

**The *trans*-Aqua-hydroxo-di- μ -hydroxo-bis-
[*fac*-triamminechromium(III)] Ion, *trans*-
[(H₂O)(NH₃)₃Cr(OH)₂Cr(NH₃)₃(OH)]³⁺, Formed by
Condensation of *fac*-Triamminetriaquachromium(III) Ions with
Base. Preparation, Characterization and X-Ray Structure
Analysis**

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trans-Aqua-hydroxo-di- μ -hydroxo-bis[*fac*-triamminechromium(III)] bromide dihydrate, *trans*-[(H₂O)(NH₃)₃Cr(OH)₂Cr(NH₃)₃(OH)]Br₃·2H₂O (I), was synthesized from *fac*-[Cr(NH₃)₃(H₂O)₃](ClO₄)₃ (II) by condensation in aqueous solution by addition of LiOH. II was synthesized from *fac*-Cr(NH₃)₃Cl₃ (III) by Hg(II)-assisted substitution of Cl⁻ with H₂O, and III was isolated from charcoal-catalyzed Cr(II)–NH₄⁺/NH₃ buffer solutions after spontaneous oxidation followed by saturation with gaseous HCl at 0 °C. The configuration of II was confirmed by its ESR spectrum (frozen glass).

The iodides of the protonated and deprotonated diol cation of I were isolated, and the two successive acid dissociation constants of the 4+-charged cation were determined by pH-titrations to be 10^{-6.0} and 10^{-7.5} M (25 °C, 1 M NaClO₄), respectively. Treatment of I with 12 M HClO₄ at 70–80 °C gave *fac*-[Cr(NH₃)₃(H₂O)₃]³⁺ quantitatively, whereas an equilibrium between the diol and the corresponding mono-ol (the mono- μ -hydroxy dimer) was established at higher pH (0–5, 25 °C) as judged from spectral and pH measurements.

The crystal structure of I was determined from X-ray diffraction on a single crystal. It crystallizes in the space group *P* $\bar{1}$ with *a*=8.836(3) Å,

b=9.314(3) Å, *c*=11.403(3) Å, α =88.10(2)°, β =96.81(2)°, γ =114.46(2)° and *Z*=2. Final refinement of 5405 diffractometer reflections (*ca.* –175 °C, MoK α radiation) led to *R*=0.048 and *R*_w=0.044. The crystals contain infinite chains of alternating *trans*-diaqua and *trans*-dihydroxo diol cations linked by short (2.45 Å) O···H–O bonds, where O are the non-bridging oxygen atoms of the two different cations both having a center of inversion.

In a recent work¹ we studied some polynuclear hydroxo-bridged chromium(III) amines obtained by charcoal/chromium(II) catalyzed reactions in aqueous NH₄⁺/NH₃ buffer solutions. Now we present the result of uncatalyzed, direct condensation of mononuclear chromium(III) amines.

The *fac*-[Cr(NH₃)₃(H₂O)₃](ClO₄)₃ seemed to be a promising starting material for such an investigation: it is very soluble in water and so are its deprotonized cations, a favourable condition for the formation of polynuclear species. Among these one might expect mono- μ -, di- μ - and maybe even the tri- μ -hydroxobridged complex, [(NH₃)₃Cr(OH)₃Cr(NH₃)₃]³⁺, with interesting magnetic properties, acid-base properties and

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reactions involving opening or formation of hydroxo bridges.

EXPERIMENTAL

Preparations. *fac*-[Cr(NH₃)₃Cl₃]. An ammine chromium(II) solution with charcoal was prepared under circumstances described elsewhere.¹ The amounts used were 15.6 g of >99.99 % pure chromium metal in 100 ml 8 M HCl; 250 ml 12 M NH₃, 230 g NH₄Cl, and 2 g charcoal in 400 ml water. The mixture was stored at room temperature for *ca.* 1 d without the admission of air, until the hydrogen evolution had ceased. Then the charcoal was filtered off. The filtrate was saturated at 0 °C with gaseous HCl, the NH₄Cl precipitate being filtered off once or twice during this procedure, and the solution was kept closed at 0 °C for *ca.* 1 week. The precipitate was filtered off, washed with 0.001 M HCl until the washings were colourless, then washed with ethanol and air-dried. The yield was somewhat varying: *ca.* 10 g of blue-gray [Cr(NH₃)₃Cl₃] (16 %), but some more could be obtained by repeating the HCl-treatment of the filtrate.

***fac*-[Cr(NH₃)₃(H₂O)₃](ClO₄)₃.** *Caution!* In the following procedure handling of the perchlorate and the 70 % HClO₄ must be done with caution:² larger amounts than prescribed should be avoided or prepared with the utmost care, avoid scraping with a glass rod against sintered glass, avoid (local) heat, and mixtures of organic solvents and 70 % HClO₄ should be diluted with water at once. We have not experienced explosions when these precautions are taken.

