The Crystal Structure, and Magnetic and Other Properties of Tri-μ-hydroxo-bis[triamminechromium(III)] Perchlorate

Peter Andersen,[a,*] Anders Døssing,[a] Sine Larsen[b] and Erik Pedersen[a]

[a]Department I, Inorganic Chemistry and [b]Department IV, Physical Chemistry, H. C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

Andersen, P., Døssing, A., Larsen, S. and Pedersen, E., 1987. The Crystal Structure, and Magnetic and Other Properties of Tri-μ-hydroxo-bis[triamminechromium(III)] Perchlorate. – Acta Chem. Scand., Ser. A 41: 381–390.

The tri-μ-hydroxo-bis[triamminechromium(III)] dimer (triol) has been precipitated as the salt $[(NH_3)_3Cr(OH)_3Cr(NH_3)_3](ClO_4)_{3-x}$ I_x (**1**) from solutions rich in the *cis*-diol, *cis*-$[(H_2O)(NH_3)_3Cr(OH)_2Cr(NH_3)_3(OH)]^{3+}$, containing minimal amounts of the triol.

The structure of **1** was determined from low-temperature X-ray diffraction data. It crystallizes in the orthorhombic space group $Pmn2_1$ with a = 7.899(2), b = 9.631(3),c = 11.630(5) Å (105 K) and Z = 2. Using 2592 observed reflections the structure was refined to R = 0.040 and R_w = 0.049. Two of the perchlorate ion sites are partially populated by iodide ions. The heavier atoms, Cr, Cl and I, are all located in crystallographic mirror planes. The symmetry of the cation is close to D_{3h}, with a Cr-Cr distance of 2.6307(11) Å.

The magnetic susceptibilities of **1** were interpreted in terms of sums of two-center interactions approximately according to the Heisenberg-Dirac-Van Vleck Hamiltonian, giving a triplet energy J = 119(1) cm^{-1}. The X-band ESR spectra of a crystalline powder of **1** diluted in $[(NH_3)_3Co(OH)_3Co(NH_3)_3](ClO_4)_3 \cdot aq$ showed a group of transitions at 3.2 kG which were interpreted as internal quintet transitions in a system with mononuclear zero-field splitting parameters $D_1 = D_2$ = 1.2 cm^{-1}.

Absorption spectra show that **1** is hydrolyzed in water at 0.8 °C to the *cis*-diol with a half-life of 5–6 min (ca. 0.5 min at 25 °C). Hydrolysis is even faster in acidic or basic solution.

Recently, we presented an investigation of reversible isomerization reactions of di-μ-hydroxo-bis[*fac*-triamineaquachromium(III)] ions (diols) in aqueous solution.[1] Among the reactions studied was the *trans*/*cis*-isomerization of $[(H_2O)(NH_3)_3Cr(OH)_2Cr(NH_3)_3(H_2O)]^{4+}$ and of the deprotonated forms of this ion, where *trans* and *cis* refer to the positons of the terminal H_2O or OH^- ligands relative to the $Cr(OH)_2Cr$ bridge plane. Equilibrium was attained from both sides, and one of the solid starting materials was synthesized and characterized as *cis*-$[(H_2O)(NH_3)_3Cr(OH)_2Cr(NH_3)_3(OH)](ClO_4)_3 \cdot H_2O$.

In order to study the structure of the cation in this salt, with special reference to the suggested intramolecular hydrogen bond between the terminal H_2O and OH^- ligands, we decided to carry out a structure analysis using single-crystal X-ray diffraction data. Suitable crystals were grown by a slight modification of our previous method[1] (see Experimental).

The structure analysis showed surprisingly that the cation in the salt is not the *cis*-diol, but the triol, $[(NH_3)_3Cr(OH)_3Cr(NH_3)_3]^{3+}$, and in the following we describe the structure analysis along with investigations of other properties of this cation.

Experimental

Syntheses. The synthesis described recently[1] was modified in order to obtain crystals large enough

*To whom correspondence should be addressed.

for single crystal structure determination: 0.64 g of *trans*-$[(H_2O)(NH_3)_3Cr(OH)_2Cr(NH_3)_3(H_2O)]I_4 \cdot 4H_2O$[2] was dissolved in 6.0 ml of water, after which six 50 μl portions of 1.5 LiOH were added at intervals of 5 min. After addition of the last portion, the solution was kept at room temperature for 30 min. With this procedure the final pH was ca. 5.8, and unwanted loss of NH_3 was avoided while ensuring a high content of the *cis*-diol isomer. To the solution was then added 2.7 g of $LiClO_4$ in small portions and the solution was kept at 0 °C for 15 min. The violet *trans*-$[(H_2O)(NH_3)_3Cr(OH)_2Cr(NH_3)_3(OH)](ClO_4)_3 \cdot aq$ was filtered off and the solution was kept at ca. 5 °C for 2–3 days for crystallization. The red crystals were washed with ethanol and air-dried. Yield: 60 mg (14 %) of $[(NH_3)_3Cr(OH)_3Cr(NH_3)_3](ClO_4)_3$ containing ca. 5 % (*w*/*w*) of iodide, analyses being in accordance with the formula $[(NH_3)_3Cr(OH)_3Cr(NH_3)_3](ClO_4)_{3-x}I_x$ (x = 0.2–0.3).

