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Bis[*trans*-dibromo(2,2-dimethylpropane-1,3-diamine-κ^2N,N')chromium(III)] dibromide hydrogen perchlorate hexahydrate

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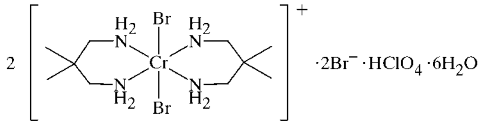
In the title compound, $[CrBr_2(C_5H_{14}N_2)_2]_2Br_2{\cdot}HClO_4{\cdot}6H_2O$, there are two independent Cr^{III} complex cations which are conformational isomers of each other. The Cr atoms lie respectively on a center of symmetry and on a mirror plane and have octahedral environments, coordinated by the N atoms of two 2,2-dimethylpropane-1,3-diamine ligands and by two Br atoms in *trans* positions. The Cr—N and Cr—Br bond lengths are in the ranges 2.078 (3)–2.089 (3) and 2.4495 (9)–2.5017 (9) Å, respectively. The crystal structure consists of two Cr^{III} complex cations, two Br^- anions, a $(ClO_4)^-$ anion and an $[H_{13}O_6]^+$ hydrogen-bonded cluster cation.

Comment

2,2-Dimethylpropane-1,3-diamine (Me_2tn) can coordinate to a central metal ion as a bidentate ligand, forming a six-membered chelate ring, similar to the situation for unsubstituted propane-1,3-diamine (tn) (House, 1986). In addition to the conformational isomerism resulting from the six-membered chelate rings, the $[CrBr_2(tn/Me_2tn)_2]^+$ complex cations can exist as *cis* or *trans* isomers. Although electronic absorption and IR spectra have been used to identify the geometrical structures of chromium(III) complexes (Choi *et al.*, 2002; Poon & Pun, 1980), assignments based on spectral data are not always conclusive (Stearns & Armstrong, 1992). Furthermore, since reports on the structural chemistry of complexes of the type $[Cr^{III}L_4Br_2]X$ are rare (Lisgarten *et al.*, 1990), we prepared the title complex, (I), which contains the $[CrBr_2(Me_2tn)_2]^+$ cation, and determined its crystal structure by X-ray analysis.

The structure analysis of (I) reveals the crystal to contain two crystallographically independent Cr^{III} complex moieties. As atom Cr1 is located at a crystallographic center of symmetry, this Cr^{III} complex cation has molecular C_i symmetry, while the other complex cation, containing atom Cr2, has molecular C_s symmetry; atoms Cr2, Br21, Br22, C22, C24, C25, C27, C29 and C30 are located on a crystallographic mirror plane. It was found that in both complex cations, the two Br atoms are coordinated to the central Cr atom in a *trans* arrangement. The Cr—Br bond lengths [2.4495 (9)–2.5017 (9) Å] are close to the value found in *trans*-[CrBr$_2$(cyclam)]Br (cyclam is 1,4,8,11-tetraazacyclotetradecane; Lisgarten *et al.*, 1990). The Cr—N bond lengths in (I) are in the range 2.078 (3)–2.089 (3) Å, which are typical values for Cr^{III}—N(primary amine) bonds. All of the six-membered chelate rings formed by the Me_2tn ligand adopt chair conformations and the two complex cations are so-called conformational isomers (C_i and C_s) due to the relative conformation of the two Me_2tn chelate rings, as shown in Fig. 1.



(I)

As well as the complex cation, the asymmetric unit of (I) also contains a Br^- ion (Br3), half a $(ClO_4)^-$ anion and three O atoms (O1, O2 and O3) corresponding to the hydrated water molecules. For charge balance, a half equivalent amount of H^+ per Cr^{III} complex cation should be included in the crystal. We suspected that such an H^+ ion was trapped between atoms O1 and O1^{iii} [symmetry code: (iii) $1 - x$, y, $-z$], because the O1$\cdots$O1^{iii} distance was only 2.347 (9) Å, pointing to the existence of a strong hydrogen-bonding interaction between these atoms (Minkwitz *et al.*, 1998). Since atom O1 is also involved in hydrogen bonds with both O2 and O3^{iv} [O1$\cdots$O2 = 2.662 (7) Å and O1$\cdots$O3^{iv} = 2.667 (7) Å; symmetry code: (iv) $\frac{1}{2} + x$, $\frac{1}{2} - y$, z], the hydrated H^+ cation in

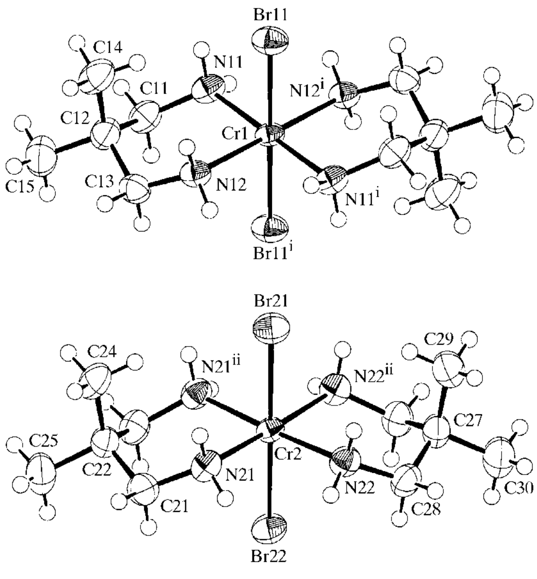


Figure 1
Perspective views of the two crystallographically independent complex cations in (I). Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $\frac{1}{2} - x$, $\frac{1}{2} - y$, $-z$; (ii) x, $-y$, z.]