1.0 g of *fac*-[Cr(NH₃)₃Cl₃] (see above) was stirred under ice-cooling with 2.5 ml 3.5 M Hg(ClO₄)₂/0.5 M HClO₄ (*e.g.*, from HgO) until the dark colour from the chloro complex disappeared. The red mixture was now dissolved in 300 ml ice-cold water, and passed down a column (50 cm × 7 cm Ø) with 5 g of Sephadex SP-C25. It was washed free of mercury with 1 l ice-cold 0.01 M HCl and then free of chloride with 1.5 l ice-cold water. The resin was transferred to a 70 cm × 2.5 cm Ø column and eluted with ice-cold 2 M NaClO₄. To the more concentrated part of the red eluate (20–25 ml) was carefully added (under cooling) three times as much, by volume, of pre-cooled 70 % HClO₄, and the solution was kept for 30 min at 0 °C for precipitation. The red precipitate was filtered off, washed twice with 10 ml ice-cold 70 % HClO₄ and finally with ether until the washings were free of acid. Yield: 1.5 g (70 %) of *fac*-[Cr(NH₃)₃(H₂O)₃](ClO₄)₃.

[*(H₂O)*(NH₃)₃Cr(OH)₂Cr(NH₃)₃(OH)]Br₃ · 2H₂O (I). The condensation of *fac*-

[Cr(NH₃)₃(H₂O)₃](ClO₄)₃ (see above) in aqueous solution with LiOH were followed under varying conditions. The total chromium concentration was varied between 0.33 and 0.43 M, C_{LiOH} between 0.33 and 0.66 M, the time of reaction between 0.3 and 16 h, and 0 °C as well as 20 °C were tried. The products were separated on Sephadex SP-C25 after slight acidification with HClO₄ and dilution with water (*ca.* 0 °C). 0.7 M NaCl/0.001 M HCl was used as eluent and two or three well separated bands showed up: a first red band containing *fac*-[Cr(NH₃)₃(H₂O)₃]³⁺, a second red-violet containing the protonated cation of I, and under certain conditions a third band presumably containing polynuclear species of higher charge. From the chromium content of these bands the following procedure was chosen in order to give maximum yield of I:

4.4 g of *fac*-[Cr(NH₃)₃(H₂O)₃](ClO₄)₃ (10 mmol) were dissolved in 16 ml water at 0 °C and 8 ml 1.5 M LiOH were added within 5–10 min drop by drop under cooling and stirring. After 1 h at 0 °C the mixture was filtered, and within 5 min 16 g of NaI were added under continued cooling. After another hour at 0 °C the precipitate was filtered off, washed free of iodide with ethanol, washed twice with ether and air-dried. Yield: 1 g (32 %) of red-violet [(OH)(NH₃)₃Cr(OH)₂Cr(NH₃)₃(H₂O)]I₃ · aq. The product could be reprecipitated or recrystallized in a small yield (*ca.* 10 %) with 1.5 waters of crystallization.

A pure bromide was prepared by dissolving 150 mg of the crude iodide in 50 ml 0.05 M LiBr (0 °C). It was concentrated in a 1 cm layer of Sephadex SP-C25 in a 10 cm × 1 cm Ø column, which had in advance been eluted with 0.05 M LiBr. The resin was now washed with 5 ml 0.05 M LiBr and slowly eluted with 2 M LiBr (0 °C). The more concentrated part of the eluate was collected and cooled in ice, and after 15–20 min (scratching might be necessary) the crystals were filtered off, washed with ethanol and air-dried. Yield: 15 mg (13 %) of I (sometimes an anhydrous salt was produced. These crystals were more reddish than those of the dihydrate, with a different powder photograph, but with the same properties in aqueous solution). Bigger crystals were obtained, in smaller yields, by working at room temperature or by elution with 1 M LiBr. The whole procedure should be finished within *ca.* 15 min due to decomposition of the dissolved complex.

Iodides of the protonated and deprotonated cation of I. 750 mg of the crude iodide above were dissolved in 16 ml 0.1 M HClO₄ at 0 °C and 15 g NaI were added within a few minutes under continued ice-cooling. After 10–15 min at 0 °C

the precipitate was filtered off, washed free of NaI with very small portions of ethanol (the product is soluble in ethanol), and air-dried. Yield: 660 mg (70 %) of violet $[(\text{H}_2\text{O})(\text{NH}_3)_3\text{Cr}(\text{OH})_2\text{Cr}(\text{NH}_3)_3(\text{H}_2\text{O})]_4 \cdot 4\text{H}_2\text{O}$.

340 mg of the crude aqua hydroxo iodide above were dissolved in as little water as possible and 500 μl 2 M NH_3 were added, all at 0 °C. Solid NaI was now added until precipitation began (ca. 1 g), and after 5 min at 0 °C the precipitate was filtered off, washed with ethanol and ether, and air-dried. Yield: 200 mg (70 %) of violet $[(\text{OH})(\text{NH}_3)_3\text{Cr}(\text{OH})_2\text{Cr}(\text{NH}_3)_3(\text{OH})]_2 \cdot \text{H}_2\text{O}$.

Chemicals and chemical analysis. All chemicals were of reagent grade or of a similar or better

quality. The charcoal was a Norit W product. The prepared compounds were analyzed, most of them on a microscale (2–5 mg): chromium by atomic absorption spectrophotometry, nitrogen after Kjeldahl, and halides by potentiometry. The analyses were all, within 1–2 % relative, in accordance with the formulae given.