It seems that the presence of iodide ions in the solution is essential for the crystallization of the triol. If the iodide is removed with $AgClO_4$, no triol is obtained; in this case only *trans*-aqua-hydroxo diol precipitates.

The ESR spectra (Fig. 4) were measured on a powder of the chromium triol diluted in $[(NH_3)_3Co(OH)_3Co(NH_3)_3](ClO_4)_3 \cdot aq$. This powder was prepared by syncrystallization from an aqueous solution of the chloride salt of the cobalt triol[3] and the perchlorate salt of the chromium triol, using $LiClO_4$ as precipitating agent. The procedure was carried out at 0 °C within a

Table 1. Crystal data for $[(NH_3)_3Cr(OH)_3Cr(NH_3)_3](ClO_4)_{2.83}I_{0.17}$.

Formula		$Cr_2O_{14.32}N_6Cl_{2.83}I_{0.17}H_{21}$	
FW/g mol^{-1}		560.21	
Space group		$Pmn2_1$ (orthorhombic)	
Cell parameters	105 K (single crystal)		296 K (powder)
Radiation	Mo*K*α		Cu*K*α
a/Å	7.899(2)		8.001(5)
b/Å	9.631(3)		9.841(4)
c/Å	11.630(5)		11.649(4)
V/Å^3	884.7(8)		917.1(7)
Calculated density (296 K)/g cm^{-3}		2.028	
Observed density (296 K)/g cm^{-3}		2.08	
Molecules per cell		2	
Data collection and refinement			
Crystal size/mm^3		0.05 × 0.10 × 0.5	
Developed forms		{100},{011}	
Radiation (Mo*K*α) λ/Å		0.71073	
Linear absorption coefficient μ/cm^{-1}		20.0	
Scan type		ω-2θ	
Scan width, Δ θ/°		1.6 + 0.350 tan θ	
Background		25 % of full scan on both sides	
Maximum scan time /s		240	
Maximum specified σ(*I*)/*I*		0.01	
θ limits		1–36	
Octants collected		$hk \pm \ell$	
No. of unique data		3567	
Internal *R*-value from averaging		R = 0.024	
No. of data with $I/\sigma(I) \geq 3.0$		2592	
No. of variables		232	
Weights		$w^{-1} = \sigma_{cs}^2(F) + 0.00063\|F\|^2$	
R		0.040	
R_w		0.049	

few seconds, and the precipitated powder was washed with ethanol and air-dried. A powder containing 2.1 mole % chromium was used for the ESR measurements.

Chemicals, elemental analyses and apparatus. The chemicals used were all of reagent grade or of a similar or better quality. All the prepared compounds were subjected to microanalysis, and analyses for Cr, Co, N, Cl and I were in accordance, within 1–2 rel. %, with the formulae given. Visible absorption spectra were recorded on a Perkin-Elmer Lambda 17 spectrophotometer with automatic disk data collection. ESR spectra were obtained on a Jeol JES-ME-1X instrument, and the magnetic susceptibilities were measured by the Faraday method in the temperature range 4.6–300 K at a field strength of 13 kG. A description of the instrument is given elsewhere.[4] The X-ray equipment is described below.

X-Ray crystallography. Characterization and data collection. The chromium triol salt crystallizes as irregularly shaped crystals. Crystals suitable for single-crystal diffraction work were obtained as described above. The compound was characterized by Weissenberg photographs and by powder photographs (Guinier-Hägg camera with Cu$K\alpha$ radiation) recorded with silicon as internal standard. These photographs showed the crystals to belong to the orthorhombic system. The systematically absent reflections $h0\ell : h + \ell = 2n + 1$ are consistent with the space groups $Pmn2_1$ and *Pmnm* (a non-standard setting of *Pmmn*).

A CAD 4 single-crystal diffractometer equipped with an Enraf-Nonius gas-flow low-temperature device was employed for the data collection. The temperature was recorded with a thermocouple and the variation was less than 1 K. Mo$K\alpha$ radiation obtained from a highly mosaic graphite crystal was used. The unit cell parameters at 105 K were determined from 18 ($17.4° \leq \theta \leq 21.1°$) reflections by least-squares refinement. The intensities of three standard reflections were measured after every 10 000 s; these measurements showed no systematic variations. The orientation of the crystal was checked after every 300 reflections.

Data reduction included corrections for background, Lorentz, polarization and absorption effects. A Gaussian numerical integration procedure[5] was used for the absorption correction. The symmetry-related reflections were averaged and the standard deviations for the measured intensities were based on counting statistics. Table 1 lists the crystal data and other information relevant to data collection and structure refinement.

