinic space group $P\bar{1}$ with two mononuclear formula units in the cell. Hydrogen atoms associated with the hydroxy and solvent water moieties were located in a difference Fourier and were refined isotropically, while hydrogen atoms bound to carbon and nitrogen atoms were placed in fixed calculated positions (C–H = 0.96 Å, N–H = 0.90 Å); all non-hydrogen atoms were refined anisotropically. The final values of the conventional R factors were $R = 0.0541$, $wR = 0.0750$ based on 3409 independent reflections with $I > 3\sigma(I)$.

***trans*-[Cr(cyca)(OH)(H$_2$O)](ClO$_4$)$_2$·H$_2$O 6.** The complex crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with two mononuclear formula units in the cell. X-Ray powder diagrams demonstrate that the Co analogue **7** is isomorphous with this Cr complex. Hydrogen atoms associated with the nitrogen and oxygen atoms were located from a difference Fourier map and were refined isotropically, while hydrogen atoms bound to carbon atoms were placed in fixed calculated positions (C–H = 0.96 Å). All non-hydrogen atoms were refined anisotropically. Three of the oxygen atoms attached to perchlorate chlorine atom Cl(1) were disordered between two positions labelled A and B, the relative occupancies being 66.7 and 33.3% respectively. Similarly, oxygen atoms attached to Cl(2) were disordered with occupancies of 61.0 and 39.0% for the positions labelled A and B, respectively. The final values of the conventional R factors were $R = 0.0387$, $wR = 0.0520$ based on 335 independent reflections with $I > 3\sigma(I)$.

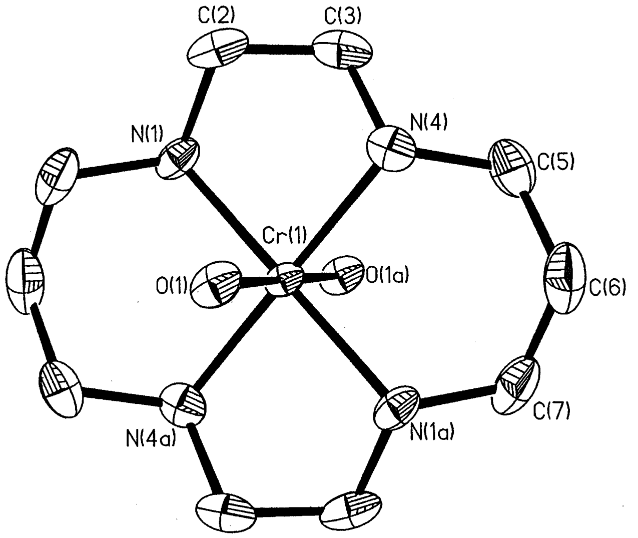

Fig. 1 View of the inner coordination sphere of the polymeric *trans*-[Cr(cyclam)(OH)(H$_2$O)]$^{2+}$ cation in the crystals of the triflate salt **1**. Hydrogen atoms are omitted for clarity. Atoms O(1) and O(1a) are the nominal OH and H$_2$O oxygen atoms, but are related by the crystallographic inversion center.

***trans*-[Cr(pico)$_2$(H$_2$O)$_2$](NO$_3$)$_3$·H$_2$O 8.** The complex crystallizes in the triclinic space group $P\bar{1}$ with one mononuclear formula unit in the cell. One of the nitrate anions [centered on N(4)] is disordered between two sites, so the site occupancy factors of N(4) and its associated oxygen atoms O(5) and O(6) were set to 0.5. Interestingly, the solvent water molecule occupies the same sites as one of the disordered oxygen atoms [O(7)] associated with this nitrate, so the occupancy of that site is unity. All hydrogen atoms, except those associated with the solvent water molecule, were located in a difference Fourier and were refined isotropically, while non-hydrogen atoms were refined anisotropically. The final values of the conventional R factors were $R = 0.0335$, $wR = 0.0467$ based on 1976 independent reflections with $I > 3\sigma(I)$.

Results and discussion

Description of the structures

***trans*-[Cr(cyclam)(OH)(H$_2$O)](CF$_3$SO$_3$)$_2$ 1.** The structure consists of *polymeric chains* in which adjacent Cr(cyclam) units are linked by hydrogen bonded $O_2H_3^-$ ions. A view of the inner coordination sphere in the cation is shown in Fig. 1, whereas the chain structure and the bridging $O_2H_3^-$ unit are depicted in

