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Two bismuth oxalate hydrates and revision of their chemical formulae

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The crystal structures of two bismuth(III) oxalate hydrates, previously described as '$Bi_2(C_2O_4)_3 \cdot H_2C_2O_4$' and '$Bi_2(C_2O_4)_3 \cdot 7H_2O$', were solved and refined from single-crystal X-ray diffraction data. The results led to the revised chemical formulae $Bi_2(C_2O_4)_3 \cdot 6H_2O$ and $Bi_2(C_2O_4)_3 \cdot 8H_2O$, respectively. Both dibismuth(III) trioxalate hexahydrate (tetraaquatri-μ-oxalato-dibismuth(III) dihydrate, $\{[Bi_2(C_2O_4)_3(H_2O)_4] \cdot 2H_2O\}_n$) and dibismuth(III) trioxalate octahydrate (tetraaquatri-μ-oxalato-dibismuth(III) tetrahydrate $\{[Bi_2(C_2O_4)_3(H_2O)_4] \cdot 4H_2O\}_n$) are characterized by a three-dimensional network of Bi atoms connected by tetradentate oxalate groups. All ligand and 'free' water molecules are located in channels and voids. The mean Bi—O bond lengths are ~2.51 Å. The lone electron pairs on all Bi^{3+} cations are stereochemically inactive.

Comment

During work on a comprehensive review of the crystal chemistry and crystal structure types of complex metal oxalates (Fleck & Kolitsch, 2003), it was noted that data for bismuth(III) oxalates are very rare and no crystal structures have been reported. The only crystallographic study is that of Polla *et al.* (1984), who prepared and studied the space-group symmetries of two compounds, *viz.* monoclinic 'bismuth hydrogen oxalate' ['$Bi_2(C_2O_4)_3 \cdot H_2C_2O_4$'; $P2_1/c$] and triclinic 'bismuth oxalate heptahydrate' ['$Bi_2(C_2O_4)_3 \cdot 7H_2O$'; $P1$ or $P\overline{1}$], and who also investigated the thermal behaviour of these compounds during heating. The formulae given were based on wet-chemical analyses of the Bi^{3+} and $C_2O_4^{2-}$ contents (water was not determined directly) and a comparison between measured and calculated densities.

The present contribution reports the structure determinations of both compounds based on single-crystal X-ray diffraction data collected at 293 K. The present refined unit-cell parameters show good agreement with those given by Polla *et al.* (1984) [$a = 9.77$ (1) Å, $b = 8.20$ (1) Å, $c = 10.23$ (1) Å, $\beta = 99.6$ (1)° and $V = 808.1$ Å^3 (monoclinic compound), and $a = 9.18$ (1) Å, $b = 9.43$ (1) Å, $c = 11.17$ (1) Å, $\alpha = 101.0$ (1)°, $\beta = 101.7$ (1)°, $\gamma = 106.3$ (1)° and $V = 876.7$ Å^3 (triclinic compound)]. The solutions of the crystal structures, however, led in both cases to a revision of the chemical formulae. The correct structural formula of '$Bi_2(C_2O_4)_3 \cdot H_2C_2O_4$' (Polla *et al.*, 1984) is $[Bi_2(C_2O_4)_3(H_2O)_4] \cdot 2H_2O$, (I), which can be simplified to $Bi_2(C_2O_4)_3 \cdot 6H_2O$. Thus the monoclinic compound contains less oxalate per formula unit than previously reported. The correct formula of the compound '$Bi_2(C_2O_4)_3 \cdot 7H_2O$' (Polla *et al.*, 1984) is $Bi_2(C_2O_4)_3 \cdot 8H_2O$, (II), *i.e.* a formula with a higher water content.

The crystal structure of (I) has space-group symmetry $P2_1/c$, and the asymmetric unit contains one Bi atom, three C atoms, six oxalate O atoms and three water O atoms; the H atoms of the latter could not be located. Two of the water O atoms, *viz.* O*W*1 and O*W*2, are bonded to the Bi atom (Table 1), whereas the third, *viz.* O*W*3, belongs to a 'free' water molecule held in the structure only by medium-to-weak hydrogen bonds [O*W*3···O*W*1 = 2.691 (4) Å and O*W*···O1 = 2.801 (4) Å] and two further possible bonds to O*W*2 (> 2.85 Å). All detected atoms are in general positions.