Structure determination and refinement. The structure was solved by combination of the heavy atom method and direct methods.[6] Assuming the space group to be $Pmn2_1$, the positions of two chromium atoms were found in the crystallographic mirror plane. Attempts to solve the structure in the space group of higher symmetry, *Pmnm*, were futile. Subsequent least-squares refinements minimizing $\Sigma w(|F_o| - |F_c|)^2$, and the difference Fourier calculations showed the positions of the chlorine, oxygen and nitrogen atoms in the structure. The z coordinate for Cr1 was fixed during all the refinements. The subsequent refinements ($R = 0.10$) resulted in perchlorate groups with physically unrealistic geometries and thermal parameters, and the corresponding difference Fourier showed large peaks close to two of the chlorine atoms. The elemental analysis had shown a small content of iodide (see above), and as the iodide and perchlorate ions are similar in size and shape it was concluded that the crystal examined contains a fraction of iodide ions in two of the sites for the perchlorate ions. The distances between the iodine and chlorine positions are ca. 0.2 Å. Iodide was introduced and the population parameters for the two partially populated perchlorate sites and iodide ions were also varied in the least-squares refinements. This improved the model significantly. Anisotropic thermal parameters were introduced for the chromium atoms and for the atoms of the ordered perchlorate group. The population parameters of adjacent chlorine and iodine are highly correlated and consequently unsuited for estimating the ratio between them. The population parameters for the partially populated perchlorate ion sites were therefore determined as the average of the population parameters of the oxygen atoms, and the population parameters for iodine were adjusted accordingly to assure electroneutrality. The population parameters with their statistical standard deviations are shown in Table 2. From these values, the linear absorption coefficient was recalculated and used in an absorption correction of the data. The final refinements were performed using these data. The iodine atoms and Cl2 were re-

Table 2. Positional[a] parameters and isotropic thermal parameters (Å^2).

Atom	*x*	*y*	*z*	B_{iso}^b
Cation				
Cr1	0.0000	0.82164(8)	0.225	0.77
Cr2	0.0000	0.58690(8)	−0.10931(8)	0.80
N1	0.0000	0.8261(5)	−0.4012(4)	1.20
N2	0.1866(4)	0.9734(3)	−0.2155(3)	1.18
N3	0.1847(5)	0.5235(4)	0.0053(3)	1.41
N4	0.0000	0.3942(5)	−0.1877(4)	1.23
O1	0.1579(3)	0.6621(3)	−0.2259(3)	1.07
O2	0.0000	0.7821(4)	−0.0583(3)	1.11
Perchlorate 1				
Cl1	0.0000	0.7054(2)	0.2966(1)	1.33
O11	0.0000	0.8456(5)	0.3447(4)	2.31
O12	0.1488(5)	0.6889(4)	0.2281(3)	2.78
O13	0.0000	0.6070(5)	0.3896(5)	2.23
Perchlorate 2, PP = 0.876(18)				
Cl2	0.0000	0.1709(1)	0.0620(1)	0.66
O21	0.0000	0.2907(5)	0.1391(4)	1.83
O22	0.0000	0.0455(6)	0.1270(5)	2.1
O23	0.1491(5)	0.1786(3)	−0.0108(3)	1.71
Perchlorate 3, PP = 0.956(30)				
Cl3	0.0000	0.1889(1)	0.5026(1)	0.81
O31	0.0000	0.3169(5)	0.5621(4)	2.09
O32	0.1494(5)	0.1096(3)	0.5314(3)	2.02
O33	0.0000	0.2153(5)	0.3794(4)	1.70
I1, PP = 0.044	0.0000	0.1995(6)	0.4836(5)	0.13
I2, PP = 0.124	0.0000	0.1536(2)	0.0573(2)	0.36

[a]The symmetry-related atoms can be generated by the symmetry operation $(-x,y,z)$. [b]For the atoms refined with anisotropic thermal parameters,

$$B_{iso} = \frac{8\pi^2}{3} \sum_i \sum_j U_{ij} \cdot a_i^* \cdot a_j^* \cdot \bar{a}_i \cdot \bar{a}_j$$

fined with isotropic thermal parameters. Anisotropic thermal parameters were used for the other chlorine, chromium, nitrogen and oxygen atoms.

A difference Fourier clearly showed the positions of all the hydrogen atoms in the structure except the hydrogen atom bonded to the bridging hydroxo group and expected to be in the crystallographic mirror plane. A careful examination of the difference Fourier showed that this hydrogen atom is distributed equally between two positions related by the symmetry of the mirror plane. The positional parameters for the hydrogen atoms were also included in the final refinements, using a common isotropic thermal parameter $B = 2.0$ Å^2. The polarity of the crystal was determined as described by Rogers.[7] In the final cycle the maximum shift was 0.19 σ, and the unit-weighted and weighted residuals were 0.040 and 0.049, respectively. The goodness-of-fit parameter, S, had a value of 1.29. The maximum peaks of 2e/Å^3 in the final difference Fourier were found close to Cl2. The SDP-system[8] provided by Enraf-Nonius was used for the crystallographic calculations. The atomic scattering factors of Cromer and Mann[9] were used as contained in the program. The anomalous dispersion corrections to the atomic scattering factors for I, Cr, Cl, O and N

Table 3. Bond lengths (Å) and bond angles(°).

