

# Hydrolytic Properties of the Triaqua[*N,N',N''*-trimethyl-1,1,1-tris(aminomethyl)ethane]chromium(III) Ion, $[\text{Cr}(\text{Me}_3\text{-tame})(\text{H}_2\text{O})_3]^{3+}$ . Crystal Structure of $[(\text{Me}_3\text{-tame})\text{Cr}(\text{H}_3\text{O}_2)_3\text{Cr}(\text{Me}_3\text{-tame})](\text{CF}_3\text{SO}_3)_3$ with Three Short Hydrogen Bonds Connecting the Two Mononuclear Units

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Treatment of the triaqua[*N,N',N''*-trimethyl-1,1,1-tris(aminomethyl)ethane]chromium(III) ion,  $[\text{Cr}(\text{Me}_3\text{-tame})(\text{H}_2\text{O})_3]^{3+}$  (**1**), with basic triflate solution produces a salt containing equal amounts of the singly and doubly deprotonated monomer complex. The salt can be formulated as  $[(\text{Me}_3\text{-tame})\text{Cr}(\text{H}_3\text{O}_2)_3\text{Cr}(\text{Me}_3\text{-tame})](\text{CF}_3\text{SO}_3)_3$  (**2**) with three short hydrogen bonds connecting the two mononuclear units.

This has been confirmed by a single-crystal X-ray structure determination. Compound **2** crystallizes in the space group *R*32 with  $a = b = 9.031(2)$ ,  $c = 41.079(8)$  Å and  $Z = 3$ . Using 4006 independent reflections the structure was refined to  $R(\text{obs}) = 0.036$  and  $R_w(\text{all}) = 0.10$ .

The cation pair in **2** has  $D_3$  site symmetry. The HO—H—OH hydrogen bonds have O—O distances equal to 2.429(2) Å. When heated to 135°C for ca. 2 h **2** loses three water molecules to form the racemic trihydroxo-bridged dimer (**3**).

The acid dissociation constants of **1** have been determined. Aqueous solutions (25°C) of **2** within a few weeks reach equilibrium with major amounts of **3** and the corresponding *meso*-isomer and minor amounts of the mono- and dihydroxo-bridged dimers.

The triaqua complex (**1**) of chromium(III) with the facially coordinating tridentate ligand *N,N',N''*-trimethyl-1,1,1-tris(aminomethyl)ethane ( $\text{Me}_3\text{-tame}$ ) has the property that it easily condenses to the trihydroxo-bridged dimer when deprotonated in aqueous solution. This has been demonstrated by Glerup and Weihe, who have investigated the magnetic and ESR spectral properties of this dimer and determined the crystal structure of the chloride.<sup>1</sup>

During studies<sup>2</sup> of the equilibria between these species we isolated a salt that contains equal amounts of the singly and doubly deprotonated monomer complex. The salt can be formulated as  $[(\text{Me}_3\text{-tame})\text{Cr}(\text{H}_3\text{O}_2)_3\text{Cr}(\text{Me}_3\text{-tame})](\text{CF}_3\text{SO}_3)_3$  (**2**) with three short hydrogen

bonds between the two mononuclear units. When heated to 135°C for ca. 2 h it loses three water molecules per two chromium atoms to give an isomer (**3**) of the trihydroxo-bridged dimer. In the following we present the crystal structure of **2** and deal with some of the hydrolytic properties of this complex.

## Experimental

**Chemicals and chemical analysis.** The chemicals were of reagent grade or of a better quality. The synthesized compounds were analyzed for Cr, C, H, N and S, and were within 1–2% in accordance with the given formulae.

**Apparatus.** Visible absorption spectra were recorded on a Perkin-Elmer Lambda 17 or Lambda 2 spectrophotometer with automatic disk data collection.  $[\text{H}^+]$  was

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measured as described elsewhere<sup>3</sup> in 1.0 M NaBr at 25°C. The titrations for the determination of the acid dissociation constants were performed from the acidic as well as the basic side. Thermogravimetry was performed on the thermobalance described by Pedersen.<sup>4</sup> The X-ray equipment is described in the X-ray section.

