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Key indicators

Single-crystal X-ray study
 T = 295 K
 Mean $\sigma(\text{C}-\text{C}) = 0.011 \text{ \AA}$
 H-atom completeness 35%
 Disorder in main residue
 R factor = 0.023
 wR factor = 0.068
 Data-to-parameter ratio = 11.8

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

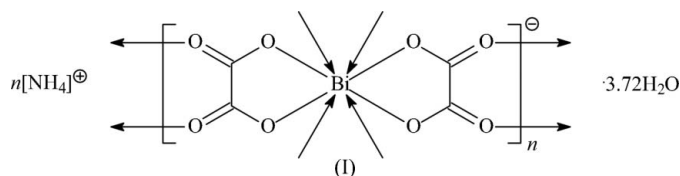
Redetermination of ammonium bisoxalato-bismuthate(III) x-hydrate from single-crystal data

In the crystal structure of the title compound, poly[ammonium di- μ_2 -oxalato-bismuthate(III) 3.72-hydrate], $\text{NH}_4[\text{Bi}(\text{C}_2\text{O}_4)_2] \cdot 3.72\text{H}_2\text{O}$, the Bi^{3+} ion and the centre of the $[\text{NH}_4]^+$ ion lie on different special positions of $\bar{4}m2$ site symmetry, and the oxalate group and one water molecule on different special positions of m site symmetry; the second water molecule lies on a special position of $2/m$ site symmetry. The Bi atom is eight-coordinate in a slightly distorted dodecahedral environment. This single-crystal redetermination improves the precision of the previous powder diffraction study [Vanhoyland *et al.* (2004). *Inorg. Chem.* **43**, 785–789], as all non-H atoms have been refined anisotropically.

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Comment

The crystal structure of ammonium bisoxalato-bismuthate(III) x-hydrate, (I), has been refined previously from X-ray powder data to an R_B index of 8% ($R_{wp} = 14\%$ if the background was subtracted); the number of water molecules, 3.71, was determined from corresponding TGA measurements of the as-synthesized material. The compound, prepared by the reaction of bismuth nitrate and ammonium oxalate in water, was obtained as a white powder (Vanhoyland *et al.*, 2004). Under hydrothermal conditions, the synthesis has afforded the compound as a crystalline material that has allowed a redetermination from single-crystal data. The structural features are statistically indistinguishable from those of the powder refinement, but are of higher precision as all non-H atoms have been refined anisotropically.



Compound (I) has the metal atom in a slightly distorted dodecahedral geometry as the atom is chelated by four oxalato groups (Fig. 1). The two sets of Bi–O bonds are statistically indistinguishable from each other (Table 1). The building block is the BiO_8 polyhedron; the polyhedra do not share any edges or vertices. The open framework (Fig. 2) features a channel along [111] that houses the ammonium cations $[\text{N} \cdots \text{O} = 2.996(3) \text{ \AA}]$ and the (partially occupied) solvent water molecules. The hydrogen-bonding interaction of the water molecules is somewhat weak $[\text{O}1 \cdots \text{O}1w = 3.037(6) \text{ \AA}; \text{O}1 \cdots \text{O}2w = 3.19(1) \text{ \AA}]$ whereas the water–water interaction is much stronger $[\text{O}1w \cdots \text{O}2w 2.69(3) \text{ \AA}]$.

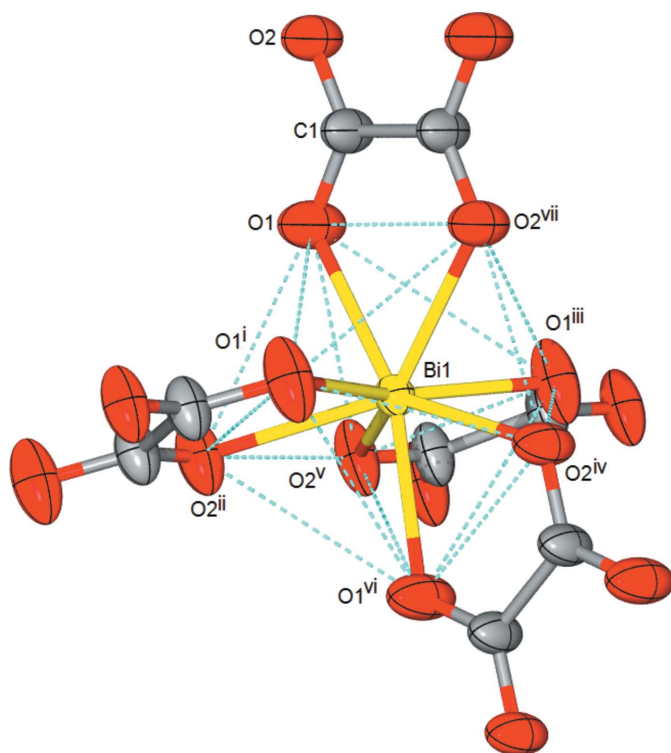


Figure 1
ORTEP plot illustrating the coordination geometry of Bi in ammonium dioxalatobismuthate(III) 3.72-hydrate. The ammonium cation and disordered water molecules are not shown. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $\frac{1}{4} + y, x - \frac{1}{4}, \frac{5}{4} - z$; (ii) $1 - x, y, z$; (iii) $\frac{1}{4} + y, \frac{3}{4} - x, \frac{5}{4} - z$; (iv) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{3}{2} - z$; (v) $\frac{3}{4} - y, \frac{1}{4} + x, z - \frac{1}{4}$; (vi) $\frac{3}{4} - y, \frac{1}{4} - x, z - \frac{1}{4}$; (vii) $\frac{1}{2} - x, \frac{1}{2} - y, \frac{3}{2} - z$.]