The atomic arrangement in (I) can be described as a three-dimensional network of Bi atoms, connected by tetradentate

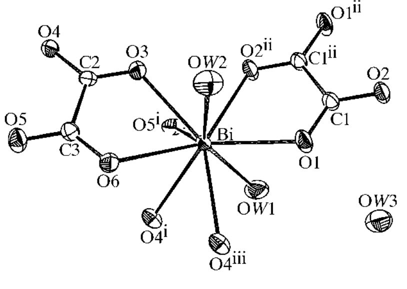

Figure 1
The connectivity in (I), shown with displacement ellipsoids at the 50% probability level. [Symmetry codes: (i) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x, -y, -z$; (iii) $x, -y - \frac{1}{2}, z - \frac{1}{2}$.]

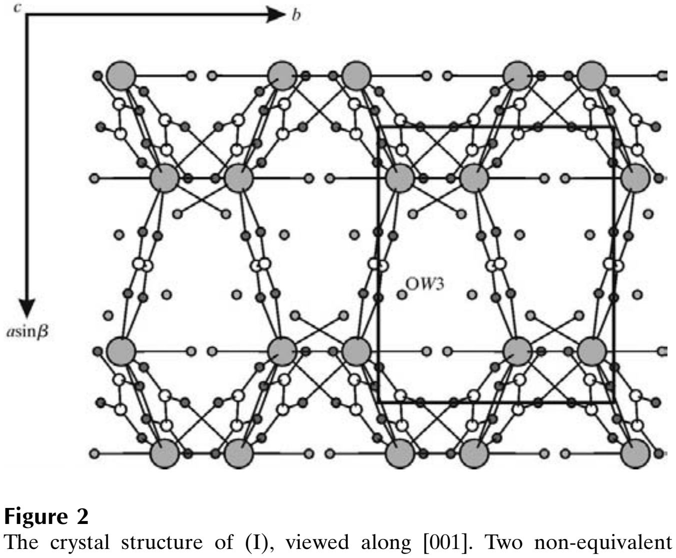

Figure 2
The crystal structure of (I), viewed along [001]. Two non-equivalent tetradentate oxalate groups connect the nine-coordinated crystallographically unique Bi atoms (large spheres) into a three-dimensional network. The 'free' water molecules, represented by atoms O*W*3, are located in channels parallel to both [100] and [001]. All Bi—O bonds are shown.

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oxalate groups (Figs. 1 and 2). The Bi atom is surrounded by nine O atoms (including two aqua ligands, O*W*1 and O*W*2) within 2.67 Å in a narrow range [2.326 (2)–2.663 (2) Å; mean Bi—O = 2.51 (11) Å]. The BiO_9 coordination polyhedron is relatively undistorted, and its coordination geometry indicates that the lone electron pair on the Bi^{3+} ion is not stereochemically active. The Bi atoms are connected *via* two tetradentate oxalate groups in two different directions, approximately along [411] and [$\bar{5}7\bar{5}$], thus creating a three-dimensional network. The three water molecules are all located in figure-of-eight-shaped channels, approximately parallel to both [100] and [001]. The C2/C3-based oxalate group shows a very small deviation from planarity [1.2 (4)°].

The calculated X-ray powder diffraction pattern shows reasonable agreement with the *d* values reported by Polla *et al.* (1984; see also ICDD-PDF 38-548, http://www.idcc.com), but the agreement with the previously reported intensities is relatively poor (possibly because of the effects of preferred orientation).

Compound (II) is triclinic (space group $P\bar{1}$). The asymmetric unit contains two Bi atoms, six C atoms, 12 oxalate O atoms and eight water molecules; the H atoms of the latter could not be located. Four of the eight water molecules, represented by atoms O*W*1, O*W*2, O*W*3 and O*W*4, are bonded to atoms Bi1 and Bi2. The remaining four water molecules, represented by atoms O*W*5, O*W*6, O*W*7 and O*W*8, can be considered as 'free' because they have no apparent bonds to the Bi atoms (all Bi—O*W* distances are greater than 4.3 Å). Atom O*W*8 occupies two sites, *viz*. O*W*8*A* and O*W*8*B*, with a separation of 0.77 (2) Å and a refined occupancy ratio of 0.31 (6):0.69 (6). All detected atoms are in general positions, as in the hexahydrate. If the different characters of the two types of water molecules are accounted for, the structural formula of the compound can be written as $[Bi_2(C_2O_4)_3(H_2O)_4]\cdot 4H_2O$.

