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Redetermination of bis[μ_3-1,3,5-triamino-1,3,5-trideoxy-*cis*-inositolato(3–)]tribismuth(III) trichloride hexahydrate

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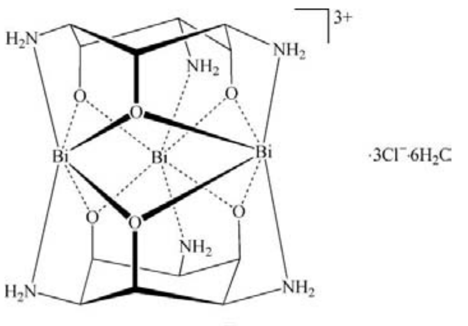
The crystal structure of the title compound, $[Bi_3(C_6H_{12}N_3O_3)_2]Cl_3\cdot6H_2O$, which was described in the space group *R*3 [Hegetschweiler, Ghisletta & Gramlich (1993). *Inorg. Chem.* **32**, 2699–2704], has been redetermined in the revised space group *R*32 as suggested by Marsh [*Acta Cryst.* (2002), B**58**, 893–899]. Accordingly, the significant difference in the Bi—N bond distances of 2.43 (2) and 2.71 (1) Å, as noted in the previous study, proved to be an artifact. As a consequence, the $[Bi_3(H_{-3}taci)_2]Cl_{6/3}$ entity (taci is 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol) adopts D_3 symmetry and the three Bi atoms lie on C_2 axes with equal Bi—N bond distances of 2.636 (3) Å.

Comment

The reaction of three equivalents of Bi^{III} with two equivalents of 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol (taci) and six equivalents of a base resulted in the spontaneous formation of the trinuclear $[Bi_3(H_{-3}taci)_2]^{3+}$ unit. The synthesis, spectroscopic characterization and crystal structure of a hydrated trichloride salt of this cation were reported several years ago (Hegetschweiler *et al.*, 1993). $[Bi_3(H_{-3}taci)_2]Cl_3\cdot6H_2O$, (I), crystallizes in a trigonal lattice, and in the 1993 study the structure was solved and refined in the space group *R*3. The trinuclear unit was located on a polar C_3 axis, with significant displacement of the three Bi centers from a mean position between the two $H_{-3}taci^{3-}$ residues. As a consequence, different Bi—O and, in particular, significantly different Bi—N bond distances were observed. These findings were, however, in contradiction to the ^1H and ^{13}C NMR characteristics, which clearly indicated a structure with a symmetric (D_{3h}) binding of the two ligand entities in solution. As usual in such situations, we explained the unexpected asymmetry in terms of a packing effect. It was, however, noted by Marsh (2002) that, in this structure, every atom except the Bi centers either lies on or is paired across an additional C_2 axis, which, if included, results in the space group *R*32. Marsh suggested that the significant displacement of the Bi atoms may be due to an inverted assignment of the anomalous scattering, resulting in a polar dispersion error. Inspection of the data set established indeed that an absolute structure had not been assigned at that time. We therefore collected diffraction data from a new crystal of the compound and evaluated the data set successfully by using the space group *R*32, as suggested by Marsh.



(I)

A view of the D_3-symmetric sandwich-type $[Bi_3(H_{-3}taci)_2]^{3+}$ unit together with two of the six chloride ligands is shown in Fig. 1. The three Bi atoms form an equilateral triangle, which is encapsulated by two triply deprotonated $H_{-3}taci^{3-}$ ligands. Both ligand entities bind the Bi centers *via* an *O*,*N*,*O*-axial–equatorial–axial coordination mode, with the alkoxo O atoms all serving as μ_2 bridges. As a consequence, the Bi centers are bonded to two N atoms and to four alkoxo O atoms (Table 1). A similar trinuclear structure has been observed for other large metal cations, such as the trivalent lanthanides (Hegetschweiler, 1999).

The hydrated trichloride salt (I) is a two-dimensional polymer with the $[Bi_3(H_{-3}taci)_2]^{3+}$ units interlinked by μ_3-Cl

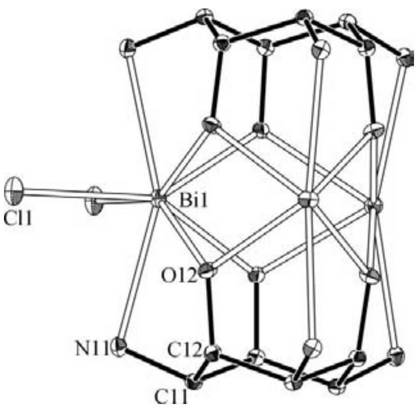


Figure 1
The $[Bi_3(H_{-3}taci)_2]Cl_{6/3}$ entity, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. For clarity, only two of the six chloride ligands are shown and H atoms have been omitted.