### Syntheses

*Me<sub>3</sub>-tame*, *Cr(Me<sub>3</sub>-tame)Cl<sub>3</sub>* and meso-[(*Me<sub>3</sub>-tame*)-*Cr(OH)<sub>3</sub>Cr(Me<sub>3</sub>-tame)*] salts. These compounds were synthesized as described elsewhere.<sup>1</sup>

[(*Cr(Me<sub>3</sub>-tame)(H<sub>2</sub>O)<sub>3</sub>*)](*CF<sub>3</sub>SO<sub>3</sub>*)<sub>3</sub> (**1**). 70 ml of *CF<sub>3</sub>SO<sub>3</sub>H* (0°C) were added dropwise under ice cooling to 20 g of *Cr(Me<sub>3</sub>-tame)Cl<sub>3</sub>* (63 mmol), after which the solution was kept at 60°C for 2 h in a flask stoppered with a *CaCl<sub>2</sub>* tube. The dark-violet solution was then cooled with ice and very slowly added to ca. 1.5 l diethyl ether under vigorous stirring (to avoid the formation of an oil). The red-violet precipitate was filtered off and washed with diethyl ether. The crude product of *Cr(Me<sub>3</sub>-tame)(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>* was kept for further use in a desiccator over *CaCl<sub>2</sub>*. Yield: 39.4 g (95%).

16.5 g of this product (25 mmol) were suspended in 400 ml of acetone. 2.5 ml of 1 M *CF<sub>3</sub>SO<sub>3</sub>H* were added and the suspension was stirred at room temperature for ca. 2 days, until the violet colour of the triflate complex had disappeared and the solution become red and clear. The solution was filtered and transferred to a beaker, which was covered with a watch glass. When the acetone had evaporated the moist red product was transferred to a glass filter where it was washed with diethyl ether until the washings were colourless. The product was dried over *CaCl<sub>2</sub>*. Yield: 15.1 g of **1** (85%).

[(*Me<sub>3</sub>-tame*)-*Cr(H<sub>3</sub>O<sub>2</sub>)<sub>3</sub>Cr(Me<sub>3</sub>-tame)*](*CF<sub>3</sub>SO<sub>3</sub>*)<sub>3</sub> (**2**). 3.0 g of **1** (4.2 mmol) were dissolved in 3.0 ml of water at 0°C. Ca. 0.50 ml of 12 M *NH<sub>3</sub>* (0°C) was added under stirring until pH 7.3. The solution was kept at 0°C for 10 min for crystallization, but no longer, as this will produce [(*Me<sub>3</sub>-tame*)-*Cr(OH)<sub>3</sub>Cr(Me<sub>3</sub>-tame)*]<sup>3+</sup>. The purple precipitate was filtered off, washed with a solution of 15 g of *NaO<sub>3</sub>SCF<sub>3</sub>* in 100 ml of abs. ethanol until the washings were colourless, then with abs. ethanol and diethyl ether and finally air-dried. Yield: 1.46 g of **2** (75%).

The product could be reprecipitated as follows: 900 mg of **2** were dissolved in 8 ml of water at 0°C. 1.5 g of *NaO<sub>3</sub>SCF<sub>3</sub>* were added, and the purple crystals were collected after 10 min as described above. Yield: 660 mg (73%).

Crystals suitable for single-crystal X-ray diffraction were made as follows: 200 mg of reprecipitated **2** were dissolved in 2 ml of water at 0°C. The solution was filtered and carefully put on top of a 0°C saturated solution of *NaO<sub>3</sub>SCF<sub>3</sub>* (ca. 2 ml) without mixing the two layers.

After 1/2 h the crystals in the interface were collected carefully as described above.

[(*Me<sub>3</sub>-tame*)-*Cr(OH)<sub>3</sub>Cr(Me<sub>3</sub>-tame)*](*CF<sub>3</sub>SO<sub>3</sub>*)<sub>3</sub>·3*H<sub>2</sub>O* (*racemate*) (**3**). 5.0 g of crude **2** (5.1 mmol) were placed in a open glass tube in an oven for 2 h at 135°C. Then the glass tube was stoppered and the red anhydrous product cooled to room temperature. This anhydrous product could be reprecipitated as a trihydrate, **3**, as follows: 400 mg of the product were dissolved in 4 ml of water at 0°C. The solution was filtered and 3.5 ml of a 0°C solution of 10 g of *NaO<sub>3</sub>SCF<sub>3</sub>* in 10 ml of water were added. After 5 min the red precipitate was filtered off and washed with diethyl ether and air-dried. Yield: 290 mg of **3** (73%).