Hydrolysis of I with 70 % HClO_4 . Ca. 5 mg of I were treated with 70 % HClO_4 at 70–80 °C as described elsewhere,¹ and the ESR spectrum (see below) of the red product showed that it was *fac*- $[\text{Cr}(\text{NH}_3)_3(\text{H}_2\text{O})_3]^{3+}$.

ESR spectra of frozen glasses. The instrument used was a Jeol JES-ME-1X, and the glasses were made by mixing equal volumes of the aqueous solution and glycerol followed by immediate cooling to –130 °C to –150 °C, where the spectra (first derivative) were recorded at 9.2 GHz from 0 to 5 kG, see Fig. 1.

Optical absorption spectra were recorded with a Cary 118 spectrophotometer, see Table 1.

pH measurements. The instrument used was a Radiometer PHM 52 with a K 401 calomel electrode with 1.0 M NaCl in the salt bridge and with a G 403 B glass electrode adjusted with perchloric acid in 1.0 M NaClO_4 at 25 °C. Typical measurements were made with ca. 30 μmol of substance in 25 ml 1.0 M NaClO_4 thermostated at 25.0 °C with the addition of 1 M HClO_4 or 1 M NaOH from a microburette.

X-Ray diffraction; structure determination of I. Powder photographs were taken using a Guinier camera with $\text{CuK}\alpha$ radiation and with silicon as internal standard. Weissenberg photographs were taken for preliminary purposes, space group determination *etc.*

Single crystal data of I were collected on a Picker FACS-1 diffractometer at ca. 100 K. The

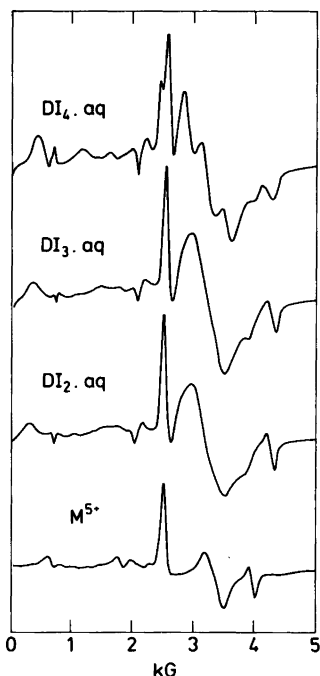


Fig. 1. First derivative ESR spectra at 9.2 GHz of frozen glasses (ca. –130 °C) of 50 % (v/v) glycerol/aqueous solution of the diols (iodides dissolved in water) and the mono-ol, M^{5+} (from D^{4+} in 4 M HClO_4 for 1 h at 25 °C followed by ion-exchange at 0–5 °C with 1 M HClO_4). The similarity between the spectra of $\text{DI}_3 \cdot \text{aq}$ and $\text{DI}_2 \cdot \text{aq}$ is probably due to a dramatic increase of the base strength of D^{2+} on cooling to –130 °C in the medium used. This phenomenon is also observed with other hydroxochromium(III) amines changing into the conjugated aqua ions on similar treatment, or with a μ -oxo changing into the μ -hydroxo compound.¹⁴

Table 1. Optical absorption spectra data for the diols (iodides dissolved in water), the mono-ol, M^{5+} (from D^{4+} in 4 M HClO_4 for 1 h at 25 °C followed by ion-exchange at 0–5 °C with 1 M HClO_4), and the *fac*- $[\text{Cr}(\text{NH}_3)_3(\text{H}_2\text{O})_3](\text{ClO}_4)_3$, *fac*, in 0.1 M HClO_4 . The first and the latter spectrum showed no changes after 5–10 min while the three others showed small changes, and for them the extrapolated values are given.

	$\lambda_{1\text{max}}/\text{nm}$	$\lambda_{2\text{max}}/\text{nm}$	ϵ_1/ϵ_2
$\text{DI}_4 \cdot \text{aq}$	544	387	1.5
$\text{DI}_3 \cdot \text{aq}$	540	400	1.4
$\text{DI}_2 \cdot \text{aq}$	540	405	1.1
M^{5+}	523	385	1.6
<i>fac</i>	512	375	1.6

Table 2. Crystal data for $[(\text{H}_2\text{O})(\text{NH}_3)_3\text{Cr}(\text{OH})_2\text{Cr}(\text{NH}_3)_3(\text{OH})]\text{Br}_3 \cdot 2\text{H}_2\text{O}$.