Cr1–N1	2.050(5)	Cr2–N4	2.068(5)
Cr1–N2	2.078(3)	Cr2–N3	2.068(3)
Cr1–O1	1.979(3)	Cr2–O1	1.980(3)
Cr1–O2	1.975(4)	Cr2–O2	1.971(4)
O1–Cr1–O2	81.71(13)	O1–Cr2–O2	81.78(12)
O1′–Cr1–O1	78.13(14)	O1′–Cr2–O1	78.07(15)
N1–Cr1–O1	90.60(14)	N4–Cr2–O1	91.51(13)
N1–Cr1–O2	170.0(2)	N4–Cr2–O2	171.3(2)
N1–Cr1–N2	92.20(13)	N4–Cr2–N3	91.12(14)
N2′–Cr1–N2	90.3(2)	N3′–Cr2–N3	89.7(2)
N2–Cr1–O1	95.69(11)	N3–Cr2–O1	96.05(12)
N2–Cr1–O2	94.79(13)	N3–Cr2–O2	95.02(12)
N2–Cr1–O1′	173.25(12)	N3–Cr2–O1′	173.62(12)
Cr1–O1–Cr2	83.30(10)	Cr1–O2–Cr2	83.63(15)

were those of Cromer and Liberman.[10] The final positional and equivalent isotropic thermal parameters are listed in Table 2. Anisotropic thermal parameters, parameters for the hydrogen atoms, and lists of observed and calculated structure amplitudes can be obtained from the authors on request.

Results and discussion

As stated in the introduction, the cation in the investigated perchlorate surprisingly is not the *cis*-aquahydroxo diol but the tri-μ-hydroxy complex (triol), $[(NH_3)_3Cr(OH)_3Cr(NH_3)_3]^{3+}$, i.e. the condensation product of the *cis*-diol. Thus, from solutions rich in *cis*-diol and with no detectable amounts of the triol present it is nevertheless the triol which precipitates on addition of perchlorate.

The triol was not detected in connection with our previous isomerization studies in aqueous solution at 25 °C,[1] because under these circumstances the triol is hydrolyzed to the *cis*-diol at a rate comparable to that of dissolution (see below).

With the new knowledge obtained from the crystal structure determination we were able to characterize the triol in more detail as follows.

The crystal structure. The bond lengths and angles are presented in Table 3. The Cr-O and Cr-N bond lengths are similar to those found in the structures of related chromium diols.[2] The symmetry of the cation (Fig. 1) is close to D_{3h}, the positions of the hydrogen atoms bonded to the bridging hydroxo groups showing the only major deviation from this symmetry. The population of two of the perchlorate sites with iodide ions does not affect the geometries of the perchlorate ions. The three ions have normal Cl-O bond lengths and O-Cl-O angles.

The packing in the crystal is determined by hydrogen bonds between the cation and the perchlorate (iodide) ions, as illustrated by the stereo pair in Fig. 2. Table 4 lists the hydrogen bonds in the structure. All the hydrogen atoms participate in hydrogen bonds to the anions. Two of these bonds are bifurcated (from O1 and N1), but the rest are of the normal linear type.

The angles between the O-H bonds and the corresponding Cr1-O-Cr2 planes which are of importance for the interpretation of the magnetic

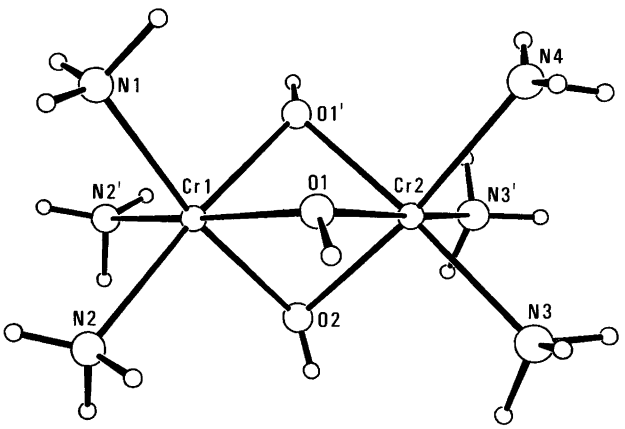

Fig. 1. Perspective ORTEP[22] drawing of the cation $[(NH_3)_3Cr(OH)_3Cr(NH_3)_3]^{3+}$ illustrating the atomic labelling. Atoms generated by the symmetry operation of the mirror plane are marked by ′. The thermal ellipsoids enclose 50 % probability. Hydrogen atoms are drawn as spheres with a common, arbitrary radius.