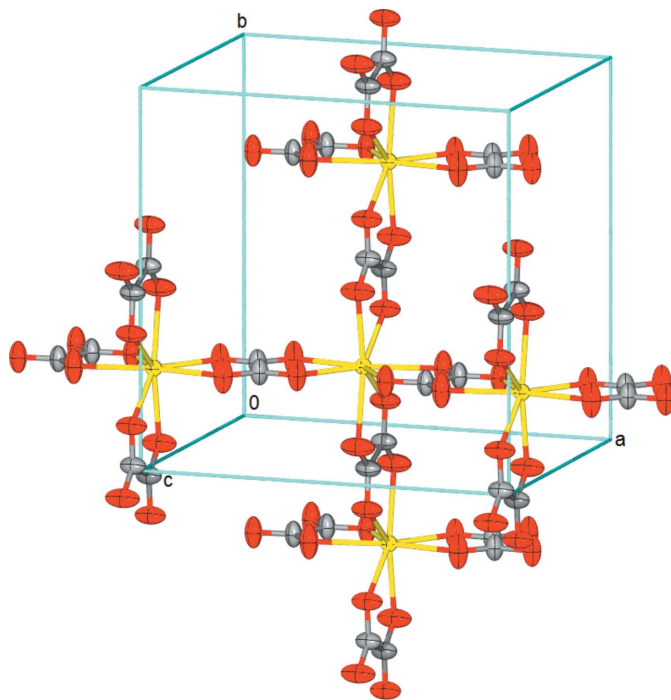


Figure 2
ORTEP plot illustrating the connectivity of the BiO_8 polyhedron. Probability level is as in Fig. 1.

Experimental

Technical grade reagents were used in the synthesis. Bismuth nitrate pentahydrate (0.25 g, 5.0 mmol), oxalic acid hydrate (0.63 g, 5.0 mmol), hydroxylamine hydrochloride (0.52 g, 7.5 mmol) and water (10 ml) were heated in a Teflon-lined Parr bomb at 383 K for 4 d. The block-shaped crystals that separated from the cool solution were collected in about 50% yield.

Crystal data

$\text{NH}_4[\text{Bi}(\text{C}_2\text{O}_4)_2] \cdot 3.72\text{H}_2\text{O}$
 $M_r = 470.38$
 Tetragonal, $I4_1/amd$
 $a = 11.674(1) \text{ \AA}$
 $c = 9.2545(8) \text{ \AA}$
 $V = 1261.2(2) \text{ \AA}^3$
 $Z = 4$

$D_x = 2.477 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 14.04 \text{ mm}^{-1}$
 $T = 295(2) \text{ K}$
 Block, colourless
 $0.24 \times 0.20 \times 0.17 \text{ mm}$

Data collection

Bruker APEX area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.123, T_{\max} = 0.199$
 (expected range = 0.057–0.092)

3231 measured reflections
 401 independent reflections
 365 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$
 $\theta_{\max} = 27.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.023$
 $wR(F^2) = 0.068$
 $S = 1.13$
 401 reflections
 34 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0476P)^2 + 3.0591P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.76 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.49 \text{ e \AA}^{-3}$

Table 1

Selected bond lengths (\AA).

Bi1—O1	2.423 (6)	O2—C1	1.24 (1)
Bi1—O2 ⁱ	2.429 (6)	C1—C1 ⁱⁱ	1.52 (2)
O1—C1	1.25 (1)		

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

One of the water molecules lies at (0.25, 0.25, 0.25) and the other at $(x, 0.25 - x, 0.375)$; the occupancies were set to 62% of these site occupancies, in accordance with the number of water molecules that were derived from TGA measurements (Vanhooyland *et al.*, 2004). The displacement parameters of the two atoms were restrained to be nearly isotropic by setting the three main U_{ij} values to within 0.01 of each other. When refined with crystallographically-imposed full site-occupancies of 0.25 and 0.50, displacement parameters of 0.22 (1) \AA^2 for O1_w and 0.35 (1) \AA^2 for O2_w were obtained. For this model, the number of water molecules in the formula unit is 6, which is in conflict with the TGA results. Therefore this model was discarded. The ammonium H atom was refined with distance restraints of N—H = 0.85 \AA and H...H = 1.39 \AA , and was included in the refinement with $U_{\text{iso}}(\text{H})$ being 1.2 times $U_{\text{eq}}(\text{N})$. The water H atoms could not be placed in chemically sensible positions and thus were not included in the refinement.

Data collection: SMART (Bruker, 2003); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT; method used to solve struc-

ture: atomic coordinates taken from published structure; program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *SHELXL97*.

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