The crystal structure of (II) is similar to that of (I) in that they are both based on a three-dimensional network formed by the connection between tetradentate oxalate groups and Bi atoms (Figs. 3 and 4). Atom Bi1 is surrounded by nine O atoms (including two aqua ligands, O*W*2 and O*W*3) within 3.5 Å in a relatively wide range [2.320 (3)–2.763 (3) Å; mean Bi1—O = 2.51 (14) Å]. Atom Bi2 also has nine O ligands (including two aqua ligands, O*W*1 and O*W*4) within 3.5 Å but in a slightly smaller range [2.349 (3)–2.681 (3) Å; mean Bi2—O = 2.51 (9) Å]. Thus the ligand environments of both Bi atoms (Table 2) are considerably more distorted than that of the Bi atom in (I). Nonetheless, the lone electron pairs on both of the Bi^{3+} ions in the octahydrate are not stereochemically active, a situation that is comparable to that in the hexahydrate. The eight water molecules are all located in voids and channels of the network, with the latter running parallel to all three major crystallographic axes.

The tetradentate oxalate group based on atoms C1 and C2 bridges atoms Bi1 and Bi2 roughly along [$\bar{3}4\bar{9}$]. The tetradentate oxalate group based on atoms C3 and C4 connects atoms Bi1 and Bi2 approximately along [$5\bar{8}\bar{4}$]. The tetradentate oxalate group based on atoms C5 and C6 connects atoms Bi1 and Bi2 approximately along [853]. All oxalate groups are non-planar, with maximum deviations from planarity of 7.1 (6) (C1/C2-based group), 4.1 (4) (C3/C4-based group) and 9.1 (4)° (C5/C6-based group). Probable hydrogen bonds are of medium-to-weak strength, having O···O distances all greater than 2.68 Å, with the single exception of the unusually short distance between atoms O*W*5 and O*W*8*A* [2.543 (4) Å].

The calculated X-ray powder diffraction pattern shows reasonable agreement with the *d* values reported by Polla *et al.* (1984; see also ICDD-PDF 38-549, http://www.idcc.com), but considerably weaker intensities for all reflections with *I* less than I_{100}.

Compounds (I) and (II) cannot be transformed directly into one another because their topologies are not similar, as shown in Figs. 1–4. This dissimilarity is also confirmed by analyses of

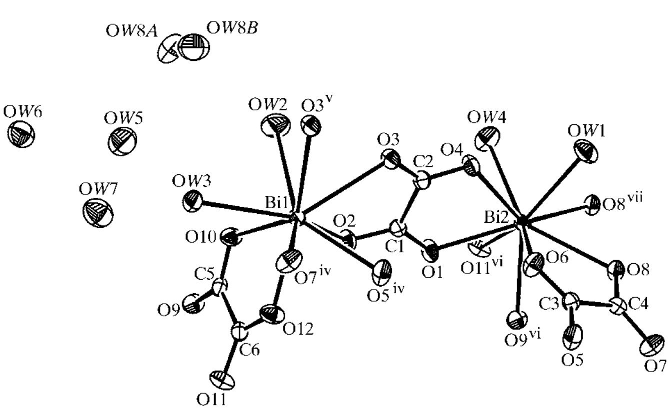

Figure 3

The connectivity in (II), shown with displacement ellipsoids at the 50% probability level. [Symmetry codes: (iv) $-x, -y+2, -z$; (v) $-x, -y+1, -z$; (vi) $-x+1, -y+2, -z$; (vii) $-x, -y+2, -z-1$.]