Molecular weight of $\text{Cr}_2\text{H}_{27}\text{N}_6\text{O}_6\text{Br}_3$: 551.0
Triclinic

ca. 100 K (diffractometer)

$a = 8.836(3) \text{ \AA}$ $\alpha = 88.10(2)^\circ$
 $b = 9.314(3) \text{ \AA}$ $\beta = 96.81(2)^\circ$
 $c = 11.403(3) \text{ \AA}$ $\gamma = 114.46(2)^\circ$
 $d_{\text{calc}} = 2.158 \text{ g/cm}^3$ for $Z=2$; $V = 848.1 \text{ \AA}^3$

Room temp. (Guinier)

$a = 8.889(2) \text{ \AA}$ $\alpha = 87.72(2)^\circ$
 $b = 9.381(2) \text{ \AA}$ $\beta = 97.11(1)^\circ$
 $c = 11.492(3) \text{ \AA}$ $\gamma = 114.59(1)^\circ$
 $d_{\text{calc}} = 2.117 \text{ g/cm}^3$ for $Z=2$
 $d_{\text{obs}} = 2.1 \text{ g/cm}^3$

$\mu(\text{MoK}\alpha) = 86.47 \text{ cm}^{-1}$, $F(000) = 540$

Space group: $P \bar{1}$ (No. 2)

Developed faces: $\{100\}$, $\{001\}$, $\{110\}$, $\{011\}$,
and $\{1\bar{1}0\}$.

instrument was equipped with a modified²² ENRAF-Nonius low-temperature device, and the variations of the temperature at 100 K were less than 1 K. Graphite-monochromated $\text{MoK}\alpha$ radiation was used. The crystal used had the dimensions $0.1 \times 0.1 \times 0.2 \text{ mm}^3$ in the a -, b - and c -direction, respectively. Some crystal data are given in Table 2 where the density of the crystals were determined by flotation in mixtures of 1-bromonaphthalene and 1,2-dibromoethane and the dimensions of the unit cell were determined on the diffractometer from 13 reflections by a least squares refinement and agree with those determined from room temperature powder photographs. A θ - 2θ scan mode was used with a rate of 1° min^{-1} in 2θ . The scan range was asymmetrical from $2\theta_0 - (0.7^\circ + 0.231^\circ \tan \theta)$ to $2\theta_0 + (1.1^\circ + 0.462^\circ \tan \theta)$ where $2\theta_0$ is the calculated peak position. Background counts were made for 20 s at each end of the scan range. Three standard reflections were measured after each 57 reflections showing no decay of the crystal.

Intensity data were collected with $3.6^\circ < 2\theta < 65^\circ$ and corrected for Lorentz and polarization effects, and a Gaussian numerical integration procedure³ was used for absorption corrections. This resulted in 6145 independent reflections. 5405 of these were classified as observed, using the criterion $I > 2\sigma(I)$, where $\sigma(I)$ is the standard deviation calculated by counting statistics. These 5405 reflections were used for the structure solution and refinements.

The following programs were used for computations: the Vanderbilt System⁴ for diffractometer operations, a data reduction program of local origin including absorption correction,³ ORTEP II⁵ for illustrations and the X-Ray System⁶ and MULTAN System⁷ for crystal structure analysis.

The atomic scattering factors used were those reported by Cromer and Mann⁸ for the uncharged atoms; for hydrogen the factor calculated by Stewart *et al.*⁹ was used. The anomalous dispersion correction for chromium and bromine were taken from Cromer and Liberman.¹⁰

Combination of the three-dimensional Patterson function and direct methods (MULTAN) gave the positions of the three bromine atoms and the two chromium atoms. Subsequent Fourier syntheses gave the positions of the ligand atoms, *i.e.* six nitrogen atoms and four oxygen atoms; two oxygen atoms from water of crystallization were found as well. The structure was refined by the method of least-squares minimizing $\sum w(|F_o| - |F_c|)^2$. After refinements of the positional and anisotropic thermal parameters for the above mentioned atoms the positions of the 27 hydrogen atoms in the structure were localized in a difference Fourier synthesis. At this stage a weighting scheme, $1/w = 3.0 \sigma^2(F) + 0.00090|F|^2$, was introduced and further refinements were carried out including the hydrogen atoms. First a refinement including the positional and isotropic thermal parameters for the hydrogen atoms was performed. In the final cycles of least-squares refinement the hydrogen atoms were given a restricted common isotropic thermal parameter equal to the average of the above obtained, $U = 0.05 \text{ \AA}^2$. This gave a final R -value of 0.048 and $R_w = 0.044$ (average shift/error: 0.03, max: 0.4). The results of this structure analysis are given in Tables 3 and 4 and Figs. 2 and 3. Lists of anisotropic thermal parameters and of observed and calculated structure amplitudes are available from the authors upon request.

RESULTS AND DISCUSSION

Mononuclear species. The mononuclear starting material, $[\text{Cr}(\text{NH}_3)_3(\text{H}_2\text{O})_3](\text{ClO}_4)_3$, contains the *facial* isomer judged from both ESR and kinetic studies. The ESR spectrum of the frozen glass¹ has a characteristic narrow transition at a field strength corresponding to $g=2$ as the main feature. This spectrum differs from those of all other mononuclear ammineaquachromium(III) complexes but is, as expected, almost identical to those of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ and $\text{Cr}(\text{NH}_3)_6^{3+}$ showing