Table 2 Principal interatomic distances (Å) and angles (°) in complex **1**

Cr(1)–O(1)	1.984(2)	Cr(1)–N(1)	2.058(3)
Cr(1)–N(4)	2.063(3)	Cr(1)–Cr(1A)	6.085(1)
O(1)–O(1B)	2.493(5)		
O(1)–Cr(1)–N(1)	90.5(1)	O(1)–Cr(1)–N(4)	90.9(1)
N(1)–Cr(1)–N(4)	85.0(1)	O(1)–Cr(1)–O(1A)	180.0
N(1)–Cr(1)–O(1A)	89.5(1)	N(4)–Cr(1)–O(1A)	89.1(1)
N(1)–Cr(1)–N(1A)	180.0	N(4)–Cr(1)–N(1A)	95.0(1)
N(4)–Cr(1)–N(4A)	180.0		

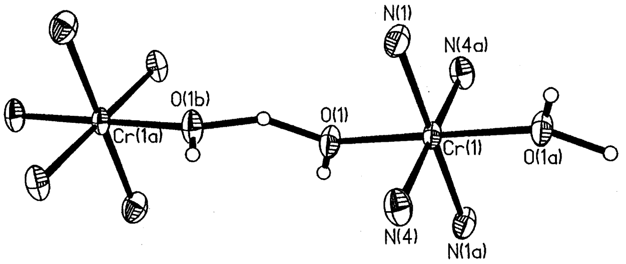

Fig. 2 View of the polymeric structure of the *trans*-$[Cr(cyclam)(OH)(H_2O)]^{2+}$ cation in the crystals of the triflate salt **1**, showing the bridging $O_2H_3^-$ ion linking adjacent Cr atoms.

Fig. 2. Principal bond distances and angles are listed in Table 2.

The geometry about the chromium(III) centers is roughly octahedral, with ligation provided by the nitrogen atoms of the ligand and the oxygen atoms of the 'water' and 'hydroxo' ligands. Adjacent chromium(III) centers are bridged by hydrogen bonds to form the polymeric unit {–Cr–HO···H···OH–Cr–HO···H···OH–Cr–}$_n$. The chromium atoms lie on a crystallographic inversion center, while the central hydrogen atom [H10] sits on a crystallographic twofold axis and is, therefore, exactly equi-distant from its two neighboring chromium atoms. The chains extend parallel to the crystallographic *c*-axis, the Cr···Cr and O(1)···O(1b) separations in the chain being 6.085 (1) [*i.e. c*/2] and 2.493 Å, respectively. This O(1)···O(1b) separation in the present chain structure is comparable with that of 2.462 Å found in the dimeric *cis* isomer,[1] but naturally the Cr···Cr distance in the chain is much greater than that of 4.925 Å in the dimeric *cis* isomer. Although the oxygen atoms nominally come from one water and one hydroxo ligand, it is apparent from the structure that the oxygen atoms in the bridges are both chemically and crystallographically equivalent, leading to symmetric bridges. Thus, the Cr(1)–O(1) bonds are all 1.984(2) Å in length and the O(1)–Cr(1)–O(1a) bond angle is constrained to 180°. This Cr–O bond length might have been expected to be intermediate between those of the monomeric dihydroxo and diaqua species, but in fact (*vide infra*) it is longer than both; this apparent lengthening may represent the difference between bridging and terminal ligands. The two independent Cr–N distances of 2.058(3) and 2.063(3) Å are similar, as expected, and the geometry of the cyclam ligand is unremarkable and consistent with that observed in a variety of other *trans*-$[M(cyclam)X_2]^{n+}$ complexes.[17]

The triflate ions in the structure are ordered, and their geometries are normal, with S–O distances in the range 1.392–1.430 Å [average, 1.41(2) Å], C–F distances of 1.257–1.323 Å [average, 1.30(4) Å], and a C–S separation of 1.792(6) Å. The O–S–O and F–C–F bond angles are in the ranges 111.1–117.3 [average 115(3)°] and 105.2–110.7° [average 107(3)°], while the O–S–C and S–C–F bond angles are in the ranges 103.0–104.4 [average 103.7(7)°] and 110.5–112.6° [average 111.4(11)°]; all of these metrical parameters are comparable to those observed in recent determinations of the structure of this anion.[18]

Table 3 Principal interatomic distances (Å) and angles (°) in complex **4**

Co(1)–O(1)	1.942(3)	Co(1)–N(1)	1.968(4)
Co(1)–N(4)	1.976(7)	Co(2)–O(2)	1.943(3)
Co(2)–N(21)	1.970(5)	Co(2)–N(24)	1.975(5)
Co(1)–Co(2)	6.078(1)	O(1)–O(2)	2.552(8)
O(1)–Co(1)–N(1)	90.1(2)	O(1)–Co(1)–N(4)	89.4(2)
N(1)–Co(1)–N(4)	85.7(2)	O(1)–Co(1)–O(1A)	180.0
N(1)–Co(1)–O(1A)	89.9(2)	N(4)–Co(1)–O(1A)	90.6(2)
N(1)–Co(1)–N(1A)	180.0	N(4)–Co(1)–N(1A)	94.3(2)
N(4)–Co(1)–N(4A)	180.0	O(2)–Co(2)–N(21)	90.8(2)
O(2)–Co(2)–N(24)	88.5(2)	N(21)–Co(2)–N(24)	85.9(2)
O(2)–Co(2)–O(2A)	180.0	N(21)–Co(2)–O(2A)	89.2(2)
N(24)–Co(2)–O(2A)	91.5(2)	N(21)–Co(2)–N(21A)	180.0
N(24)–Co(2)–N(21A)	94.1(2)	N(24)–Co(2)–N(24A)	180.0