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the crystal of (I) forms an $[H_{13}O_6]^+$ cluster cation (Fig. 2). Although both Eigen-type and chain-like structures of $[H_9O_4]^+$ clusters are often observed (Frank & Reiss, 1997; Hassaballa *et al.*, 1998), the H-shaped $[H_{13}O_6]^+$ cluster cation found in the crystal of (I) has, to the best of our knowledge, not been reported previously.

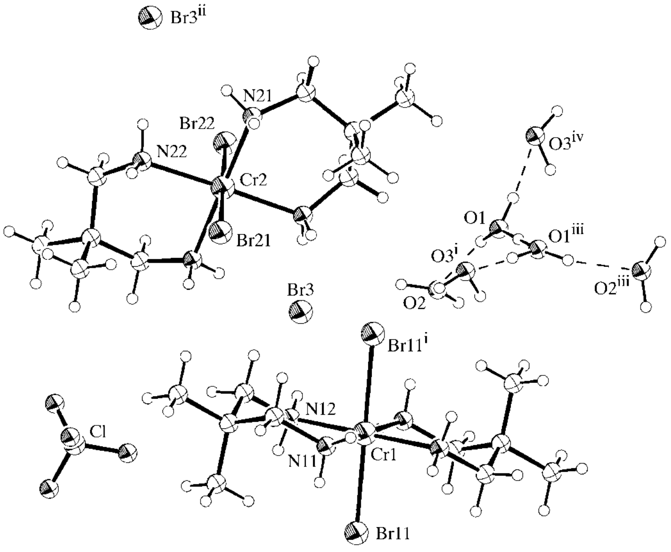

Figure 2
A view of a complete set of ions in (I). [Symmetry codes: (i) $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (ii) $x, -y, z$; (iii) $1-x, y, -z$; (iv) $\frac{1}{2}+x, \frac{1}{2}-y, z$.]

Hence, (I) can be formulated as $[H_{13}O_6]$\{*trans*-$[CrBr_2(Me_2tn)_2]$\}$_2Br_2(ClO_4)$. For help in visualizing the complete structure of this compound, a drawing showing the $[H_{13}O_6]^+$ cluster cation and the two conformational isomers of the Cr^{III} complex cation, together with two Br^- anions and a $(ClO_4)^-$ anion, is included as Fig. 2.

Experimental

The starting material *trans*-$[CrCl_2(Me_2tn)_2]ClO_4$ was synthesized according to the literature method of House (1986). The complex *trans*-$[CrCl_2(Me_2tn)_2]ClO_4$ (1.0 g) and NaOH (1.0 g) were suspended in water (10 ml) and the suspension heated at 333 K for 15 min. HBr (48%, 10 ml) and $HClO_4$ (60%, 5 ml) were added to the mixture. The solution was concentrated at 333 K until green crystals appeared. The reaction mixture was then placed in an ice bath and the crystalline product which was deposited was filtered off, washed with cold 2-propanol and then with diethyl ether. Recrystallization of the crude product from 0.5 *M* HBr solution afforded green crystals of (I) suitable for X-ray analysis.

Crystal data

$[CrBr_2(C_5H_{14}N_2)_2]_2Br_2\cdot HClO_4\cdot 6H_2O$
$M_r = 1200.74$
Monoclinic, $C2/m$
$a = 22.3862$ (8) Å
$b = 24.7393$ (8) Å
$c = 8.3230$ (3) Å
$\beta = 91.624$ (1)°
$V = 4607.6$ (3) Å^3
$Z = 4$
$D_x = 1.731$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 876 reflections
$\theta = 1.6$–27.5°
$\mu = 5.78$ mm^{-1}
$T = 293$ (2) K
Plate, green
0.32 × 0.32 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID Imaging Plate diffractometer
ω scans
Absorption correction: multi-scan (Higashi, 1995)
$T_{min} = 0.188$, $T_{max} = 0.560$
20 618 measured reflections
5320 independent reflections
4188 reflections with $I > 2\sigma(I)$
$R_{int} = 0.052$
$\theta_{max} = 27.5°$
$h = -26 \rightarrow 26$
$k = -30 \rightarrow 32$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.108$
$S = 1.05$
5320 reflections
228 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0520P)^2 + 9.0033P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.73$ e Å^{-3}
$\Delta\rho_{min} = -0.60$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Br11—Cr1	2.4876 (4)	Cr1—N11	2.084 (3)
Br21—Cr2	2.5017 (9)	Cr2—N21	2.078 (3)
Br22—Cr2	2.4495 (9)	Cr2—N22	2.089 (3)
Cr1—N12	2.078 (3)		
N12—Cr1—N11	91.46 (12)	N22—Cr2—N22^i	88.94 (18)
N12—Cr1—Br11	90.59 (9)	N21—Cr2—Br22	91.47 (9)
N11—Cr1—Br11	90.24 (9)	N22—Cr2—Br22	91.20 (10)
N21—Cr2—N21^i	89.79 (18)	N21—Cr2—Br21	88.45 (9)
N21—Cr2—N22	90.57 (13)	N22—Cr2—Br21	88.87 (10)
N21—Cr2—N22^i	177.29 (14)		