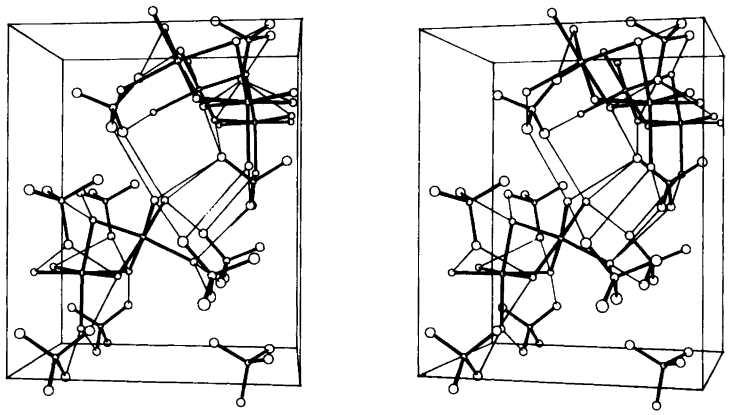

Fig. 2. ORTEP stereo drawing showing the packing in $[(NH_3)_3Cr(OH)_3Cr(NH_3)_3](ClO_4)_3$. The hydrogen bonds are indicated as thin lines. The unit cell is viewed along *c*.

data are 30(4)° for the O1-H1 group and 48(15)° for the O2-H2 group.

It is remarkable that the compound crystallizes with the heavier atoms of the complex cation and the three perchlorate ions in a crystallographic mirror plane. The structure of $[(NH_3)_3Co(OH)_3Co(NH_3)_3]I_3$[11] shows a similar mode of crystallization. Weissenberg photographs of this cobalt triol were compared with those of the chromium triol perchlorate, and this comparison revealed that the two structures are virtually isostructural. This is in accordance with the observation that iodide ions can replace perchlorate ions in the present structure.

Table 4. Hydrogen bonds in $[(NH_3)_3Cr(OH)_3Cr(NH_3)_3](ClO_4)_{3-x}I_x$.

D–H···A	D–A/Å	D–H–A/°
N1–H11–O13[a]	3.221(7)	134(5)
N1–H12–O23[b]	3.051(4)	139(5)
N1–H12–O32[c]	3.076(6)	138(5)
N2–H21–O32[c]	3.236(5)	152(4)
N2–H22–O23[d]	3.108(5)	173(4)
N2–H23–O33[b]	3.263(4)	175(5)
N3–H31–O21	3.095(6)	150(5)
N3–H32–O12	3.055(5)	157(5)
N3–H33–O13[b]	3.097(5)	157(5)
N4–H41–O23	3.151(6)	149(2)
N4–H42–O12[b]	3.049(4)	170(5)
O1–H1–O21[b]	3.158(4)	137(5)
O1–H1–O33[b]	3.193(4)	133(4)
O2–H2–O32[e]	3.138(4)	151(9)

[a](*x*,*y*,*z*-1). [b](½-*x*, 1-*y*,*z*-½). [c](*x*, 1+*y*,*z*-1). [d](*x*, 1+*y*,*z*). [e](*x*-½, 1-*y*,*z*-½).

The dinuclear chromium(III) diols are well characterized structurally, and have Cr-Cr distances of around 3.00 Å and bridge O-O distances of around 2.55 Å. In the present chromium triol, the average bridge O-O distance is the same and the Cr-Cr distance is 2.6307(11) Å, which is similar to that found in the structures of the few other known chromium triols. The dithionate[12] and iodide[13] salts of the N,N′,N″-trimethyl-1,4,7-triazacyclononane complex have Cr-Cr separations of 2.6064(6) and 2.642(2) Å, respectively, and in the 1,5,9-triazacyclododecane complex[14] this separation is 2.666(3) Å. For comparison, the Co-Co separation in the related $[(NH_3)_3Co(OH)_3Co(NH_3)_3]^{3+}$ complex is 2.57 Å and 2.565 Å in the iodide and dithionate[15] salts, respectively.

Magnetic susceptibilities. The magnetic susceptibilities of $[(NH_3)_3Cr(OH)_3Cr(NH_3)_3](ClO_4)_{3-x}I_x$ in the range 4.6–300 K are shown in Fig. 3. This has been interpreted in terms of antiferromagnetic coupling between two nearest centers, combined with partial magnetic saturation at 13 kG. The susceptibilities were fitted to the expression:

$$\chi'_A(T) = -\frac{N}{2H}\frac{\sum_i \frac{\partial E_i}{\partial H}\exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)} + K + \frac{C}{T} \quad (1)$$