### X-Ray crystallography

*Characterization.* Compound **2**, [(*Me<sub>3</sub>-tame*)-*Cr(H<sub>3</sub>O<sub>2</sub>)<sub>3</sub>Cr(Me<sub>3</sub>-tame)*](*CF<sub>3</sub>SO<sub>3</sub>*)<sub>3</sub>, crystallizes as purple hexagonal plates. They were characterized by precession photographs taken with Ni-filtered *CuKα* radiation and by powder diffraction: the latter diagrams were taken with a Guinier-Hägg powder camera using *CuKα* radiation and silicon as an internal standard. These photographs could be indexed according to a rhombohedral cell with the condition for reflections  $-h+k+l=3n$ . No other systematic absences were observed.

The density of the crystals were measured by flotation in a mixture of bromobenzene and tribromomethane. This measurement, combined with the volume of the unit cell, gave  $Z=3$ . The precession photographs showed the Laue symmetry  $\bar{3}m$ . The crystal data are presented in Table 1.

*Data collection and reduction.* A single crystal of the approximate dimensions  $0.45 \times 0.24 \times 0.16$  mm<sup>3</sup> and bound by the faces (100), (001), (00 $\bar{1}$ ), (010), (1 $\bar{1}$ 0), ( $\bar{1}$ 10) and ( $\bar{1}$ 50) was selected for the data collection. Attempts to cool the crystal to 122 K resulted in a phase transition, and the data were collected at the ambient temperature, 22°C.

A CAD4 diffractometer and graphite-monochromated *MoKα* radiation was used. The unit-cell parameters and orientation matrix were determined from a least-squares refinement of the setting angles of 20 reflections with  $\theta$  in the range 15.7–18.2°. Based on analysis of reflection profiles the  $\omega/2\theta$  scan mode and scan range,  $\Delta\omega = 1.2^\circ + 0.35^\circ \tan \theta$ , were selected. The intensities of three standard reflections were measured every 10000 s, and the orientation of the crystal was checked after every 300 reflections. These repeated measurements did not show any systematic variations. Data reduction, which was performed with the DREADD programs,<sup>5</sup> included corrections for Lorentz, polarization and background effects.

*Structure determination and refinement.* The presence of only three formula units in the unit cell and the knowl-

Table 1. Crystal data and a summary of data collection and refinement results for [(Me<sub>3</sub>-tame)Cr(H<sub>3</sub>O<sub>2</sub>)<sub>3</sub>Cr(Me<sub>3</sub>-tame)]-(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>.

Formula	Cr <sub>2</sub> C <sub>19</sub> F <sub>9</sub> H <sub>51</sub> O <sub>15</sub> S <sub>3</sub> N <sub>6</sub>	
FW/g mol <sup>-1</sup>	974.82	
Space group	R32 (No. 155)	
Cell parameters (295 K, single crystal and powder, respectively):		
Radiation	MoKα	CuKα
$a = b/\text{Å}$	9.031 (2)	9.029 (3)
$c/\text{Å}$	41.079 (8)	41.049 (18)
$V/\text{Å}^3$	2901.8 (11)	2898.2 (14)
Calculated density (295 K)/g cm <sup>-3</sup>	1.676	
Observed density (295 K)/g cm <sup>-3</sup>	1.68	
Molecules per cell, Z	3	
Data collection and SHELXL92 refinement:		
Crystal size/mm <sup>3</sup>	0.45 × 0.24 × 0.16	
Radiation (MoKα) λ/Å	0.710 73	
Linear absorption coefficient, μ/cm <sup>-1</sup>	8.11	
θ limits/°	1–40	
Octants collected	±h k ±l	
No. of measurements	12499	
No. of independent measurements	4006 with $I > 3.0\sigma(I)$	
Internal R-value	0.036	
No. of parameters	104	
Weights	$w^{-1} = \sigma^2( F ^2) + 0.0584P^2$ where $P = \{ F_o ^2 + 2 F_c ^2\}/3$	
Flack parameter	0.49 (2)	
$R^a$ (obs)	0.036	
$R_w^b$ (all)	0.10	
$S_{\text{all}}$	0.972	
(Shift/error) <sub>max</sub>	–0.001	
$\Delta\rho_{\text{max}}/e \text{ Å}^{-3}$	0.88	
$\Delta\rho_{\text{min}}/e \text{ Å}^{-3}$	–0.35	