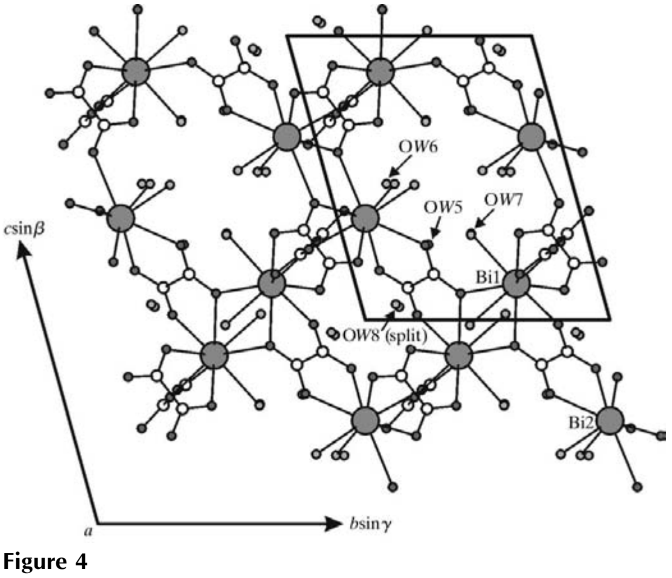

Figure 4

The crystal structure of (II), viewed along [100]. Three non-equivalent tetradentate oxalate groups link two nine-coordinated crystallographically unique Bi atoms (large spheres) in several different directions, thus forming a three-dimensional network. The four 'free' water molecules are labelled; atom O*W*8 is disordered (see text). All Bi—O bonds are shown and the unit cell is outlined.

the directions of the strongest interatomic connections and of the shortest Bi$\cdots$Bi distances. In (I), the Bi sublattice can be described as a corrugated layer parallel to the (100) plane (*cf.* Fig. 2), with a shortest Bi$\cdots$Bi distance of 4.413 (1) Å. In contrast, in (II), each Bi1 (Bi2) atom has only one other Bi1 (Bi2) atom as its next cationic neighbour within 6.0 Å [Bi1$\cdots$Bi1 = 4.534 (2) Å and Bi2$\cdots$Bi2 = 4.431 (1) Å].

A noteworthy observation was made after the intensity data collections of both compounds; the previously colourless transparent thick-tabular crystal of the monoclinic oxalate then exhibited a pale-brown colour (darker brown at the crystal edges) and revealed an hour-glass internal structure, but without having lost its transparency. The triclinic oxalate exhibited a very similar pale-brown colour and was also still completely transparent. These observations can be tentatively explained by the genesis of point defects due to irradiation with the X-ray beam. A similar colour-change phenomenon was recently observed in our laboratory for the basic lead nitrate $Pb_{13}O_8(OH)_6(NO_3)_4$, whose colour changed from pale yellow before the data collection to brown–orange afterwards (Kolitsch & Tillmanns, 2003). Similarly, no loss of transparency was noted.

Experimental

Both title compounds crystallized at room temperature from the same aqueous solution of $Bi(NO_3)_3\cdot 5H_2O$ and oxalic acid dihydrate. Compound (I) formed as small thick-tabular slightly rounded colourless crystals. Compound (II) crystallized as colourless prisms arranged in sprays.

Compound (I)

Crystal data

$[Bi_2(C_2O_4)_3(H_2O)_4]\cdot 2H_2O$
$M_r = 790.12$
Monoclinic, $P2_1/c$
$a = 9.776$ (2) Å
$b = 8.211$ (2) Å
$c = 10.224$ (2) Å
$\beta = 99.75$ (3)°
$V = 808.8$ (3) Å^3
$Z = 2$
$D_x = 3.244$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3097 reflections
$\theta = 2.0$–32.6°
$\mu = 21.82$ mm^{-1}
$T = 293$ (2) K
Fragment, colourless
0.09 × 0.07 × 0.04 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*HKL SCALEPACK*; Otwinowski & Minor, 1997)
$T_{\min} = 0.244$, $T_{\max} = 0.476$
5650 measured reflections
2924 independent reflections
2670 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.013$
$\theta_{\max} = 32.6°$
$h = -14 \rightarrow 14$
$k = -12 \rightarrow 12$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.048$
$S = 1.06$
2924 reflections
119 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.021P)^2 + 1.95P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.74$ e Å^{-3}
$\Delta\rho_{\min} = -1.85$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00226 (18)

Table 1
Selected interatomic distances (Å) for (I).