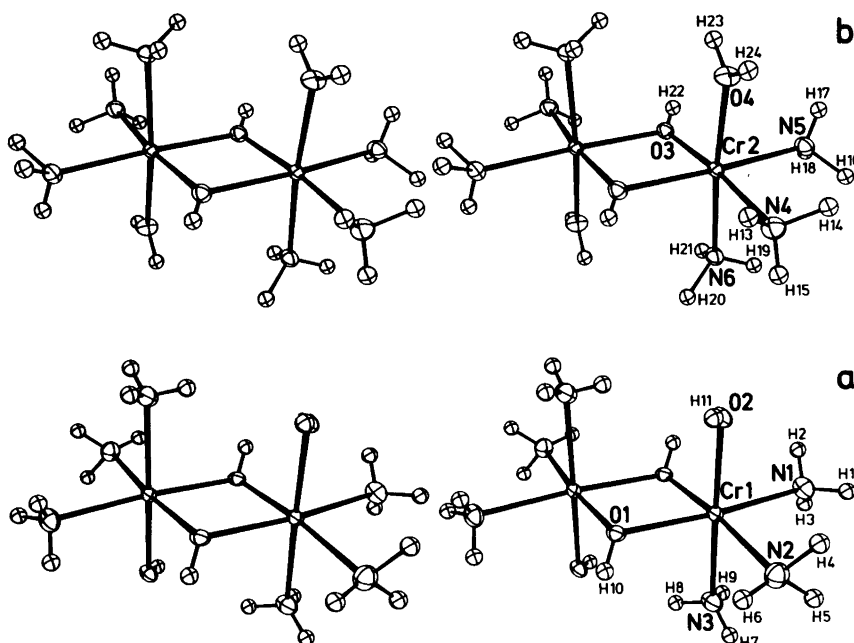


Fig. 2. Stereoscopic drawing of the two different centrosymmetric cations in *trans*- $[(\text{H}_2\text{O})(\text{NH}_3)_3\text{Cr}(\text{OH})_2\text{Cr}(\text{NH}_3)_3(\text{OH})]\text{Br}_3 \cdot 2\text{H}_2\text{O}$, i.e., the *trans*-dihydroxo (a) and the *trans*-diaqua diol (b). The thermal ellipsoids enclose 50 % probability with the exception of hydrogen atoms, which are shown as spheres with 0.15 Å radius.

nearly isotropic surroundings of chromium,¹ the holohedrized symmetry being O_h in all three cases. Kinetic studies of this triamminetriaqua ion show three kinetically equivalent water ligands¹¹ contrary to the two types of water

ligands in the triamminetriaqua isomer¹² obtained from $\text{Cr}(\text{NH}_3)_3(\text{O}_2)_2$ via trichloro or aquadichloro compounds.¹³

The ease with which the *fac*- $\text{Cr}(\text{NH}_3)_3\text{Cl}_3$ is isolated from the charcoal-catalyzed mixture is probably due to the presence of polynuclear species with 3 NH_3 in a *facial* configuration¹ combined with its low solubility in water compared to most other chloro- and aquachlorochromium(III) amines. From earlier works¹ we experienced that treatment of polynuclear chromium(III) amines with concentrated hydrochloric acid quantitatively gave the mononuclear constituents with retention of the configuration with respect to NH_3 . The reason why we call this $\text{Cr}(\text{NH}_3)_3\text{Cl}_3$ *facial* is based on the fact that the $\text{Hg}(\text{II})$ - or $\text{Ag}(\text{I})$ -assisted substitution of Cl^- by H_2O gives pure *fac*- $\text{Cr}(\text{NH}_3)_3(\text{H}_2\text{O})_3^{3+}$ (as judged from the ESR and visible spectrum), while the $\text{Cr}(\text{NH}_3)_3\text{Cl}_3$ obtained from $\text{Cr}(\text{NH}_3)_3(\text{O}_2)_2$ gives the *mer*- $\text{Cr}(\text{NH}_3)_3(\text{H}_2\text{O})_3^{3+}$ by a similar treatment. A further argument is that the frozen glass ESR spectrum (ca. -130°C) of the *fac*- $\text{Cr}(\text{NH}_3)_3\text{Cl}_3$ dissolved in *N*-methylform-

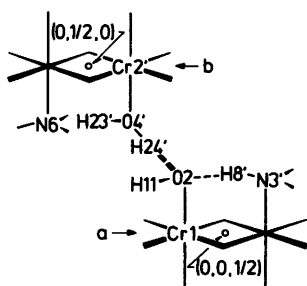


Fig. 3. Illustration of the short hydrogen bond (2.45 Å) between the two independent cations in $\text{DBr}_3 \cdot 2\text{H}_2\text{O}$ resulting in infinite chains of alternating *trans*-dihydroxo (a) and *trans*-diaqua diols (b). ' refers to atoms whose positions are centrosymmetrically related to those given in Table 3; the respective symmetry centers are marked by \circ together with their coordinates.

Table 3. $[(\text{H}_2\text{O})(\text{NH}_3)_3\text{Cr}(\text{OH})_2\text{Cr}(\text{NH}_3)_3(\text{OH})]\text{Br}_3 \cdot 2\text{H}_2\text{O}$. Final fractional coordinates and thermal parameters with e.s.d. The expression for the temperature factors are $\exp\{-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{23}klb^*c^*)\}$. $U_{\text{eq}} = (U_{11}a^{*2}a^2 + \dots + 2U_{23}b^*c^*bc \cos \alpha)/3$. The labeling of the atoms in the cations is explained in Fig. 2.