<sup>a</sup> $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$  calculated for reflections with  $I > 3.0\sigma(I)$ . <sup>b</sup> $R_w = [\Sigma w(|F_o|^2 - |F_c|^2)|\Sigma|F_o|^2]^{1/2}$ .

edge of the possible symmetries of the complex cations restricted the possible space groups to *R*32 and *R*3. The two other space groups, *R*3̄ and *R*3*m*, would impose unrealistic symmetry restraints on the cations. Though the Laue symmetry indicated that the space group is *R*32, initial refinements were started in *R*3, as the structure could be described without any disorder in this space group, e.g. the complex cation on a three-fold axis and the anion in a general position.

The Patterson function provided the positions for the two chromium atoms and two of the three sulfur atoms of the anions. They were all found on the three-fold axis. From subsequent refinements and difference Fourier calculations the remaining non-hydrogen atoms were located except those of the last triflate ion.

Analysis of the structure showed that a two-fold axis relates the two halves of the cation pair and the two triflate ions on the three-fold axis. The difference Fourier showed density corresponding to the third triflate ion in a plane perpendicular to the *c*-axis between the other two triflate ions. This structure is in agreement with the apparent Laue symmetry 3̄*m*. It turned out to be impossible to describe the third triflate ion with a simple model, and further refinements of the structure were continued in the space group *R*32. Anisotropic displace-

ment parameters were gradually introduced for all the non-hydrogen atoms.

The difference Fourier showed that the third triflate ion is located around the two-fold special axis position (*x*, 0, ½) with Wyckoff notation *e* and a multiplicity 1/9. The crystallographic symmetry implies a heavy disorder of this anion with the S and C atoms overlapping. Several models were employed to describe this disorder, including one with a mixed carbon–sulfur atom. The best model was considered to be one where the carbon and sulfur atoms were described as carbon atoms with anisotropic displacement parameter and a (refined) multiplicity.

Positions for the fluorine and oxygen atoms bonded to these atoms were shown in the difference Fourier, and the further refinements included their positional and isotropic thermal parameters as well as their multiplicities. The positions of the hydrogen atoms of the cation were also found in the difference Fourier. They were introduced in idealized positions with a fixed thermal parameter of 5 Å<sup>2</sup>. The use of unit weights, giving higher weights to the small high-order reflections, was essential in order to obtain convergence. Apparently these reflections are important for the description of the structure. After the final cycle the residuals were  $R = 0.045$  and  $R_w = 0.043$ . The residual density had peaks in the range 0.9 to  $-1.0 e \text{ Å}^{-3}$ . The

Table 2. Positional parameters and displacement parameters.

Atom	x	y	z	$10^2 U_{\text{eq}}^a / \text{\AA}^2$
Cation:				
Cr	0.00000	0.00000	0.05646(1)	2.695(7)
N	0.19732(15)	0.17261(16)	0.08779(3)	3.52(2)
O5	0.03179(18)	0.18885(14)	0.02894(3)	4.05(2)
C1	0.00000	0.00000	0.17108(6)	6.07(8)
C2	0.00000	0.00000	0.13361(5)	4.09(4)
C3	0.18501(21)	0.11181(27)	0.12197(4)	4.41(4)
C4	0.37494(21)	0.24486(27)	0.07566(5)	5.20(4)
Triflate ion:				
S	0.00000	0.00000	0.39170(1)	3.35(1)
C5	0.00000	0.00000	0.34752(7)	5.25(6)
F1	0.10647(33)	0.15296(23)	0.33591(4)	9.71(8)
O1	-0.03621(19)	0.13399(17)	0.39979(4)	5.19(3)
Disordered triflate ion with site occupancy factors (s.o.f.):				
	s.o.f.			$10^2 U_{\text{iso}} / \text{\AA}^2$
CS	0.29(2)	0.1233(10)	0.00000	6.3(3)
F2	0.07(2)	-0.1088(28)	0.0450(28)	4.9(9)
F3	0.17(1)	-0.1319(11)	-0.0571(16)	6.0(3)
F4	0.26(2)	-0.1777(22)	-0.0206(26)	11.6(7)
O2	0.41(2)	0.1245(18)	-0.0848(14)	9.6(4)
O3	0.11(2)	0.2455(58)	0.0396(58)	12.7(20)
O4	0.23(2)	0.1447(25)	-0.0322(29)	11.8(8)

$$^a U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \bar{a}_i \bar{a}_j.$$

largest peaks were found close to the disordered triflate ion.