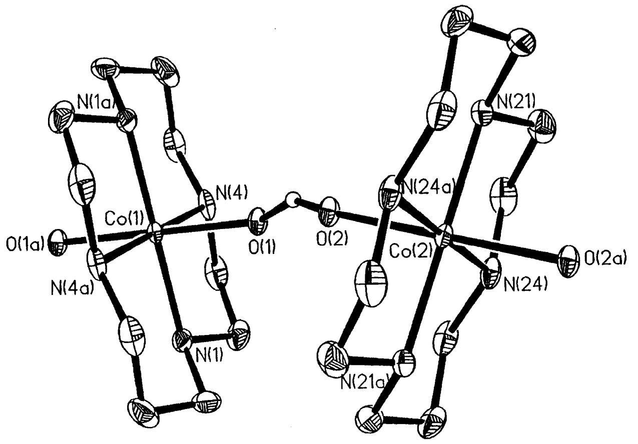

Fig. 3 View of the structure of the *trans*-$[Co(cyclam)(OH)(H_2O)]^{2+}$ cation in the crystals of the perchlorate salt **4**, showing the bridging $O_2H_3^-$ ion linking adjacent Co atoms. Atoms Co(1) and Co(2) are crystallographically independent, but each lies on an inversion center.

***trans*-$[Co(cyclam)(OH)(H_2O)](ClO_4)_2$ 4.** The structure of this complex also consists of *polymeric chains* in which adjacent Co(cyclam) units are linked by hydrogen bonded $O_2H_3^-$ ions. A view of the chain structure and the bridging $O_2H_3^-$ unit is presented in Fig. 3. Principal bond distances and angles are listed in Table 3.

With two independent molecules in $P\bar{1}$, the cobalt atoms could be in general positions in the cell, but in fact there are two independent cobalt atoms, each lying on a crystallographic inversion center. The geometry about the two independent cobalt(III) centers is roughly octahedral, with ligation again provided by the nitrogen atoms of the ligand and the oxygen atoms of the 'water' and 'hydroxo' ligands. The chains are formed by Co(1)–O···H···O–Co(2) units in which adjacent cobalt(III) centers are bridged by hydrogen bonds to form the polymeric unit {–Co(1)–HO···H···OH–Co(2)–HO···H···OH–Co(1)–}$_n$. The chains extend parallel to the crystallographic *c*-axis, the Co(1)···Co(2) separations in the chain being 6.078(1) Å [*i.e. c*/2] while the O(1)···O(2) distance is 2.552 Å. These values are very similar to those of 6.085 and 2.493 Å, respectively, in the chromium chain structure of **1**, above. Since the cobalt atoms lie on crystallographic inversion centers, the oxygen atoms in the bridges are again both chemically and crystallographically equivalent, leading to symmetric bridges. Thus, the Co(1)–O(1) and Co(2)–O(2) bond lengths of 1.942(3) and 1.943(3) Å are equal, and the O(1)–Co(1)–O(1a) and O(2)–Co(2)–O(2a) bond angles are constrained to 180°. The four independent Co–N distances of 1.968(4) to 1.976(7) Å [average 1.972(4) Å] are similar; all of these bond lengths at cobalt are shorter than the equivalent distances at chromium in **1**, as expected.

The perchlorate ions in the structure are apparently ordered and well behaved, and their Cl–O bond lengths and O–Cl–O angles of 1.357(8)–1.429(9) Å and 104.5(4)–117.6(4)° [average

