

## SHORT STRUCTURAL PAPERS

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Bismuth Basic Nitrate  $[\text{Bi}_6(\text{H}_2\text{O})(\text{NO}_3)\text{O}_4(\text{OH})_4](\text{NO}_3)_5$ 

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**Abstract.**  $[\text{Bi}_6(\text{H}_2\text{O})(\text{NO}_3)\text{O}_4(\text{OH})_4](\text{NO}_3)_5$ , monoclinic,  $P2_1/c$ ,  $a = 9.313$  (2),  $b = 13.514$  (7),  $c = 19.575$  (5) Å,  $\beta = 114.12$  (1)°,  $D_m = 5.32$  (5),  $D_c = 5.405$  Mg m<sup>-3</sup>,  $Z = 4$ ,  $\mu(\text{Mo } K\alpha) = 44.65$  mm<sup>-1</sup>,  $R = 0.052$  for 1989 reflexions [ $I > 2\sigma(I)$ ]. In the polycation of this structure the six Bi atoms are located at the corners of an octahedron with the O atoms and OH groups above the centres of the octahedral faces. Each O atom of the OH groups has three Bi neighbours arranged pyramidally at longer distances, while the remaining O atoms are linked to three nearly coplanar Bi atoms at shorter distances. Furthermore a  $\text{NO}_3^-$  group and the water molecule are bound to two neighbouring Bi atoms.

**Introduction.** This work is part of a systematic study of bismuth basic nitrates (Lazarini, 1978, 1979). It is hoped that the known crystal structures of various Bi basic nitrates will help to explain the mechanism of the hydrolysis of bismuth(III) nitrate. In the previous papers the important role of the polycations in crystal structures of Bi basic nitrates was emphasized. The first solid hydrolysis product of  $\text{Bi}(\text{NO}_3)_3$  at pH values below 1.2,  $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot 4\text{H}_2\text{O}$  (Lazarini, 1979), contains polycations which seem to be the product of intramolecular condensation of  $[\text{Bi}_6(\text{OH})_{12}]^{6+}$  ions, present in solutions of Bi basic salts (Levy, Danford & Agron, 1959; Maroni & Spiro, 1968). At pH values between 1.2 and 2.4 another hydrolysis product,  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ , can be obtained. Its crystal structure (Lazarini, 1978) contains polycations in which pairs of  $[\text{Bi}_6\text{O}_5(\text{OH})_3]^{5+}$  groups are joined through two bridging O atoms. Crystals of the title compound can be prepared by heating a suspension of  $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot 4\text{H}_2\text{O}$  at 323 K for several days (Rutten, 1902). The considerably smaller unit-cell volume of the title compound, 2248.5 Å<sup>3</sup>, compared to that of  $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot 4\text{H}_2\text{O}$ , 2443.7 Å<sup>3</sup>, which cannot be entirely explained by the lower crystalline-water content, was a

good reason to start the crystal structure analysis. Gattow & Kiel (1968) have not succeeded in solving this structure from two-dimensional data.

A well-developed crystal selected for the intensity measurements was characterized by the following planes (the distances from the crystal faces to an arbitrary origin inside the crystal are given in parentheses):  $\pm\{011\}$  (0.0525 mm),  $\pm\{0\bar{1}1\}$  (0.0525 mm),  $\pm\{102\}$  (0.0650 mm),  $\pm\{110\}$  (0.0950 mm), and  $\pm\{\bar{1}10\}$  (0.0950 mm). The intensity data were collected at 293 (1) K with an Enraf-Nonius CAD-4 diffractometer. The experimental conditions were: graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å),  $\omega$ - $2\theta$  scan,  $\theta_{\min} = 1^\circ$ ,  $\theta_{\max} = 25^\circ$ ,  $2\theta$  scan width ( $^\circ$ ) =  $0.6 + 0.2 \tan \theta$ , aperture (mm) =  $3.0 + 1.0 \tan \theta$ , maximum scan time 30 s, background:  $\frac{1}{4}$  of the scan time at each of the scan limits. A set of 3913 independent reflexions were recorded and, of these, 1989 with  $I > 2\sigma(I)$  (calculations based on counting statistics) were used in the refinement. The usual corrections were applied for Lorentz and polarization effects. Great attention was given to absorption correction [ $\mu(\text{Mo } K\alpha) = 44.65$  mm<sup>-1</sup>]. The transmission factors, calculated from the measured crystal dimensions (Gaussian-grid method, 392 sampling points, crystal volume 0.00163 mm<sup>3</sup>) range from 0.0199 to 0.0704. The unit-cell parameters were obtained from a least-squares fit of the  $\theta$  values of 15 reflexions measured on the diffractometer. The space group  $P2_1/c$  was determined from systematic absences ( $h0l: l = 2n + 1; 0k0: k = 2n + 1$ ).