For these calculations the SDP system<sup>6</sup> was used. The atomic scattering factors, including correction for anomalous dispersion, were from Ref. 7 and were used as contained in the program. It was attempted to determine the polarity of the crystal as described by Rogers,<sup>8</sup> but this did not provide any indication. This observation and the large disorder of one of the triflate ions indicate that the crystal could be a racemic twin. At this stage the beta version of SHELXL92<sup>9</sup> became available to us. Among the features of the program, which is designed to make refinements on  $|F|^2$ , is the possibility to refine on data from twinned crystals. We used this option in SHELXL92 for the final refinements. This gave a Flack parameter<sup>10</sup> of 0.49(2), indicating that the individuals of the twinned crystal were of almost equal magnitude. All 4006 reflections were used in the refinement, which included anisotropic displacement parameters for all the ordered non-hydrogen atoms. The parameters of the hydrogen atoms were not refined. Seven atomic positions were used to describe the disordered triflate ion. Their isotropic displacement parameters and population parameters were included in the refinement. Realizing that these peaks may not correspond to actual atomic positions we used the sum of the product of population parameters and atomic numbers as an indication for the total charge density. These values are within the experimental accuracy, in agreement with the expected values.

As we were able to achieve a better description of the structure with inclusion of a twin refinement, the results reported here are from the SHELXL92 calculations. Further details from the refinements are listed in Table 1. The final positional parameters are listed in Table 2, and selected bond lengths and bond angles in Table 3. Lists of the observed and calculated squares of structure amplitudes, anisotropic displacement parameters and

Table 3. Selected bond lengths (in Å) and bond angles (in °) with e.s.d.

Cr-O5	1.944(1)	C1-C2	1.539(3)
Cr-N	2.117(1)	S-C5	1.815(3)
N-C4	1.483(2)	S-O1	1.441(1)
N-C3	1.492(2)	C5-F1	1.316(2)
C2-C3	1.534(2)		
O5-Cr-O5'	89.59(5)	N-C3-C2	113.07(13)
O5-Cr-N	90.39(5)	C3-C2-C3'	110.75(9)
O5-Cr-N'	93.13(6)	C1-C2-C3	108.16(10)
N-Cr-N'	86.91(5)	C5-S-O1	103.33(7)
Cr-N-C3	114.88(10)	O1-S-O1'	114.85(5)
Cr-N-C4	116.53(11)	S-C5-F1	111.24(16)
C3-N-C4	110.07(13)	F1-C5-F1'	107.65(17)
D-H--A	D-A	H--A	∠ D-H-A
O5--H1--O5''	2.429(2)	1.585(1)	162.25(6)
O5-H2--O1	2.860(2)	1.998(2)	150.24(9)
N-H3--O1	3.045(2)	2.193(2)	149.32(9)

Symmetry operations: '( -y, x - y, z) '( -x, y - x, -z).

positional parameters for the hydrogen atoms are available from the authors.

## Results and discussion

*Description of the crystal structure.* The packing of the ions in **2** is shown in Fig. 1. The cations and two of the anions are placed around the three-fold axes. The disordered triflate ion is found around the two-fold axis,  $(x, 0, \frac{1}{2})$ . The three oxygen atoms of the ordered, staggered triflate ion form hydrogen bonds to an oxygen atom as well as to a nitrogen atom of the cation: O1—H2—O5 being 2.860(2) and O1—H3—N 3.045(2) Å. The disordered triflate ion does not form hydrogen bonds to neighbouring groups.

The most striking feature of the cations (Fig. 2) is the short intermolecular hydrogen bonds between the three equivalent pairs of oxygen atoms, O5—H1—O5'' being 2.429(2) Å. This leads to a Cr—Cr distance of 4.639(1) Å. The centres between these oxygen pairs are on the three two-fold axes intersecting at the three-fold axis. The maximum electron density of H1 was, however, found to be

evenly distributed 0.4 Å from the centre close to the line between the two oxygen atoms. The positions of all the other hydrogen atoms were determined unambiguously. The two moieties of the hydrogen-bonded cation pair are related symmetrically to give the entire pair  $D_3$  site symmetry. This is in agreement with the observation that the dehydrated trihydroxo-bridged, dinuclear product is not the *meso*-form with  $C_{3h}$  symmetry (see below).