Table 4 Principal interatomic distances (Å) and angles (°) in complex **5**

Cr(1)–O(11)	1.945(3)	Cr(1)–N(11)	2.066(4)
Cr(1)–N(14)	2.071(4)	Cr(2)–O(21)	1.950(3)
Cr(2)–N(21)	2.072(3)	Cr(2)–N(24)	2.077(4)
O(11)–Cr(1)–N(11)	90.2(2)	O(11)–Cr(1)–N(14)	91.2(1)
N(11)–Cr(1)–N(14)	85.0(2)	O(11)–Cr(1)–O(11A)	180.0
N(11)–Cr(1)–O(11A)	89.8(2)	N(14)–Cr(1)–O(11A)	88.8(1)
N(11)–Cr(1)–N(11A)	180.0	N(14)–Cr(1)–N(11A)	95.0(2)
N(14)–Cr(1)–N(14A)	180.0	O(21)–Cr(2)–N(21)	91.1(1)
O(21)–Cr(2)–N(24)	90.1(1)	N(21)–Cr(2)–N(24)	85.3(1)
O(21)–Cr(2)–O(21A)	180.0	N(21)–Cr(2)–O(21A)	88.9(1)
N(24)–Cr(2)–O(21A)	89.9(1)	N(21)–Cr(2)–N(21A)	180.0
N(24)–Cr(2)–N(21A)	94.8(1)	N(24)–Cr(2)–N(24A)	180.0

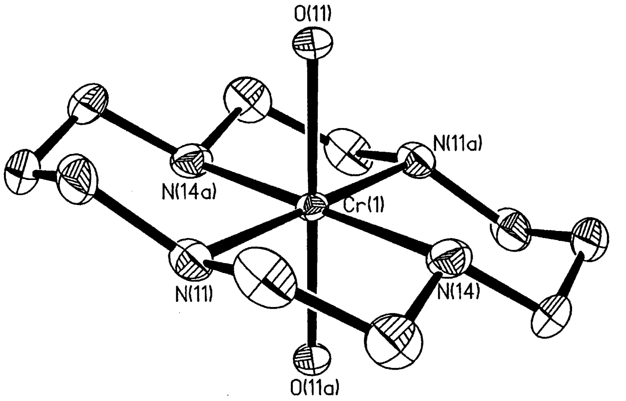

Fig. 4 View of the inner coordination sphere in one of the two independent *trans*-[Cr(cyclam)(OH)$_2$]$^+$ cations in the crystals of the perchlorate salt **5**; the other cation [centered around Cr(2)] is substantially similar. Hydrogen atoms are omitted and carbon atoms are unlabeled for clarity . Atoms O(11) and O(11a) *etc.*, are related by the crystallographic inversion center at Cr(1).

values, 1.40(2) Å and 109(3)°, respectively] are consistent with those observed in other structures.[1,19]

***trans*-[Cr(cyclam)(OH)$_2$]ClO$_4$·H$_2$O 5.** The structure of the complex consists of *monomeric* *trans*-[Cr(cyclam)(OH)$_2$]$^+$ cations, perchlorate ions, and solvent water molecules. A view of one cation is shown in Fig. 4. Principal bond distances and angles are listed in Table 4.

As was the case for complex **4**, above, with two independent molecules in $P\bar{1}$, the metal atoms could be in general positions in the cell, but here again there are two independent chromium atoms, each lying on a crystallographic inversion center. The geometry about the two independent centers is roughly octahedral, with ligation again provided by the nitrogen atoms of the ligand and the oxygen atoms of the hydroxo groups. The Cr(1)–O(11) and Cr(2)–O(21) bond lengths of 1.945(3) and 1.950(3) Å do not differ significantly, and are shorter than the value of 1.971 Å in the diaqua complex (*vide infra*) as expected. The Cr–N distances of 2.066(4)–2.077(4) Å [average 2.072(4) Å] are slightly longer than those in **1**, but the difference is small.

Interestingly, the shortest Cr · · · Cr separation of 6.048 Å in this monomer is slightly smaller than the intra-chain Cr · · · Cr and Co · · · Co distances in **1** and **4**, above. Here, however, the shortest O · · · O separation of 3.279 Å is far larger than the O · · · O distances in the O$_2$H$_3^-$ units in the chains or in the dimers formed by the corresponding *cis* isomers.[1]

The perchlorate ions in the structure also are apparently ordered and well behaved, and their Cl–O bond lengths and O–Cl–O angles of 1.326(10)–1.397(4) Å and 100.7(5)–117.9(7)° [average values, 1.35(3) Å and 109(7)°, respectively] are consistent with those observed above in **4** and in other structures.[1,19]

***trans*-[Cr(cyca)(OH)(H$_2$O)](ClO$_4$)$_2$·H$_2$O 6.** Like those of the analogous cyclam complexes (**1**–**4**) above, the structure in this complex again consists of *polymeric chains* in which adjacent Cr(cyca) units are linked by hydrogen bonded ionic units, but in this case the bridging units are O$_3$H$_5^-$ ions formed by the coordinated OH and H$_2$O ligands and the solvent water molecule. A view of the inner coordination sphere in the cation is shown in Fig. 5, while the chain structure and the bridging O$_3$H$_5^-$ unit are depicted in Fig. 6. Principal bond distances and angles are listed in Table 5.