Atom	x	y	z	$100 \times U_{\text{eq}}$
Br1	0.26808(5)	0.71813(5)	0.51585(4)	1.59(2)
Br2	0.50781(5)	0.54745(5)	0.25006(4)	1.59(2)
Br3	0.33996(6)	0.11292(6)	0.01153(4)	2.41(2)
Cr1	0.14978(8)	0.11564(7)	0.44818(6)	1.09(3)
Cr2	0.08328(8)	0.54417(7)	-0.11112(5)	0.96(3)
O1	0.0121(3)	-0.1126(3)	0.4452(3)	1.21(14)
O2	0.0136(4)	0.1385(4)	0.3036(3)	1.43(14)
O3	-0.0805(4)	0.3615(4)	-0.0396(3)	1.30(14)
O4	-0.0815(4)	0.6138(4)	-0.1970(3)	1.51(14)
O5	0.0053(5)	0.0923(4)	0.8492(3)	2.43(18)
O6	0.6406(4)	0.1707(5)	0.8095(3)	2.88(19)
N1	0.2726(5)	0.3574(5)	0.4635(3)	1.71(19)
N2	0.3215(5)	0.1006(5)	0.3429(4)	1.77(18)
N3	0.3000(5)	0.0924(5)	0.5965(4)	1.85(19)
N4	0.2644(5)	0.7510(5)	-0.1700(3)	1.67(18)
N5	0.0681(5)	0.4137(4)	-0.2604(3)	1.56(17)
N6	0.2711(5)	0.4812(5)	-0.0337(3)	1.50(18)
H1	0.346(8)	0.400(7)	0.406(6)	
H2	0.200(8)	0.390(8)	0.454(6)	
H3	0.307(9)	0.379(8)	0.512(6)	
H4	0.329(8)	0.157(8)	0.268(6)	
H5	0.417(8)	0.167(8)	0.371(6)	
H6	0.296(8)	0.009(8)	0.337(6)	
H7	0.381(8)	0.083(8)	0.579(6)	
H8	0.239(8)	0.033(8)	0.647(6)	
H9	0.314(8)	0.153(8)	0.644(6)	
H10	0.052(8)	-0.162(8)	0.467(6)	
H11	0.007(8)	0.089(8)	0.259(6)	
H13	0.238(8)	0.833(8)	-0.151(6)	
H14	0.253(8)	0.742(7)	-0.255(6)	
H15	0.360(8)	0.776(8)	-0.149(6)	
H16	0.172(8)	0.464(7)	-0.303(5)	
H17	-0.002(8)	0.421(8)	-0.309(6)	
H18	0.058(7)	0.271(7)	-0.257(5)	
H19	0.319(8)	0.461(8)	-0.089(6)	
H20	0.353(8)	0.578(8)	0.028(5)	
H21	0.244(8)	0.411(8)	-0.007(6)	
H22	-0.136(8)	0.334(9)	-0.069(6)	
H23	-0.181(8)	0.553(8)	-0.120(5)	
H24	-0.046(8)	0.722(8)	-0.232(5)	
H25	0.087(8)	0.092(8)	0.891(6)	
H26	-0.088(8)	0.057(8)	0.896(6)	
H27	0.587(8)	0.237(8)	0.803(6)	
H28	0.598(8)	0.103(8)	0.864(6)	

amide is similar to the above mentioned nearly isotropic spectra.¹⁴

The diol. The *trans*-aqua-hydroxo-di- μ -hydroxo-bis[*fac*-triamminechromium(III)] ion, *trans*-

$[(\text{H}_2\text{O})(\text{NH}_3)_3\text{Cr}(\text{OH})_2\text{Cr}(\text{NH}_3)_3(\text{OH})]^{3+}$ is the main product (30–35 %) from condensation of *fac*-triamminechromium(III) under the conditions described in the experimental section.

Table 4. $[(\text{H}_2\text{O})(\text{NH}_3)_3\text{Cr}(\text{OH})_2\text{Cr}(\text{NH}_3)_3(\text{OH})]\text{Br}_3 \cdot 2\text{H}_2\text{O}$. Selected bond lengths (Å), contact distances (Å), and bond angles (°) with e.s.d.