*Isomerism.* When Me<sub>3</sub>-tame coordinates with a three-fold axis through the metal centre two different conformations may result as illustrated in Fig. 3. The arrangement in Fig. 3a can be designated as  $\lambda, SSS$  and that in Fig. 3b as  $\delta, SSS$ , where  $\lambda$  and  $\delta$  describe the conformation of the (H<sub>2</sub>)C—N bonds relative to the three-fold axis and *S* (or *R*) the configuration around each of the three nitrogen atoms. A different configuration exists in mixed forms such as  $\lambda, RSS$  with loss of the three-fold symmetry. Models indicate that in these forms and in the conformer of Fig. 3b the distance between a CH<sub>3</sub>(N) group and a CH<sub>2</sub> group is significantly smaller than the corresponding distance in the isomer of Fig. 3a.

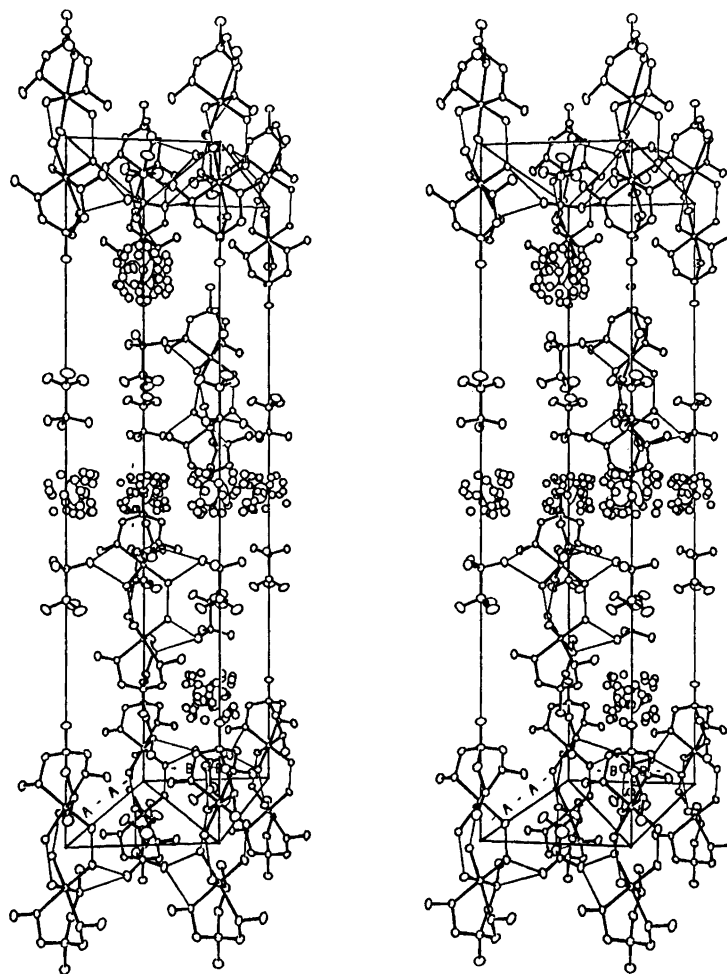


Fig. 1. ORTEP stereo view showing the packing in  $[(\text{Me}_3\text{-tame})\text{Cr}(\text{H}_3\text{O}_2)_3\text{Cr}(\text{Me}_3\text{-tame})](\text{CF}_3\text{SO}_3)_3$ . The hydrogen bonds are indicated by thin lines. All the partially occupied atoms of the disordered triflate ions are shown.