Table 5 Principal interatomic distances (Å) and angles (°) in complex **6**

Cr(1)–O(1)	1.965(3)	Cr(1)–N(1)	2.083(3)
Cr(1)–N(2)	2.064(3)	Cr(2)–O(2)	1.974(2)
Cr(2)–N(3)	2.086(3)	Cr(2)–N(4)	2.070(3)
O(1)–Cr(1)–N(1)	93.7(1)	O(1)–Cr(1)–N(2)	89.8(1)
N(1)–Cr(1)–N(2)	85.5(1)	O(1)–Cr(1)–O(1A)	180.0
N(1)–Cr(1)–O(1A)	86.3(1)	N(2)–Cr(1)–O(1A)	90.2(1)
N(1)–Cr(1)–N(1A)	180.0	N(2)–Cr(1)–N(1A)	94.5(1)
N(2)–Cr(1)–N(2A)	180.0	O(2)–Cr(2)–N(3)	86.3(1)
O(2)–Cr(2)–N(4)	90.1(1)	N(3)–Cr(2)–N(4)	85.2(1)
O(2)–Cr(2)–O(2A)	180.0	N(3)–Cr(2)–O(2A)	93.7(1)
N(4)–Cr(2)–O(2A)	89.9(1)	N(3)–Cr(2)–N(3A)	180.0
N(4)–Cr(2)–N(3A)	94.8(1)	N(4)–Cr(2)–N(4A)	180.0

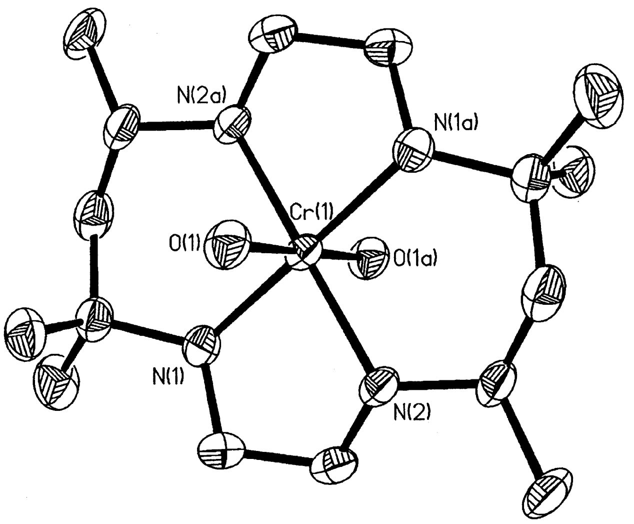

Fig. 5 View of the inner coordination sphere of the polymeric *trans*-[Cr(cyca)(OH)(H$_2$O)]$^{2+}$ cation in the crystals of the hydrated perchlorate salt **6**. Hydrogen atoms are omitted for clarity. Atoms O(1) and O(1a) are the nominal OH and H$_2$O oxygen atoms, but are related by the crystallographic inversion center.

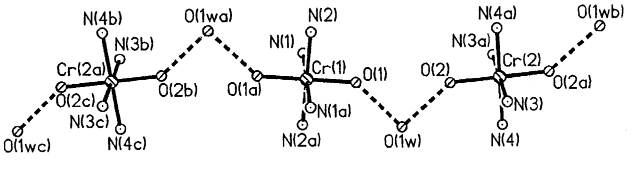

Fig. 6 View of the polymeric structure of the *trans*-[Cr(cyca)-(OH)(H$_2$O)]$^{2+}$ cation in the crystals of the hydrated perchlorate salt **6**, showing the bridging O$_3$H$_5^-$ ion linking adjacent Cr atoms.

The geometry about the chromium(III) centers is again roughly octahedral, with ligation provided by the nitrogen atoms of the ligand and the oxygen atoms of the 'water' and 'hydroxo' ligands. The chromium atoms each lie on crystallographic inversion centers. As a result of the presence of the larger bridging unit, the Cr(1) · · · Cr(2) separation in the chain of 7.738(2) Å is approximately 1.65 Å longer than that in **1** above. Examination of molecular models had suggested to us that the chain structure found in **1**–**4** could not occur in **6** or **7** because the steric requirements of the axial methyl groups at C(5) and C(12) would prevent two adjacent Cr(cyca) units from approaching each other; evidently, the presence of the intervening water molecule, to form the O$_3$H$_5^-$ unit, represents the

Table 6 Principal interatomic distances (Å) and angles (°) in complex **8**

Cr(1)–O(1)	1.971(2)	Cr(1)–N(1)	2.063(2)
Cr(1)–N(2)	2.065(2)		
O(1)–Cr(1)–N(1)	90.1(1)	O(1)–Cr(1)–N(2)	92.1(1)
N(1)–Cr(1)–N(2)	80.4(1)	O(1)–Cr(1)–O(1A)	180.0
N(1)–Cr(1)–O(1A)	89.9(1)	N(2)–Cr(1)–O(1A)	87.9(1)
N(1)–Cr(1)–N(1A)	180.0	N(2)–Cr(1)–N(1A)	99.6(1)
N(2)–Cr(1)–N(2A)	180.0		