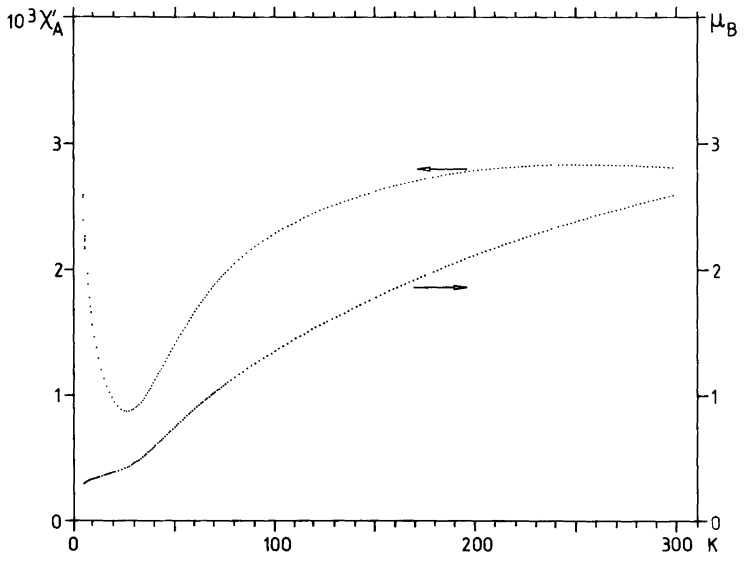

Fig. 3. Magnetic susceptibility per chromium (left scale, cgs units) and effective moment (right scale, Bohr magnetons) of $[(NH_3)_3Cr(OH)_3Cr(NH_3)_3](ClO_4)_{3-x}I_x$. The calculated values of χ'_A were all well within the extension of the · marks for the parameters representing all three models referred to in Table 5.

by minimization of

$$\sum_j \frac{[\chi^{obsd}(T_j) - \chi'_A(T_j)]^2}{\sigma^2(\chi(T_j)) + \left[\frac{\partial\chi^{obsd}}{\partial T}(T_j)\right]^2 \sigma^2(T_j)} \qquad (2)$$

In (1), the E_i values are the energies of the sixteen components of the ground-state manifold obtained from the isotropic Zeeman term $\beta g \mathbf{H} \cdot \mathbf{S}$ in the Hamiltonian by addition of exchange terms according to three different models. A Heisenberg-type model is

$$\mathcal{H} = J\,\mathbf{S}_1 \cdot \mathbf{S}_2 - j\,(\mathbf{S}_1 \cdot \mathbf{S}_2)^2 \qquad (3)$$

in which the triplet, quintet and septet energies are $J + 6.5j$, $3J + 13.5j$, and $6J + 9j$, respectively. In the following, (3) is referred to as model 2. If j is fixed at zero we call it model 1. A generalized Hamiltonian has the eigenvalues $E(S')$ at zero field, where S' has the values 0–3 in this case with two spins of 3/2. This is called model 3.

The results of the data fits are shown in Table 5, apart from values of g, K (additive constant) and C (constant accounting for the mole fraction of monomeric impurities) which in all cases were as slightly below 2.00, approximately zero, and 0.5 %, respectively. Also given in Table 5 are the calculated variances per degree of freedom, *var/f*.

Models 2 and 3 fit the data equally well according to a v^2 test, as seen from *var/f*, and do so significantly better than model 1. However,

Table 5. Exchange parameters for $[(NH_3)_3Cr(OH)_3Cr(NH_3)_3](ClO_4)_{3-x}I_x$.

Model 1	
J/cm^{-1}	128.2(5)
var/f	24.51
f	188
Model 2	
J/cm^{-1}	99.7(10)
j/cm^{-1}	2.97(10)
var/f	5.42
f	187
Model 3	
$E(1)$/cm^{-1}	119.1(4)
$E(2)$/cm^{-1}	340.3(2:)
$E(3)$/cm^{-1}	625(5)
var/f	5.20
f	186

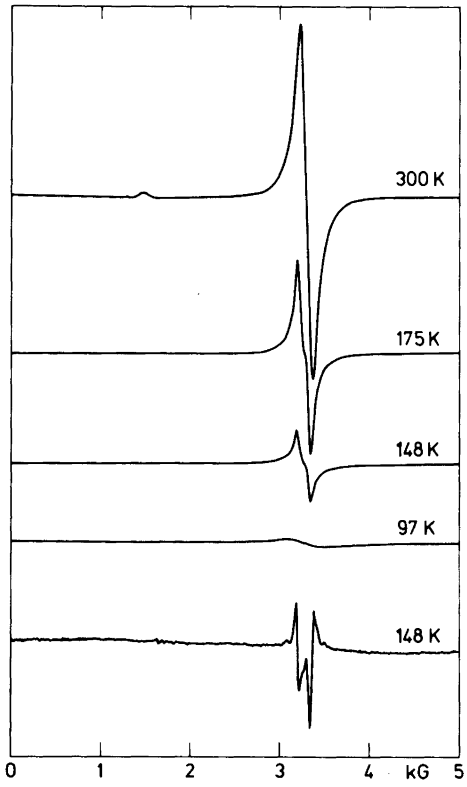

Fig. 4. First derivative (at the bottom a second derivative) ESR spectra at 9.2 GHz of a crystalline powder of $[(NH_3)_3Co(OH)_3Cr(NH_3)_3](ClO_4)_3 \cdot aq$ containing 2.1 mole % of the chromium analogue. The arbitrary scale for the four first derivative spectra is approximately the same. The small transition at 1.5 kG (300 K) has not been interpreted.

model 1, with only one exchange parameter, gives a fair description of the data.

The exchange parameters are comparable to those found for other chromium(III) triols.[16-18]

ESR spectrum. Examples of ESR spectra are shown in Fig. 4. In view of the magnitude of the exchange coupling, chromium triol salts are expected to be magnetically dilute at the temperatures of measurement. Nevertheless, the triol was diluted in a diamagnetic host lattice as described in the syntheses section. The intensity vs. temperature curve was interpreted in terms of

$$I \propto \frac{\Delta E}{kT} \exp(-E/kT),$$

showing that the states in question all have an energy of 365(35) cm^{-1}. This energy corresponds to the quintet energy, viz. $J = 122(12)$ cm^{-1}, in good agreement with the susceptibility data. The field range of our magnet (0–7.2 kG) did not allow detection of signals from any of the other spin states.