Symmetry code: (i) $x, -y, z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N11—H11M···O2^i	0.90	2.57	3.438 (6)	163
N11—H11N···Br3^{ii}	0.90	2.77	3.661 (3)	169
N12—H12M···Br3	0.90	2.62	3.496 (3)	163
N12—H12N···Br3^{iii}	0.90	3.06	3.567 (3)	117
N21—H21M···Br3^{iv}	0.90	2.58	3.475 (3)	177
N21—H21N···Br11^v	0.90	2.90	3.580 (3)	134
N22—H22N···Br3^{iv}	0.90	2.62	3.516 (3)	176
O1—H00···O1^{vi}	1.17	1.17	2.347 (9)	180
O1—H01A···O3^{vii}	0.90	1.77	2.667 (7)	175
O1—H01B···O2	0.90	1.82	2.662 (7)	155
O2—H02A···O42^{iii}	0.90	2.05	2.89 (1)	157
O2—H02B···Br3	0.90	2.61	3.420 (5)	150
O3—H03A···Br3^{iii}	0.90	2.70	3.383 (5)	133
O3—H03A···Br22^{iii}	0.90	3.02	3.575 (5)	121

Symmetry codes: (i) $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (ii) $x, y, z-1$; (iii) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$; (iv) $x, -y, z$; (v) $\frac{1}{2}-x, y-\frac{1}{2}, -z$; (vi) $1-x, y, -z$; (vii) $\frac{1}{2}+x, \frac{1}{2}-y, z$.

The water H atoms were located from difference syntheses and refined as parts of rigid groups, with O—H = 0.90 Å and $U_{iso}(H) = 0.044$ Å^2. The position of the H$^+$ ion (H00) was fixed at the midpoint between atoms O1 and O1($1-x, y, -z$). Other H atoms were placed geometrically and refined using a riding model, with N—H = 0.90 Å, C—H = 0.96 (for methyl H) or 0.97 Å (for methylene H), and $U_{iso}(H) = 1.2U_{eq}$(N or C). The H atoms of the methyl groups (C24, C25, C29 and C30) were treated as positionally disordered over two sites.

Data collection: *PROCESS–AUTO* (Rigaku, 1998); cell refinement: *PROCESS–AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation & Rigaku, 2000); program(s) used to solve

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structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1970); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1082). Services for accessing these data are described at the back of the journal.

References

Choi, J. H., Hong, Y. P. & Park, Y. C. (2002). *Spectrochim. Acta A*, **58**, 1599–1606.

Frank, W. & Reiss, G. J. (1997). *Inorg. Chem.* **36**, 4593–4595.

Hassaballa, H., Steed, J. W., Junk, P. C. & Elsegood, M. R. (1998). *Inorg. Chem.* **37**, 4666–4671.

Higashi, T. (1995). *DIFABS.* Rigaku Corporation, 3-9-12 Akishima, Tokyo, Japan.

House, D. A. (1986). *Inorg. Chem.* **25**, 1671–1674.

Johnson, C. K. (1970). *ORTEP.* Report ORNL-3794, 2nd revison. Oak Ridge National Laboratory, Tennessee, USA.

Lisgarten, J. N., Palmer, R. A., Hemmings, A. M. & Gazi, D. M. (1990). *Acta Cryst.* C**46**, 396–399.

Minkwitz, R., Schneider, S. & Kornath, A. (1998). *Inorg. Chem.* **37**, 4662–4665.

Molecular Structure Corporation & Rigaku (2000). *TEXSAN*. Version 1.11. MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA, and Rigaku Corporation, 3-9-12 Akishima, Tokyo 196-8666, Japan.

Poon, C. K. & Pun, K. C. (1980). *Inorg. Chem.* **19**, 568–569.

Rigaku (1998). *PROCESS–AUTO*. Rigaku Corporation, 3-9-12 Akishima, Tokyo 196-8666, Japan.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Stearns, D. M. & Armstrong, W. H. (1992). *Inorg. Chem.* **31**, 5178–5184.