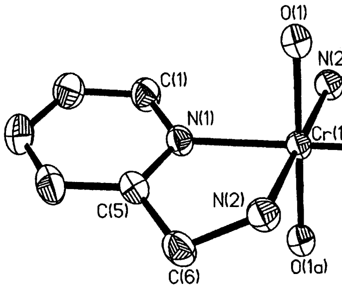

Fig. 7 View of the inner coordination sphere in the *trans*-[Cr(pico)$_2$(H$_2$O)$_2$]$^{3+}$ cation in the crystals of the nitrate salt **8**. Hydrogen atoms are omitted for clarity. Atoms O(1) and O(1a) *etc.*, are related by the crystallographic inversion center at Cr(1).

system's response to this steric constraint. The O(1)···O(1W) and O(2)···O(1W) separations of 2.663 and 2.639 Å, respectively, are longer than the O(1)···O(1b) separation in the $O_2H_3^-$ chain structure in **1**–**4**, which may reflect weaker bonding. The Cr(1)–O(1) and Cr(2)–O(2) bonds of 1.965(3) and 1.974(2) Å are slightly different, but not enough to suggest the presence of alternating dihydroxo and diaqua units in the crystal.

The four independent Cr–N distances are in the range 2.064(3)–2.086(3) Å, and while we are unaware of any previous determination of the structure of the cyca ligand, its geometry is unremarkable and consistent with our expectations. As was noted above, the perchlorate anions in the structure are each disordered in two sets of positions around a single Cl–O bond; this form of disorder is not uncommon in perchlorate structures.[19]

***trans*-[Cr(pico)$_2$(H$_2$O)$_2$](NO$_3$)$_3$·H$_2$O 8.** This structure contains monomeric *trans*-[Cr(pico)$_2$(H$_2$O)$_2$]$^{3+}$ cations, nitrate anions, and water molecules. A view of the cation is shown in Fig. 7. Principal bond distances and angles are listed in Table 6.

Since there is only one molecule per cell in the centrosymmetric space group $P\bar{1}$, the chromium centers are constrained to lie on a crystallographic inversion center. As was noted above, the Cr–OH$_2$ bond lengths of 1.971(2) Å are longer than the Cr–OH distances of 1.945–1.959 Å in **5**. The Cr–N distances of 2.063(2) and 2.065(2) Å are consistent with those in **1** and **5**.

The coordinated water molecules form hydrogen bonds to nitrate anions and the solvent water molecule, but not to each other; consequently, the closest approach between two adjacent Cr atoms is greater than 7.06 Å. The coordinated water molecule forms two hydrogen bonds. One interaction is formed by O(1)–H(1B)···O(4), with associated O(1)···O(4) and H(1B)···O(4) distances and O(1)–H(1B)···O(4) angle of 2.637 Å, 1.88 Å, and 168°, respectively. The other hydrogen bond is to O(7), which is the site alternately occupied by a nitrate anion and the solvent water molecule. The O(1)···O(7) and H(1A)···O(7) distances and O(1)–H(1A)···O(7) angle associated with this hydrogen bond are 2.588 Å, 1.92 Å, and 171°, respectively. These metrical parameters associated with the hydrogen bonding are indicative of strong hydrogen bonds.[20] The fully occupied nitrate anion is planar, with N–O bond lengths of 1.220(3), 1.244(3) and 1.268(2) Å, and O–N–O bond angles from 118.3(2) to 122.8(2)°. It is, perhaps, noteworthy that the longest N–O bond is to O(4), which is involved in the strong hydrogen bond discussed above. The present observations that the N(3)–O(4) bond is the longest and the O–N–O bond angles involving O(4) are smaller than the other O–N–O angle are all consistent with earlier observations of both hydrogen bonded and coordinated nitrates.[17]

Magnetic susceptibility. The temperature dependence of the magnetic susceptibility of powdered samples of complexes **1** and **8** was measured in the range 4.5–300 K. As would be anticipated for a monomeric Cr(III) complex, the effective magnetic moment of the monomeric complex **8** at room temperature is approximately 3.9 μ_B (similar to the anticipated spin-only value of $\sqrt{15} = 3.87$), and remains essentially constant over the entire temperature range. Alternatively, the magnetic susceptibility increases with decreasing temperature, consistent with the Curie–Weiss law. The magnetic moment of *trans*-[Cr(cyclam)(OH)(H$_2$O)](CF$_3$SO$_3$)$_2$ **1** declines a little from 290 to 20 K. The decrease in moment below 20 K could in principle be caused either by saturation effects in combination with zero-field-splitting (zfs) or by antiferromagnetic interactions through the hydrogen bonds between the individual complexes. However, in the present case the zfs has been determined by EPR spectroscopy *vide infra* and is too small ($D = 0.265$ cm^{-1}) to explain the decrease in magnetic moment, and we must conclude that we have antiferromagnetic interactions in a linear chain. This result is not unexpected since, as was noted earlier, we and others have previously observed antiferromagnetic interactions through hydrogen bonds in the similar *cis*-complexes[1–3] and the existence of magnetic interactions through hydrogen bonding has been established in a wide variety of complexes.[4] The obvious choice for a Hamiltonian operator to describe this kind of interaction is given in eqn. (1),