The X-band transition at 3.2 kG is split into two relatively intense components 130(5) G apart and two weak components 350(20) G apart, as particularly evident from the second derivative spectrum in Fig. 4 (bottom). A simple spin Hamiltonian for the system, assuming axial symmetry, is

$$\mathcal{H} = \sum_{1,2} \mathcal{H}_i + J\mathbf{S}_1 \cdot \mathbf{S}_2 \qquad (4)$$

with

$$\mathcal{H}_i = \beta g \mathbf{H} \mathbf{S}_i + D_i [S_{iz}^2 - \tfrac{1}{3} S_i (S_i + 1)] \qquad (5)$$

This Hamiltonian leads to the following effective zero-field splitting parameters: $D(S) = -\frac{12}{5}D_i$, 0 and $\frac{2}{5}D_i$ for S $(= S_1 + S_2) = 1$, 2 and 3, respectively.[19] The accidentally degenerate quintet states (at zero field) are split only to second order via interaction between the components $S = 2$, $M_S = 0$ and $S = 0$, $M_S = 0$. For $J \gg D_i$, the component $S = 2$, $M_S = 0$ is shifted $4D_i^2/3J$ above the $M_S = \pm 1$ and $M_S = \pm 2$ components. Diagonalization of the 16×16 matrix shows that D $(= D_1 = D_2) \approx [g_\perp \beta (H_2^\perp - H_1^\perp) J]^{1/2}$ and $D \approx [\frac{3}{8} g_\parallel \beta (H_2^\parallel - H_1^\parallel) J]^{1/2}$ for perpendicular and parallel orientations, respectively, where H_1 and H_2 are the two field positions for each set of quintet lines observed.

In our case $4D^2/3J$ is 0.016 cm^{-1}, corresponding to $D_i = 1.20(3)$ cm^{-1}. This value is not far from the value of Kremer[18] for a related triol. In contrast to him we did not need to include new zero-field terms for the coupled spin states.

Other properties. Triol crystals large enough for collection of single-crystal X-ray diffraction data were obtained only as described in the Experimental. Reprecipitation with ions such as Br^-, I^-, ClO_4^- and $S_2O_6^{2-}$ resulted in powders because the procedure had to be completed within a few minutes at ca. 0 °C in order to give any precipitate at all. Elemental analysis of different samples of

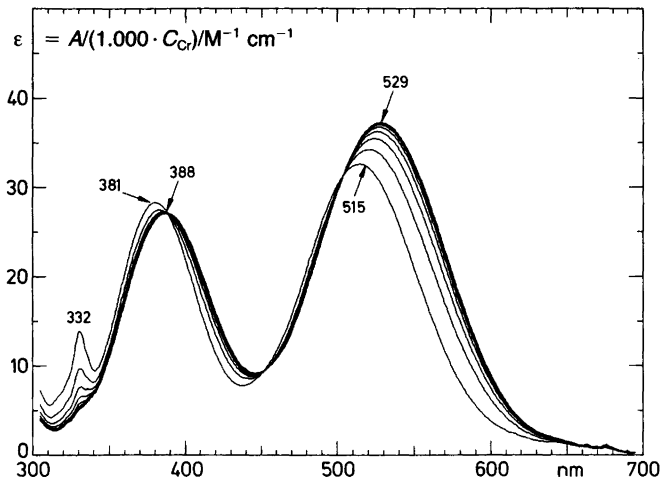

Fig. 5. Absorption spectra of $[(NH_3)_3Cr(OH)_3Cr(NH_3)_3](ClO_4)_{3-x}I_x$ in water (0.005 M) at 0.8 °C. The first spectrum (λ_{max} = 515, 381 and 332 nm) was measured 1 min after mixing, and the following seven spectra at 5 min intervals (480 nm per min).

the perchlorate precipitated from diol iodide solutions showed a content of iodide of around 5 % (*w*/w) and a water content of 0–1 molecules per triol molecule. The Guinier powder photographs of these $[(NH_3)_3Cr(OH)_3Cr(NH_3)](ClO_4)_{3-x}I_x$ ($x \approx 0.2$) samples were all identical, but different from that of the iodide, and were indexed in accordance with the single-crystal data.

Fig. 5 shows the spectral changes for an aqueous solution of the triol at 0.8 °C. The first and the last spectrum represent nearly pure triol and *cis*-aquahydroxo diol, respectively. The absorption spectrum of the triol shows similarities to those of other chromium(III) triols,[14] e.g. with respect to the characteristic narrow band at 332 nm. The half-life of the triol dissolved in water is 5–6 min at 0.8 °C and ca. 0.5 min at 25 °C.