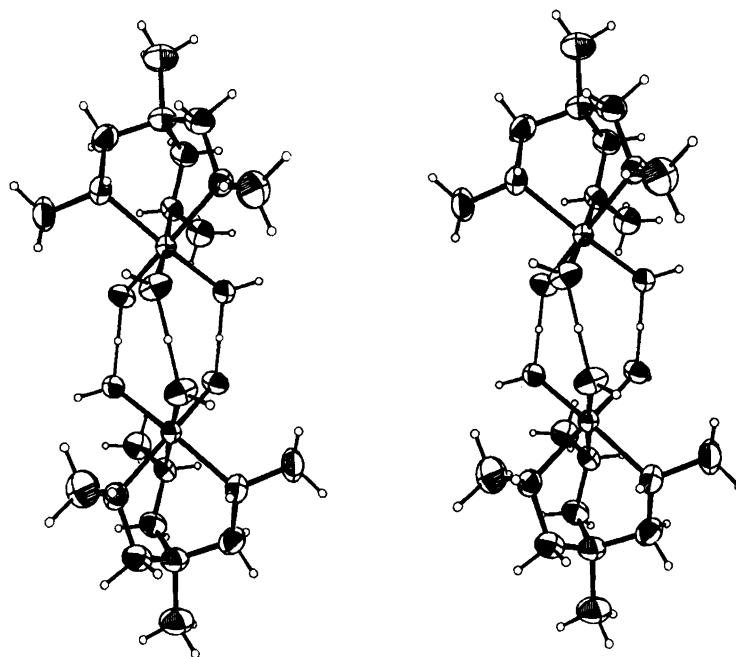


Fig. 2. ORTEP stereo drawing of the cation pair,  $[(\text{Me}_3\text{-tame})\text{Cr}(\text{H}_3\text{O}_2)_3\text{Cr}(\text{Me}_3\text{-tame})]^{3+}$ . The thermal ellipsoids enclose 50% probability. The hydrogen atoms are drawn as spheres with a common, arbitrary radius. The hydrogen bonds are shown as thin lines, and for simplicity the hydrogen atoms between the oxygen atoms are placed at the two-fold axes (see text). The labelling of the non-hydrogen atoms is given in Table 2 (cf. the z-coordinate).

Examples of different isomers have been found: The present compound, **2**, contains the monomeric moieties of the cation pairs either as  $\lambda, SSS$  forms or as  $\delta, RRR$ . A structure determination<sup>1</sup> of  $[(\text{Me}_3\text{-tame})\text{Cr}(\text{OH})_3\text{-Cr}(\text{Me}_3\text{-tame})]\text{Cl}_3 \cdot 4\text{H}_2\text{O}$  isolated by Glerup and Weihe shows that in this salt the dimer is a *meso*-form with one moiety being  $\lambda, SSS$  and the other  $\delta, RRR$ . Recently Galsbøl *et al.*<sup>11</sup> have synthesized  $\text{Rh}(\text{Me}_3\text{-tame})\text{Cl}_3$  and the triaqua derivative in two forms with different physical and chemical properties. As judged from  $^{13}\text{C}$  NMR spectra one form has a three-fold axis, while the other adopts a lower symmetry. The trichloro compound of low symmetry can be obtained in low yields by treatment

of the other isomer with hot base, probably due to deprotonation of the amine.

*Condensation to the trihydroxo-bridged dimer.* The present triflate salt, **2**, can be dehydrated at  $135^\circ\text{C}$  (see Experimental), losing three water molecules, to give an anhydrous triflate of the trihydroxo-bridged dimer, (**3**),  $[(\text{Me}_3\text{-tame})\text{Cr}(\text{OH})_3\text{Cr}(\text{Me}_3\text{-tame})](\text{CF}_3\text{SO}_3)_3$ , which can be reprecipitated as a trihydrate. The dimer, **3**, has properties different from those of the *meso*-form isolated by Glerup and Weihe.<sup>1</sup> The triflate and other salts of **3** are more soluble than those of the *meso*-form, and we were not able to grow crystals big enough for a structure determination. The UV/VIS spectra of **3** and of the *meso*-isomer are given in Fig. 4. By cleaving the two isomers in noncomplexing acidic solution at room temperature the same mononuclear triaqua complex, **1**, is obtained. We therefore expect **3** to be the racemic isomer of the trihydroxo-bridged dimer, and the arrangement of the monomers in **2**, favourable for the formation of this isomer, supports this conclusion. There are many examples of solid-state association of aquahydroxo metal complexes held together by hydrogen bonds, and several dihydroxo-bridged dimers of chromium(III), cobalt(III), rhodium(III) and iridium(III) have been synthesized in this manner.<sup>12</sup>

