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Redetermination of the Structure of Bismuth(III) Nitrate Pentahydrate, $Bi(NO_3)_3.5H_2O$

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Abstract. $M_r = 485{\cdot}067$, triclinic, $P\bar{1}$, $a = 6{\cdot}520\ (8)$, $b = 8{\cdot}642\ (8)$, $c = 10{\cdot}683\ (9)$ Å, $\alpha = 100{\cdot}82\ (6)$, $\beta = 80{\cdot}78\ (6)$, $\gamma = 104{\cdot}77\ (7)$°, $V = 567{\cdot}7$ Å^3, $Z = 2$, $D_m = 2{\cdot}90\ (5)$, $D_x = 2{\cdot}837$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 150$ cm^{-1}, $F(000) = 452$, $T = 293\ (1)$ K; $R = 0{\cdot}087$ for 2228 observed diffractometer data. In the crystal structure each Bi^{3+} ion is coordinated bidentately by three NO_3^- ions and by four H_2O molecules, the fifth H_2O molecule is linked by weak hydrogen bonds [2·67 (2) and 2·78 (2) Å] to two other H_2O molecules. The NO_3^- ions are nearly planar.

Introduction. The crystal structure of bismuth(III) nitrate pentahydrate was determined by Herpin & Sudarsanan (1965) using the film technique. The visually estimated intensities were not corrected for absorption and a final R value of 0·14 was achieved for only 1600 reflexions. The redetermination of the crystal structure was undertaken to enable a precise comparison between the structure of this important bismuth compound and those of the related bismuth basic nitrates (Lazarini, 1978, 1979*a*,*b*) to be made.

Experimental. The crystals, grown from a saturated acid solution, decompose slightly in the air and in the X-ray beam as well. The refinement of a set of data, taken with a small and unprotected crystal, failed, therefore a new set of data was collected with a relatively big crystal, sealed together with a small amount of mother liquor into a glass capillary. D_m measured pycnometrically in CCl_4. The crystal was characterized by the following planes (in parentheses are the distances from the planes to the centre of the crystal): ±(010) (0·114 mm), ±$(01\bar{6})$ (0·472 mm), (515) (0·248 mm), $(\bar{5}1\bar{5})$ (0·248 mm), (011) (0·280 mm) and $(01\bar{1})$ (0·361 mm). Lattice parameters obtained from least-squares fit of the θ values of 30 reflexions. Intensities of 3002 independent reflexions ($-14 \le h \le 14$, $-12 \le k \le 12$, $-9 \le l \le 0$) measured, CAD-4 diffractometer (Mo $K\alpha$ radiation, ω–2θ scan, $0 < \theta < 30°$), 2228 with $I > 3\sigma(I)$ used in structural analysis. Intensities of three standard reflexions ($\bar{3}02$, $0\bar{3}5$, $3\bar{1}2$) measured after every 237 reflections decreased by 7·5%. Absorption correction applied (Gaussian grid method, 3038 points), maximum and minimum transmission factors 0·0812 and 0·0110 respectively. Crystal structure determined by usual Patterson–Fourier procedure and refined by full-matrix least squares (based on F^2) with anisotropic thermal parameters for Bi and O and isotropic for N to an R value of 0·087 (150 parameters). Isotropic extinction parameter ($9{\cdot}7 \times 10^{-3}$), crystal-size parameter (1·22) and $\sigma(F)$ weighting function included in last stage of refinement ($wR = 0{\cdot}090$). Maximum and average parameter shift to error ratio in final cycle 1·9 (scale) and 0·30 respectively. Final difference Fourier map flat ($+2{\cdot}2 \ge \Delta\rho \ge -1{\cdot}8$ e Å^{-3}). Atomic scattering factors for neutral atoms of Cromer & Mann (1968) and anomalous-dispersion corrections of Cromer & Liberman (1970) used. All calculations performed on DEC-1091 computer at the University of Ljubljana using *SHELX*76 (Sheldrick, 1976).

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Table 1. *Final positional parameters* ($\times 10^4$) *and isotropic thermal parameters* (Å^2 $\times 10^3$) *with e.s.d.'s in parentheses*

For Bi and O the equivalent isotropic thermal parameter is given [calculated as $U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$], for N the isotropic thermal parameter is given.