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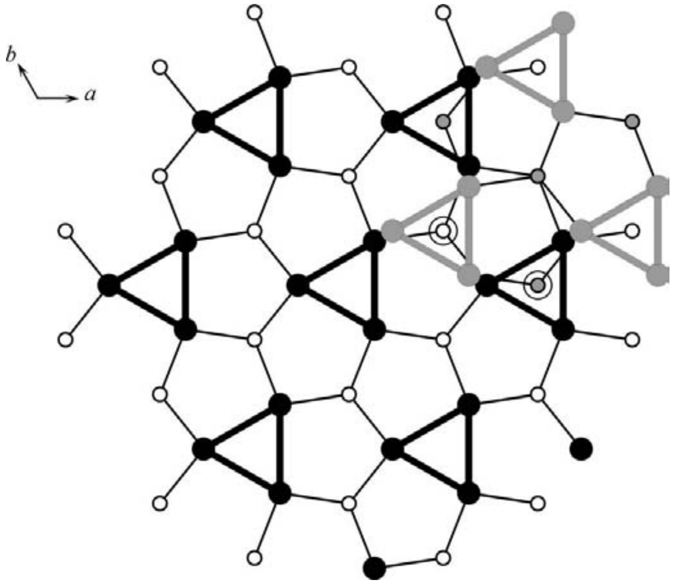

Figure 2
A view of the approximately planar layer formed by the bridging Cl1 atoms (small open circles) and the Bi_3 triangles (black). A small section of a second layer is shown in grey. Two positions of the tetrahedral holes which are equally filled with Cl2 and water O atoms (O300) are shown as large open circles.

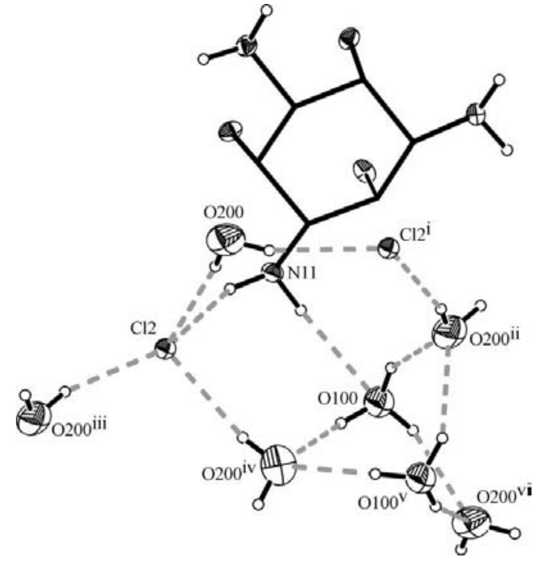

Figure 3
A section of the hydrogen-bonding network. Displacement ellipsoids of the O, N and Cl atoms are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary size. Only one H_{-3}taci unit of the cation is shown, using a stick model for the cyclohexane backbone. C-bound H atoms have been omitted for clarity. [Symmetry codes: (i) $y + \frac{1}{3}$, $x + \frac{2}{3}$, $-z + \frac{5}{3}$; (ii) $-x + y + 1$, $-x + 2$, z; (iii) $-x + y$, $-x + 1$, z; (iv) $-y + 1$, $x - y + 1$, z; (v) $x - y + \frac{4}{3}$, $-y + \frac{8}{3}$, $-z + \frac{5}{3}$; (vi) x, $y + 1$, z.]

bridges. These bridging interactions result in the formation of layers, oriented perpendicular to the crystallographic *c* axis (Fig. 2), with an almost planar arrangement of the Bi_3 triangles and the bridging Cl1 atoms. The symmetry of such an idealized plane can be described by the hexagonal plane group *p*31*m* (No. 15). On the basis of a stacking sequence *ABCABC*... of such layers, the entire structure can be regarded as a distorted cubic close packing of $[Bi_3(H_{-3}taci)_2]^{3+}$ cations, with the bridging Cl1 anions located in trigonal holes and water molecules (O100) in octahedral holes. Atom Cl2 and an additional water molecule (O300) are randomly distributed in the tetrahedral holes with site occupancies of 50% each. A 50% occupancy for atom Cl2 is in agreement with charge balance considerations and was also confirmed by careful comprehensive elemental analysis, establishing unambiguously a Bi:taci:Cl molar ratio of 3:2:3. A further water molecule (O200) is located on a twofold axis between two trinuclear cations. The Cl2 counter-ions and the water molecules, together with the amine groups of the complex cation, form a three-dimensional network of hydrogen bonds (Fig. 3 and Table 2). The Cl1 bridges and the alkoxo groups of the taci residues are not involved in hydrogen bonding.

Although the crystallographic symmetry for the $[Bi_3(H_{-3}taci)_2]^{3+}$ cation is D_3, it approaches D_{3h} symmetry quite closely. The additional vertical mirror planes that are required for the point group symmetry of D_{3h} correspond to the mirror lines of the above-mentioned plane group *p*31*m*. This type of symmetry is, however, broken by the particular *ABCABC*... stacking, and, as a consequence, the entire structure is chiral. The evaluation reported here thus fully confirms the considerations of Marsh.