Bi—O2$^{\rm viii}$	2.326 (2)	C1—O1	1.243 (4)
Bi—O5$^{\rm ix}$	2.380 (2)	C1—O2	1.253 (4)
Bi—O3	2.435 (2)	C1—C1$^{\rm viii}$	1.553 (6)
Bi—O*W*1	2.449 (3)	C2—O3	1.246 (4)
Bi—O4$^{\rm ix}$	2.527 (2)	C2—O4	1.257 (4)
Bi—O1	2.537 (2)	C2—C3	1.553 (4)
Bi—O6	2.614 (2)	C3—O6	1.245 (4)
Bi—O*W*2	2.658 (3)	C3—O5	1.254 (4)
Bi—O4$^{\rm x}$	2.663 (2)		

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

Compound (II)

Crystal data

$[Bi_2(C_2O_4)_3(H_2O)_4]\cdot 4H_2O$
$M_r = 826.15$
Triclinic, $P\overline{1}$
$a = 9.194$ (2) Å
$b = 9.458$ (2) Å
$c = 11.176$ (2) Å
$\alpha = 101.15$ (3)°
$\beta = 101.76$ (3)°
$\gamma = 106.17$ (3)°
$V = 880.9$ (4) Å^3
$Z = 2$
$D_x = 3.115$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5313 reflections
$\theta = 2.0$–32.6°
$\mu = 20.06$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.18 × 0.03 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*HKL SCALEPACK*; Otwinowski & Minor, 1997)
$T_{\min} = 0.123$, $T_{\max} = 0.585$
10 808 measured reflections
6122 independent reflections
4981 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.029$
$\theta_{\max} = 32.6°$
$h = -13 \rightarrow 13$
$k = -14 \rightarrow 14$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.067$
$S = 1.01$
6122 reflections
264 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.029P)^2 + 0.6P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.73$ e Å^{-3}
$\Delta\rho_{\min} = -1.87$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0050 (2)

Table 2
Selected interatomic distances (Å) for (II).

Bi1—O12	2.320 (3)	Bi2—O8$^{\rm vii}$	2.681 (3)
Bi1—O2	2.335 (3)	C1—O1	1.246 (5)
Bi1—O10	2.426 (3)	C1—O2	1.265 (5)
Bi1—O5$^{\rm iv}$	2.430 (3)	C1—C2	1.545 (6)
Bi1—O7$^{\rm iv}$	2.564 (3)	C2—O3	1.251 (5)
Bi1—O*W*3	2.577 (3)	C2—O4	1.253 (5)
Bi1—O3	2.597 (3)	C3—O5	1.247 (5)
Bi1—O*W*2	2.614 (4)	C3—O6	1.251 (5)
Bi1—O3$^{\rm v}$	2.763 (3)	C3—C4	1.557 (5)
Bi2—O6	2.349 (3)	C4—O8	1.248 (5)
Bi2—O1	2.398 (3)	C4—O7	1.251 (5)
Bi2—O9$^{\rm vi}$	2.450 (3)	C5—O9	1.250 (5)
Bi2—O4	2.496 (3)	C5—O10	1.260 (5)
Bi2—O*W*1	2.498 (4)	C5—C6	1.548 (6)
Bi2—O*W*4	2.543 (4)	C6—O11	1.237 (5)
Bi2—O11$^{\rm vi}$	2.553 (3)	C6—O12	1.262 (5)
Bi2—O8	2.577 (3)		

Symmetry codes: (iv) $-x, 2 - y, -z$; (v) $-x, 1 - y, -z$; (vi) $1 - x, 2 - y, -z$; (vii) $-x, 2 - y, -1 - z$.

The highest electron-density peak in title compound (I) is 1.43 Å from the O1-atom site and the deepest hole is 0.88 Å from the Bi-atom site. The highest electron-density peak in title compound (II) is 1.48 Å from the O2-atom site and the deepest hole is 0.79 Å from the Bi1-atom site.

For both title compounds, data collection: *COLLECT* (Nonius, 2002); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Shape Software, 1999) and *ORTEP*-3 *for Windows* (Farrugia, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1420). Services for accessing these data are described at the back of the journal.

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