Cr1–O1	1.963(3)	Cr2–O3	1.950(3)
Cr1–O1'	1.975(3)	Cr2–O3'	1.964(3)
Cr1–O2	1.983(3)	Cr2–O4	1.975(4)
Cr1–N1	2.058(4)	Cr2–N4	2.083(4)
Cr1–N2	2.093(5)	Cr2–N5	2.083(4)
Cr1–N3	2.086(4)	Cr2–N6	2.074(5)
O1–H10	0.71(8)	O3–H22	0.53(6)
O2–H11	0.68(7)	O4–H23	0.82(6)
		O4–H24	1.01(7)
N–H average	0.88(7)	O5/O6–H average	0.90(7)
O4–O2	2.450(5)	Br–O	3.3–3.4
O2–O5	2.750(4)	Br–N	3.4–3.6
O3–O6	2.786(4)		
N3–O2	3.042(6)		
N5–O5	3.062(6)		
Cr1–O1–Cr1'	98.46(16)	Cr2–O3–Cr2'	100.15(14)
O1–Cr1–O1'	81.54(13)	O3–Cr2–O3'	79.85(13)
O1–Cr1–O2	90.16(12)	O3'–Cr2–O4	93.51(15)
O1'–Cr1–O2	94.03(14)	O3–Cr2–O4	95.75(14)
O1–Cr1–N2	94.54(15)	O3'–Cr2–N4	94.21(15)
O1–Cr1–N3	90.33(14)	O3'–Cr2–N6	89.88(16)
O1'–Cr1–N1	91.31(16)	O3–Cr2–N5	92.32(14)
O1'–Cr1–N3	88.08(16)	O3–Cr2–N6	89.15(15)
O2–Cr1–N1	89.61(15)	O4–Cr2–N5	89.02(16)
O2–Cr1–N2	89.36(16)	O4–Cr2–N4	85.82(15)
N1–Cr1–N2	92.64(17)	N4–Cr2–N5	93.58(15)
N1–Cr1–N3	90.16(16)	N5–Cr2–N6	88.21(17)
N2–Cr1–N3	88.55(18)	N4–Cr2–N6	89.57(16)
O1–Cr1–N1	172.8(2)	O3'–Cr2–N5	171.97(17)
O1'–Cr1–N2	174.8(3)	O3–Cr2–N4	173.9(3)
O2–Cr1–N3	177.9(6)	O4–Cr2–N6	174.46(19)
Cr1–O1–H10	117(4)	Cr2–O3–H22	111(7)
Cr1'–O1–H10	110(6)	Cr2'–O3–H22	121(9)
Angle between O1–H10 and plane O1–Cr1–Cr1'		52(5)	
Angle between O3–H22 and plane O3–Cr2–Cr2'		46(8)	

“*trans*” is used here as a modification of the term used with mononuclear complexes, since there is no simple way of expressing this part of the configuration in this dinuclear ion. Disregarding the configuration of the terminal hydroxo and aqua group the ion might be characterized more precisely as the di- μ -hydroxo- $\{fac\}$ -[triammine-aquachromium(III)] $\{fac\}$ -[triamminehydroxochromium(III)] ion. This dinuclear diol ion is below called D^{3+} and its corresponding protonated and deprotonated forms D^{4+} and D^{2+} , respectively.

The configuration of these ions was found from

the X-ray structure analysis of $\text{DBr}_3 \cdot 2\text{H}_2\text{O}$ described below. However, some conclusions on the nature of the condensation product could be drawn from other observations.

Treatment of $\text{DBr}_3 \cdot 2\text{H}_2\text{O}$ with 70 % HClO_4 gave *fac*- $[\text{Cr}(\text{NH}_3)_3(\text{H}_2\text{O})_3]^{3+}$ quantitatively and the rate with which the polynuclear complex was eluted on Sephadex SP-C25 with 0.7 M NaCl/0.001 M HCl indicated a charge less than 5+, when compared with other similar separations.^{1,15} Titration of $\text{DI}_3 \cdot 1.5 \text{H}_2\text{O}$ with HClO_4 or NaOH showed that it could take up as well as give off a proton with the two acid dissociation

constants $K_{D1}=10^{-6.0}$ and $K_{D2}=10^{-7.5}$ M, respectively (1.0 M NaClO₄, 25.0 °C). The isolation of the iodides of D⁴⁺ and of D²⁺ and titration of them confirmed this.

Of the three possible dimers with 3 NH₃ on each chromium atom, Cr(OH)₃Cr³⁺, (H₂O)Cr(OH)₂Cr(OH)³⁺ and (OH)(H₂O)Cr(OH)Cr(H₂O)(OH)³⁺ (omitting NH₃), there seemed no doubt that we were dealing with the diol. As discussed below we observed an equilibrium between the diol and the mono-ol, but we never observed the triol. One reason for this might be that the diol was the *trans*-aquahydroxo isomer, and this was confirmed by the X-ray structure analysis of DBr₃·2H₂O.

X-Ray investigation. This analysis showed that there are two different complex molecules, *a* and *b*, in the unit cell, each situated at a center of inversion. The two ions are shown in Fig. 2. They are linked together through a very short hydrogen bond O2...H24'-O4' of 2.450 Å. The difference Fourier (not including hydrogen atoms) showed one peak on the line between O2 and O4' *ca.* 1.0 Å from O4', and the final least-squares refinement placed H24, within the experimental uncertainty, on this line with the distances O4'-H24'=1.01(7) Å and O2-H24'=1.45(7) Å.