Concluding remarks. We have for many years in vain tried to synthesize this ammonia triol of chromium(III). In an early work[20] we found some evidence for the existence of the triol in charcoal-catalyzed chromium(III) ammine solutions, but this evidence could just as well be interpreted in favour of the diol. The absorption spectra of those solutions show no content of the triol but are rather similar to those of the *trans*-diol. The relatively small changes in the spectra with pH – one of our arguments at that time in favour of the triol – are characteristic also for the *trans*-diol.[2]

We now know that the equilibrium between the ammonia diol and triol is strongly in favour of the diol, and that the conversion of the triol to the diol in solution is fast compared to other chromium(III) reactions. Only under favourable conditions is it possible to isolate the triol in the crystalline state from solutions containing a high concentration of the 3+ charged *cis*-diol but no spectrally detectable amounts of the triol. In addition, these chromium ammine complexes are inclined to lose ammonia in neutral or basic solution. These are probably the main reasons why this simple dinuclear complex, in contrast to the corresponding cobalt(III) complex, has remained undiscovered for so many years. The first chromium triol (with the tridentate ligand N,N′,N″-trimethyl-1,4,7-triazacyclononane) was discovered only a few years ago.[13]

The isolation of the ammonia triol has provided us with the possibility of studying the kinetic behaviour of all the dinuclear hydroxo-bridged *fac*-triamminechromium(III) complexes, including the monool and diol already available,[1] and this is being done parallel with a kinetic investigation of the corresponding 1,4,7-triazacyclononane system, where we have so far observed and isolated that *trans*- and *cis*-diol[1] without any sign of the monool or triol.

A recent determination[21] of the structure of the iodide of the *cis*-aquahydroxo diol with this nonane ligand has shown that this complex has the proposed structure[1] with an intramolecular hydrogen bond with a short terminal O-O distance (2.45 Å).

Acknowledgements. The authors are grateful to

Mr. Flemming Hansen for help with the experimental crystallographic work, and to K. Jørgensen and K. M. Nielsen for their contribution to the analytical and synthetic work. We thank the Danish Natural Science Research Council for grants (Nos. 11–1837, 511–15964 and 11–5962) towards the purchase of the X-ray diffractometer, the low temperature equipment and the UV/VIS spectrophotometer, respectively.

References

1. Andersen, P., Døssing, A. and Nielsen, K. M. *Acta Chem. Scand., Ser. A 40* (1986) 142.
2. Andersen, P., Nielsen, K. M. and Petersen, A. *Acta Chem. Scand., Ser. A 38* (1984) 593 and references therein.
3. Wieghardt, K. and Siebert, H. *Inorg. Synth. 23* (1985) 107.
4. Josephsen, J. and Pedersen, E. *Inorg. Chem. 16* (1977) 2534.
5. Coppens, P., Leiserowitz, L. and Rabinovich, D. *Acta Crystallogr. 18* (1965) 1035.
6. Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J. P. and Woolfson, M. M. *MULTAN-80: A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data.* The Universities of York, England and Louvain, Belgium 1980.
7. Rogers, D. *Acta Crystallogr., Sect. A 37* (1981) 734.
8. Frenz, B. A. *SDP. Users Guide,* Enraf-Nonius, Delft, The Netherlands 1982.
9. Cromer, D. T. and Mann, J. B. *Acta Crystallogr., Sect. A 24* (1968) 321.
10. Cromer, D. T. and Liberman, D. *J. Chem. Phys. 53* (1970) 1891.
11. Andersen, P. *Acta Chem. Scand. 21* (1967) 243.
12. Glerup, J., Kalsbeek, N. and Larsen, S. *To be published.*
13. Wieghardt, K., Chaudhuri, P., Nuber, B. and Weiss, J. *Inorg. Chem. 21* (1982) 3086.
14. Wieghardt, K., Guttmann, M. and Ventur, D. *Z. Anorg. Allg. Chem. 527* (1985) 33.
15. Thewalt, U. *Z. Anorg. Allg. Chem. 412* (1975) 29.
16. Bolster, D. E., Gütlich, P., Hatfield, W. E., Kremer, S., Müller, E. W. and Wieghardt, K. *Inorg. Chem. 22* (1983) 1725.
17. Riesen, H., Güdel, H. U., Chaudhuri, P. and Wieghardt, K. *Chem. Phys. Lett. 110* (1984) 552.
18. Kremer, S. *Inorg. Chem. 24* (1985) 887.
19. Owen, J. and Harris, E. A. In: Geschwind, S., Ed., *Electron Paramagnetic Resonance,* Plenum Press, New York 1972, Chap. 6.
20. Schäffer, C. E. and Andersen, P. *Proc. Symp. Theory and Structure of Complex Compounds, Wroclaw, Poland 1962,* Pergamon, Oxford 1964, p. 571.
21. Andersen, P., Døssing, A. and Larsen, S. *To be published.*
22. Johnson, C. K. *ORTEP: A Fortran Ellipsoid Plot Program for Crystal Structure Illustrations,* Report ORNL-3794, Second Rev., Oak Ridge National Laboratory, Oak Ridge, TN 1970.

Received April 15, 1987