$$\hat{H} = J\sum_{i=1}^{n}\hat{S}_i\cdot\hat{S}_{i+1} + g\mu_B\sum_{i=1}^{n+1}\hat{S}_i\cdot\hat{H} \qquad (1)$$

but regrettably this kind of equation cannot be solved analytically.

There are several kinds of strategies for solving this operator. In the present case, however, since the interaction is small we have chosen to treat the linear chain as consisting of dinuclear units even though the crystal structure does not support this view. The susceptibilities are then calculated by means of eqn. (1) without the summations and eqn. (2).

$$\chi = -\frac{H}{T}\frac{\sum_i \frac{\partial E_i}{\partial H}\exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)} \qquad (2)$$

The use of eqn. (2) takes account of saturation effects, *i.e.* the susceptibility is calculated correctly even at low temperatures when $|J/kT|$ is not much smaller than one. This process leads to the values $J = 2$ cm^{-1} and $g = 1.98$, indicative of a weak antiferromagnetic interaction between the Cr(III) centers.

Simulation of EPR spectra. The EPR spectra of the complexes are interpreted by computer simulation of the following spin Hamiltonian.

$$H = H_a + H_b + H_{ex} \qquad (3)$$

Here,

$$\hat{H}_{ex} = J\hat{S}_a\cdot\hat{S}_b + D_e(2\hat{S}_{az}\hat{S}_{bz} - \hat{S}_{ax}\hat{S}_{bx} - \hat{S}_{ay}\hat{S}_{by}) + E_e(\hat{S}_{ax}\hat{S}_{bx} - \hat{S}_{ay}\hat{S}_{by}) \qquad (4)$$

and

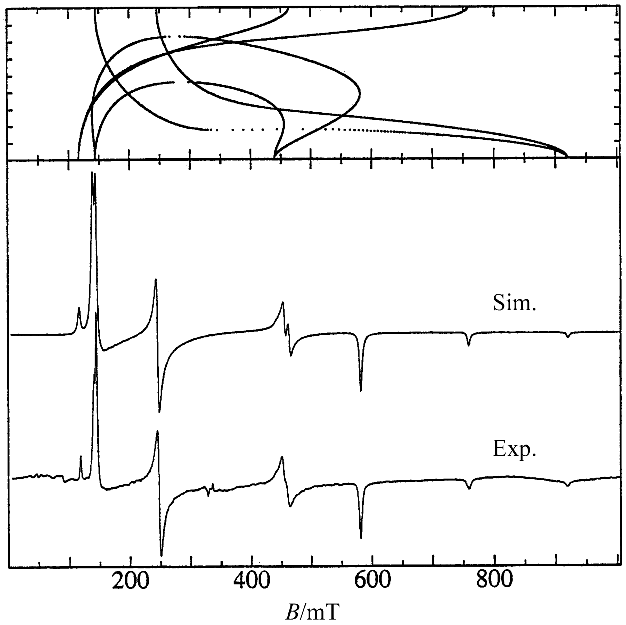

Fig. 8 EPR spectrum of the chromium complex $[Cr(cyclam)(OH)(H_2O)](CF_3SO_3)_2$ **1** diluted (2%) in the cobalt(III) analogue **3**. The top portion of the figure shows the resonance conditions as a function of the angle between the molecular z-axis and the applied field. The lower curve is the observed spectrum, whereas the center curve is the spectrum simulated with the parameters $g = 1.98$, $D = 0.2695\ cm^{-1}$ and $E = 0.0444\ cm^{-1}$.

$$H_a = g\mu_B S_a \cdot H + D_a[S_{az}^2 + 1/3S_a(S_a + 1)] \qquad (5)$$

with a similar Hamiltonian operator for atom b. The actual computer simulations have been briefly described previously.[21]