In the ion *a* (Figs. 2a and 3) the non-bridging oxygen atom, O2, is tetrahedrally surrounded by Cr1, H11, H24' and by H8' from the N3' ammonia ligand having N3'-O2=3.042 Å with H8' pointing towards O2. In the ion *b* (Figs. 2b and 3), however, the non-bridging oxygen atom, O4', has approximately planar surroundings of Cr2', H23', and H24', and the corresponding ammonia ligand (N6) has no hydrogen atom pointing towards O4' (N6-O4'=3.189 Å).

According to these observations, as outlined in Fig. 3, DBr₃·2H₂O is built of infinite hydrogen-bonded chains of alternating *trans*-dihydroxo D²⁺ (ion *a* with Cr1) and *trans*-diaqua D⁴⁺ (ion *b* with Cr2). This is not unreasonable in view of the relatively small difference between pK_{D1} and pK_{D2}. The Cr1-O2 distance is, however, not significantly different from the Cr2-O4 distance unlike what is found in other aquahydroxochromium(III) complexes,²³ and considering the short hydrogen bond and the uncertainty on the position of H24 it is doubtful whether H24 should be regarded as "belonging" to only one of the complex ions.

Bond distances and angles are otherwise in agreement with those of related compounds,¹⁶ and a selection is given in Table 4 together with some contact distances. In addition to these, the structure is characterized by a three-dimensional network of Br-N (*ca.* 3.5 Å) and Br-O (*ca.* 3.4 Å) contacts.

The mono-ol. From the pH-measurements and the behaviour of the optical spectra with time in the pH range 0-5 (25 °C, 1 M HClO₄/NaClO₄) it appeared that the D⁴⁺ and D³⁺ ions are not the only polynuclear chromium species present when starting with DBr₃·2H₂O. For example, solutions of DBr₃·2H₂O at pH=5 grew more acidic, ending with pH≈4 after *ca.* 1 h, and the visible spectrum at pH=0 changed within a few hours into another, showing isobestic points. The reverse reaction was observed if a 4 M HClO₄ solution of DBr₃·2H₂O after 1 h was diluted to be 1 M in HClO₄. Separations at 0 °C of such solutions on Sephadex SP-C25 with 0.5-1.0 M HClO₄ showed two bands, namely a violet one containing the D⁴⁺ ion followed by a red band containing probably the mono-ol ion [(H₂O)₂-(NH₃)₃Cr(OH)Cr(NH₃)₃(H₂O)₂]⁵⁺ (M⁵⁺). Spectral data and ESR spectra of some of the complex ions mentioned in this section are given in Table 1 and Fig. 1, respectively.

In the 4 M HClO₄ solution mentioned above the product is nearly 100 % M⁵⁺ whereas the product from a 0.01 M HClO₄ solution is nearly 100 % D⁴⁺.

We are at present investigating these reactions between Dⁿ⁺ and M^{m+} where one difficulty is that we so far have not been able to isolate salts of the mono-ol ion, and another difficulty is the loss of ammonia at higher pH (>*ca.* 5), a difficulty which Schwarzenbach *et al.* also met in their investigation of the analogous triamminecobalt(III) system.¹⁷

Springborg *et al.* have successfully studied such chromium(III) diol/mono-ol reactions with *e.g.* the [(NH₃)₄Cr(OH)₂Cr(NH₃)₄]⁴⁺ ion,¹⁸ and their conclusions concerning the low pK_a of their diaqua mono-ol as a result of the formation of an intramolecular hydrogen bond between the terminal OH and H₂O in the conjugate base explain the pH-changes observed in our system. Such a hydrogen bridge has recently been demonstrated by a single crystal X-ray diffraction structure analysis of [(H₂O)_{en}2Ir(OH)-Iren₂(OH)]₂-(S₂O₆)₃(ClO₄)₂·aq.¹⁹

The triol. During this work we have not observed any signs of the presence of the triol, $(\text{NH}_3)_3\text{Cr}(\text{OH})_3\text{Cr}(\text{NH}_3)_3^{3+}$. Chromium(III) seems to have a general difficulty in forming triol dimers (contrary to cobalt(III)). This was also observed by, e.g., Wieghardt *et al.*²⁰ who in similar experiments using the tridentate ligand 1,4,7-triazacyclononane likewise isolated the *trans*-diaqua diol and a trinuclear complex, but no triol. However, with the corresponding 1,4,7-trimethylated ligand Wieghardt *et al.*²¹ isolated the first well-described chromium(III) triol and associated its stability with the steric hindrance for the formation of the *trans*-diaqua complex with this ligand.

In an early work²⁴ we argued for the existence of the ammonia triol in solutions with a high content of polynuclear chromium(III) amines, obtained by charcoal-catalyzed oxidation of $\text{Cr}(\text{II})\text{-NH}_3/\text{NH}_4\text{Cl}$ solutions with $C_{\text{NH}_3} \approx 3$ M (this early work is the basis for the synthesis of *fac*- $\text{Cr}(\text{NH}_3)_3\text{Cl}_3$ presented above). One of the arguments was the small spectral changes of such solutions by adding acid. However, with our present knowledge (the immediate spectral change of I on adding acid is rather small too, see Table 1) we might have overestimated the content of triol in such solutions. An analysis of these solutions with to-day's techniques¹ might give the answer.

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