The acid dissociation constants of the  $[\text{Cr}(\text{Me}_3\text{-tame})(\text{H}_2\text{O})_3]^{3+}$  ion were determined in 1.0 M NaBr at  $25^\circ\text{C}$ . The  $-\log(K_a/M)$  values  $\text{p}K_1 = 4.780(5)$ ,  $\text{p}K_2 = 7.306(5)$  and  $\text{p}K_3 = 9.412(7)$  are close to those of other *fac*- $[\text{CrL}_3(\text{H}_2\text{O})_3]^{3+}$  compounds where  $\text{L}_3$  is an amine

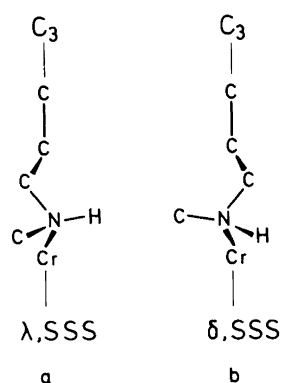


Fig. 3. An illustration of the two conformers of  $\text{Cr}^{\text{III}}(\text{Me}_3\text{-tame})$  with three-fold symmetry.  $\delta$  and  $\lambda$  refer to the conformation of the  $(\text{H}_2)\text{C}-\text{N}$  bond relative to  $\text{C}_3$ -axis and  $S$  (or  $R$ ) to the configuration around the nitrogen atoms.

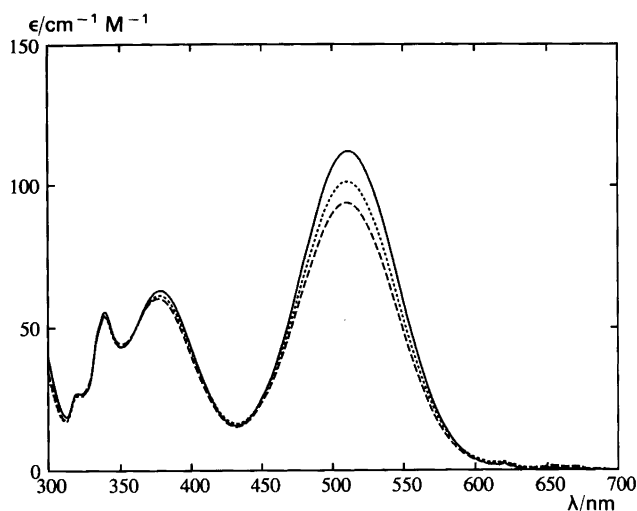
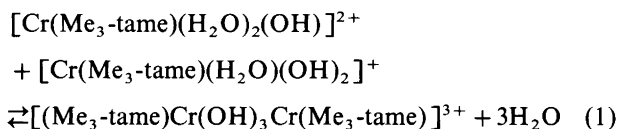


Fig. 4. Optical spectra of the meso- (—) and the racemic isomer (----) of  $[(\text{Me}_3\text{-tame})\text{Cr}(\text{OH})_3\text{Cr}(\text{Me}_3\text{-tame})]^{3+}$  (from the triflates) in 1 M NaBr at room temperature immediately after dissolution and after 2 days (.....).

ligand.<sup>13</sup> The triflate salt, **2**, reacts in aqueous solution to give both isomers of the trihydroxo-bridged dimer in approximately equal amounts (HPLC),<sup>2</sup> with equilibrium (1) being reached from both sides within a few weeks at room temperature.



The equilibrium constant of reaction (1) in 1.0 M NaBr at 25°C was determined to be  $10^{5.6} \text{ M}^{-1}$ . At  $[\text{H}^+] = 10^{-7.3} \text{ M}$  only minor amounts of other hydroxo-bridged species are present, and from such solutions salts of the less soluble trihydroxo-bridged meso-isomer are easily isolated. As Fig. 4 shows, the two trihydroxo-bridged

dimers isomerize within 1–2 days in neutral solution at room temperature to give a meso/racemic ratio of 0.7 (if mixed RS forms can be neglected). This is faster than the equilibrium with the monomer, eqn. (1), is reached, and a mechanism involving deprotonation at the nitrogen atoms is therefore likely. The above mentioned reactions are at present being studied over a wider  $[\text{H}^+]$  range.<sup>2</sup>

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