EPR spectra. To pursue the treatment of the magnetism further we have investigated the EPR spectra of the *trans*-aquahydroxo complex **1**. The powder spectrum just shows a very broad line centered around $g \approx 2$. A frozen glass spectrum of the compound dissolved in DMF (dimethylformamide) can be identified as a spectrum from the monomeric unit. This result is in contrast with that for the *cis*-aquahydroxo complex[1] where the frozen glass EPR spectra in DMF are from the quintet state which emerge as a result of the antiferromagnetic coupling within the dimeric units. The EPR spectra of complex **1** diluted in the similar Co^{III} complex **3** in the concentration range of 2–75% has been investigated. At 2% concentration the spectrum in Fig. 8 recorded at 80 K is essentially a monomeric spectrum, as can be seen from the simulation with the parameters $g = 1.98$, $D = 0.2695\ cm^{-1}$, $E = 0.044\ cm^{-1}$. When the Cr^{III} concentrations are increased several new lines appear, while at the same time the lines from the monomeric complexes shift a little resulting in slightly smaller parameters. The two small lines observed at 0.64 and 0.68 T are important, because they can be used in a trial and error process of simulating the quintet spectrum of the dimeric unit. The line at highest field determines the value of the parameter D_e while the the next line determines the value of E_e, when D_e is fixed. In Fig. 9 is given the spectrum at 30% Cr^{III} concentration recorded at 80 K. The simulated spectrum is the sum of a monomeric spectrum and a dimeric spectrum, *i.e.* the spectrum within the quintet state which emerges as a result of the antiferromagnetic interaction. As has frequently been seen before only the spectrum within the quintet state is observed.[1,21–23] The parameters for the monomeric complex have been slightly reduced to $D = 0.2500\ cm^{-1}$ and $E = 0.0416\ cm^{-1}$. The parameters for the dimeric complex are $g = 1.98$, $D = 0.2500\ cm^{-1}$, $E = 0.0416\ cm^{-1}$ and $J = 2\ cm^{-1}$, $D_e = -0.0715\ cm^{-1}$ and $E_e = 0.0350\ cm^{-1}$. It is noteworthy that these J and g values obtained from the EPR spectral analysis are entirely consistent with those obtained from the magnetic susceptibility data, even though the structure of **1** is an infinite chain.

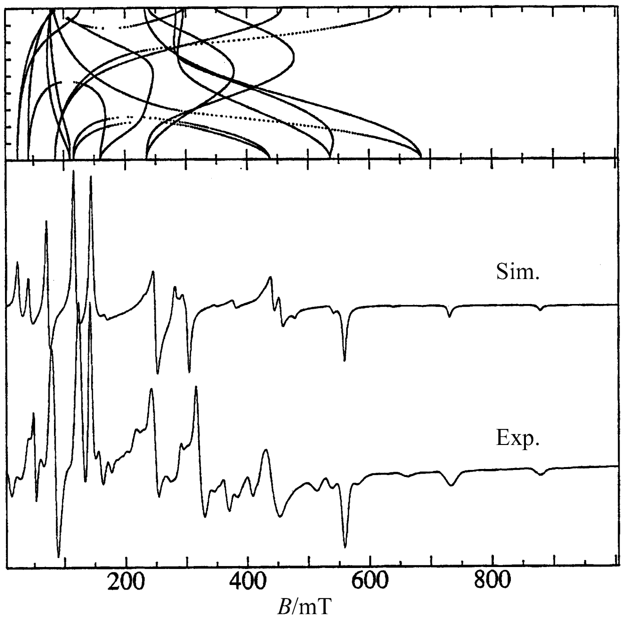

Fig. 9 EPR spectrum of the chromium complex $[Cr(cyclam)(OH)(H_2O)](CF_3SO_3)_2$ **1** diluted (30%) in the cobalt(III) analogue **3**. The top portion of the figure shows the resonance conditions as a function of the angle between the molecular z-axis and the applied field. The lower curve is the observed spectrum, whereas the center curve is the spectrum simulated with the parameters $g = 1.98$, $D = 0.2500\ cm^{-1}$ and $E = 0.0416\ cm^{-1}$ for the monomeric component and $g = 1.98$, $D = 0.2500\ cm^{-1}$, $E = 0.0416\ cm^{-1}$ and $J = 2\ cm^{-1}$, $D_e = -0.0715\ cm^{-1}$, $E_e = 0.0350\ cm^{-1}$ for the dimeric component.

Conclusion

The present series of structural results provide compelling support for the suggestion[5] that complexes of the types *trans*-$[Cr(A)_4(OH)(H_2O)]^{2+}$ and their cobalt analogues will exhibit chain structures, while the related diaqua and dihydroxo complexes are monomeric. While, as earlier workers had concluded,[5] the μ-$O_2H_3^-$ ion is the normal bridging unit, in those complexes where formation of this unit is precluded by geometric constraints, the longer μ-$O_3H_5^-$ ion may be found. Moreover, the EPR results demonstrate that EPR spectroscopy provides a reliable diagnostic tool to demonstrate the existence of weak magnetic interactions due to the formation of polymeric structures in the solid state.

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