	x	y	z	U_{eq}/U
Bi	1888 (1)	3486 (1)	2312 (1)	17 (1)
N(1)	1038 (33)	6604 (22)	2037 (19)	33 (4)
O(11)	1559 (27)	5724 (20)	1004 (15)	34 (9)
O(12)	837 (31)	6037 (21)	3087 (15)	36 (9)
O(13)	522 (45)	7913 (25)	2058 (22)	74 (10)
N(2)	−1611 (29)	1758 (20)	4093 (17)	24 (3)
O(21)	−1533 (24)	3203 (18)	3913 (15)	26 (7)
O(22)	−255 (30)	1072 (21)	3455 (19)	45 (9)
O(23)	−3069 (29)	1090 (21)	4831 (20)	40 (9)
N(3)	3313 (32)	1586 (22)	−451 (19)	34 (4)
O(31)	3558 (28)	3104 (18)	−68 (15)	30 (7)
O(32)	2263 (37)	632 (23)	295 (20)	52 (9)
O(33)	4111 (42)	1113 (23)	−1533 (18)	50 (9)
O(*W*1)	5309 (22)	5222 (16)	2058 (14)	26 (7)
O(*W*2)	2915 (25)	4392 (18)	4354 (14)	31 (7)
O(*W*3)	4353 (24)	1912 (17)	2606 (16)	27 (7)
O(*W*4)	8430 (24)	2465 (17)	1067 (12)	27 (7)
O(*W*5)	6781 (31)	7577 (19)	4071 (17)	37 (9)

Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Bi–O(11)	2·66 (1)	Bi–O(*W*1)	2·36 (1)
Bi–O(12)	2·43 (2)	Bi–O(*W*2)	2·32 (1)
Bi–O(21)	2·57 (1)	Bi–O(*W*3)	2·44 (1)
Bi–O(22)	2·59 (2)	Bi–O(*W*4)	2·67 (1)
Bi–O(31)	2·60 (1)	O(*W*5)–O(*W*1)	2·78 (2)
Bi–O(32)	2·99 (2)	O(*W*5)–O(*W*2^{i})	2·67 (2)
N(1)–O(11)	1·27 (2)	O(11)–N(1)–O(12)	117 (2)
N(1)–O(12)	1·28 (2)	O(11)–N(1)–O(13)	123 (2)
N(1)–O(13)	1·25 (2)	O(12)–N(1)–O(13)	119 (2)
N(2)–O(21)	1·28 (2)	O(21)–N(2)–O(22)	117 (2)
N(2)–O(22)	1·23 (2)	O(21)–N(2)–O(23)	120 (2)
N(2)–O(23)	1·23 (2)	O(22)–N(2)–O(23)	123 (2)
N(3)–O(31)	1·27 (2)	O(31)–N(3)–O(32)	118 (2)
N(3)–O(32)	1·25 (2)	O(31)–N(3)–O(33)	119 (2)
N(3)–O(33)	1·23 (3)	O(32)–N(3)–O(33)	122 (2)

Symmetry code: (i) $1 - x$, $1 - y$, $1 - z$.

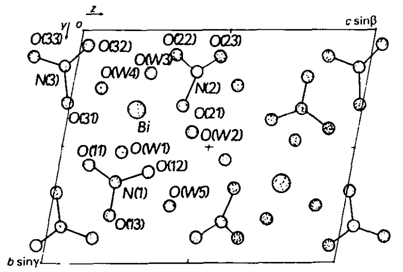

Fig. 1. The projection of the structure along **a**.

The final atomic parameters are in Table 1.* The projection of a part of the structure along **a** with the atom-numbering system is shown in Fig. 1. Some important interatomic distances and angles are given in Table 2.

Discussion. The mainly ionic crystal structure of the title compound consists of Bi^{3+} ions, NO_3^- ions and H_2O molecules. The Bi^{3+} ion is coordinated by four H_2O molecules, by two nearly symmetrically bidentate NO_3^- ions and by one asymmetrically bidentate NO_3^- ion. The coordination polyhedron is thoroughly irregular. Nine of the Bi–O distances are in the range between 2·32 (1) and 2·67 (2) Å, while the tenth Bi–O distance of the asymmetrically bidentate NO_3^- ion is much longer, 2·99 (2) Å. This distance is within the sum of van der Waals radii (about 3·4 Å, Bondi, 1964), but the interaction is obviously weak, considering the sum of ionic radii (about 2·6 Å, Shannon & Prewitt, 1969) or the corresponding contacts in bismuth basic nitrates and double nitrate (Lazarini, 1978, 1979*a*,*b*; Lazarini & Leban, 1982). The fifth H_2O molecule is linked by weak hydrogen bonds [2·67 (2) and 2·78 (2) Å] to two other H_2O molecules. The NO_3^- ions are nearly planar.

The results of this structure determination differ slightly from the results of the earlier determination (Herpin & Sudarsanan, 1965) in which only three of the H_2O molecules have been considered to coordinate to the Bi^{3+} ion. The title compound seems to be isostructural with tetraaquatrinitratoyttrium(III) hydrate (Eriksson, 1982).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42197 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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