Experimental

The title compound was prepared as described previously (Hegetschweiler *et al.*, 1993). Colorless crystals suitable for X-ray diffraction study were taken directly from the mother liquor. In addition, a dried sample (monohydrate) of composition $[Bi_3(H_{-3}taci)_2]Cl_3\cdot H_2O$ was prepared for elemental analysis (performed by Dr Thomas Kull, Solvias AG, Basel, Switzerland). Analysis found: Bi 56.9, C 13.16, Cl 9.67, H 2.44, N 7.75%; $C_{12}H_{26}Bi_3Cl_3N_6O_7$ requires: Bi 57.0, C 13.11, Cl 9.67, H 2.38, N 7.64%. The ^{1}H and ^{13}C NMR characteristics of this sample correspond to those presented in the former report (Hegetschweiler *et al.*, 1993).

Crystal data

$[Bi_3(C_6H_{12}N_3O_3)_2]Cl_3\cdot 6H_2O$
$M_r = 1189.76$
Trigonal, *R*32
$a = 8.0903$ (11) Å
$c = 35.612$ (7) Å
$V = 2018.6$ (6) Å^3

$Z = 3$
Mo $K\alpha$ radiation
$\mu = 19.93$ mm^{-1}
$T = 100$ (2) K
0.26 × 0.18 × 0.10 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: Gaussian (*XPREP*; Bruker, 2003)
$T_{min} = 0.048$, $T_{max} = 0.186$

24418 measured reflections
1983 independent reflections
1981 reflections with $I > 2\sigma(I)$
$R_{int} = 0.043$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.049$
$S = 1.15$
1983 reflections
63 parameters
2 restraints

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 1.69$ e Å^{-3}
$\Delta\rho_{min} = -2.19$ e Å^{-3}
Absolute structure: Flack (1983), 824 Friedel pairs
Flack parameter: −0.009 (8)

Table 1
Comparison of selected bond distances (Å) for $[Bi_3(H_{-3}taci)_2]Cl_3\cdot6H_2O$ presented both in our previous study (space group *R*3, 304 K) and in the present investigation (space group *R*32, 100 K).

	Hegetschweiler *et al.* (1993)	This work
Bi—O	2.28 (2)–2.40 (1)	2.329 (2), 2.331 (2)
Bi—N	2.43 (2), 2.71 (1)	2.636 (3)
Bi—Cl	3.000 (3), 3.002 (3)	2.9871 (4)
C—C	1.50 (3)–1.55 (2)	1.533 (4)
C—N	1.52 (3), 1.53 (3)	1.473 (4)
C—O	1.40 (2), 1.43 (2)	1.424 (4)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H11*A*···Cl2	0.92	2.68	3.480 (3)	146
N11—H11*B*···O100	0.92	2.31	3.167 (5)	154
O100—H100···O200^{ii}	0.852 (10)	2.11 (5)	2.871 (6)	149 (10)
O200—H200···Cl2^{i}	0.850 (11)	2.26 (3)	3.084 (3)	165 (9)

Symmetry codes: (i) $y+\frac{1}{3}, x+\frac{2}{3}, -z+\frac{5}{3}$; (ii) $-x+y+1, -x+2, z$.

As reported previously (Hegetschweiler *et al.*, 1993), the title compound crystallizes in a trigonal lattice; in the present study, the space group *R*32 was chosen according to the considerations of Marsh (2002). A total of six low-angle reflections ($3.43 < \theta < 8.61°$) with F_o^2 significantly smaller than F_c^2 were excluded from the data set. Based on elemental analysis, the total occupancy for the two Cl-atom positions is only 1.5. This could be realized either by a 75% occupancy for both positions or individually by 50% for one position and 100% for the other. Inspection of the relevant electron density clearly established that the position of atom Cl1 is fully occupied, whereas the electron density of atom Cl2 is somewhat reduced. We therefore assigned a fixed site-occupation factor of 1.0 to atom Cl1 and 0.5 to atom Cl2. However, it appeared that the 50% occupancy of Cl2 did not account for the entire amount of electron density observed. We therefore added a further O atom (O300) at this position, also with a site-occupation factor of 0.5. The two atoms, *viz.* Cl2 and O300, were refined with identical positional and displacement parameters. Obviously, a chloride counter-ion and a water molecule occupy this position at random with equal probability. The H atoms of the corresponding water molecule (O300) could not be observed and were not considered in the refinement. The H atoms of the remaining water molecules (O100 and O200) were located in difference Fourier maps. They were refined isotropically with O—H bond distances restrained to 0.85 (1) Å and U_{iso} values fixed at $1.5U_{eq}$ of the parent O atom. Since O100 is located on a crystallographic threefold axis, its H atom (H100) received a site-occupation factor of 0.67. The positions of the C- and N-bonded H atoms were calculated and refined using a riding model, with C—H distances of 1.00 Å and N—H distances of 0.92 Å, and with U_{iso} values fixed at $1.2U_{eq}$ of the parent atom. The largest electron-density peak was located 0.25 Å from the disordered Cl2/O300 system.

Data collection: *COLLECT* (Bruker, 2006); cell refinement: *COLLECT*; data reduction: *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3118). Services for accessing these data are described at the back of the journal.

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