The positions of six Bi atoms of the asymmetric unit were determined using *MULTAN* (Declercq, Germain, Main & Woolfson, 1973). After partial refinement by the least-squares method the O and N atoms were found from a difference Fourier map. The structure was then refined by full-matrix least-squares techniques with anisotropic thermal parameters for Bi, isotropic for O and N atoms and with an anomalous-dispersion correction for Bi. The function minimized in the least-squares procedure was  $\sum w(F_o - F_c)^2$ . The weighting

scheme applied was as follows: for  $|F_o| < 150$ ,  $w_F = (|F_o|/150)^{2.9}$ ; for  $150 \leq |F_o| \leq 700$ ,  $w_F = 1.0$ ; for  $|F_o| > 700$ ,  $w_F = (700/|F_o|)^{2.9}$ ; for  $\sin \theta < 0.15$ ,  $w_s = (\sin \theta/0.15)^{2.8}$ ; for  $0.15 \leq \sin \theta \leq 0.30$ ,  $w_s = 1.0$ ; for  $\sin \theta > 0.30$ ,  $w_s = (0.30/\sin \theta)^{2.2}$ ;  $w = 0.1w_Fw_s$ . An isotropic extinction parameter (Larson, 1967) was also included in the final stage of the refinement [ $g = 3.69(7) \times 10^{-3}$ ]. Final  $R$  values are:  $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.052$  and  $R_w = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2} = 0.041$  for 1989 reflexions and 188 parameters. The average parameter shift-to-error ratio was 0.19 in the final cycle. A final difference Fourier map revealed no peaks greater than  $1.1 \text{ e } \text{\AA}^{-3}$ .

All calculations were performed on the CDC Cyber 72 computer of RRC Ljubljana with the XRAY system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) and with MULTAN (Declercq, Germain, Main & Woolfson, 1973). Atomic scattering factors for neutral atoms tabulated by Cromer & Mann (1968) were applied together with the values of  $f'$  and  $f''$  for anomalous-dispersion corrections of Cromer & Liberman (1970).

The positional parameters of the Bi atoms are listed in Table 1 and those of O and N atoms in Table 2.\* The

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33998 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final positional parameters ( $\times 10^4$ ) for Bi atoms with standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Bi(1)	1230 (2)	1202 (1)	1416 (1)
Bi(2)	1259 (2)	3987 (1)	1501 (1)
Bi(3)	1587 (1)	2716 (1)	-82 (1)
Bi(4)	4561 (1)	2511 (1)	2833 (1)
Bi(5)	5081 (2)	3923 (1)	1335 (1)
Bi(6)	4988 (2)	1241 (1)	1209 (1)

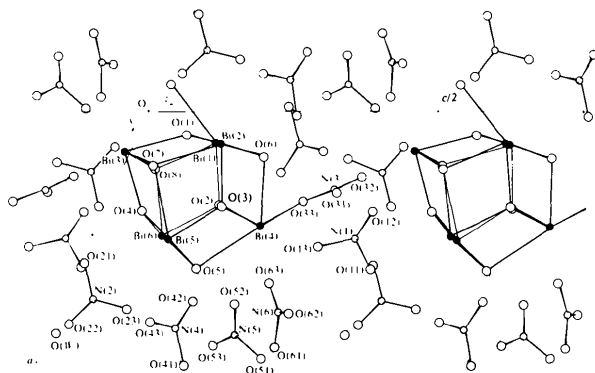


Fig. 1. A projection of the structure along  $b/2$ .

structure in the projection along  $b/2$  and the atom numbering system used are shown in Fig. 1. Some important interatomic distances and angles are given in Table 3.

**Discussion.** It is obvious from the crystal-structure analysis that the considerably smaller unit-cell volume of  $[\text{Bi}_6(\text{H}_2\text{O})(\text{NO}_3)\text{O}_4(\text{OH})_4](\text{NO}_3)_5$  compared to that of  $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot 4\text{H}_2\text{O}$  is a consequence of much shorter distances between the polycations and  $\text{NO}_3^-$  anions or water molecules. The distances from the O(W) atom of the  $\text{H}_2\text{O}$  molecule and O(33) atom of a  $\text{NO}_3^-$  group to two neighbouring Bi atoms fall in the range of Bi-OH distances. Other close contacts between Bi atoms and some of the  $\text{NO}_3^-$  anions, as well as the possible hydrogen bonds (dotted lines in Fig. 1) are listed in Table 3. The fact, that some of the  $\text{NO}_3^-$  groups should be bound to Bi atoms has already been established by IR spectroscopy (Kiel, 1967). The geometry of the  $\text{Bi}_6\text{O}_4(\text{OH})_4$  part of the polycation is very similar to the  $[\text{Bi}_6\text{O}_4(\text{OH})_4]^{6+}$  polycation or to the

Table 2. Final positional parameters ( $\times 10^4$ ) and thermal parameters ( $\text{\AA}^2 \times 10^3$ ) for O and N atoms with standard deviations in parentheses

The isotropic temperature factor is in the form:  
 $\exp[-8\pi^2 U(\sin \theta/\lambda)^2]$ .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
O(1)	937 (27)	2590 (20)	849 (12)	16 (5)
O(2)	3795 (34)	1434 (17)	1988 (14)	14 (6)
O(3)	3772 (37)	3701 (21)	2001 (16)	20 (7)
O(4)	3988 (23)	2645 (17)	666 (11)	12 (5)
O(5)	6254 (25)	2571 (20)	2067 (12)	14 (5)
O(6)	1783 (28)	2642 (20)	2351 (13)	18 (6)
O(7)	2140 (39)	4173 (20)	528 (16)	15 (7)
O(8)	2237 (34)	962 (18)	550 (13)	12 (6)
O(11)	6041 (44)	3419 (25)	5084 (19)	34 (8)
O(12)	3918 (43)	4244 (25)	4658 (19)	45 (9)
O(13)	5361 (40)	4122 (24)	3971 (18)	38 (8)
O(21)	6034 (39)	4034 (23)	100 (17)	34 (7)
O(22)	8498 (33)	4121 (19)	291 (15)	19 (6)
O(23)	7864 (37)	3500 (22)	1156 (17)	31 (7)
O(31)	3185 (36)	2330 (23)	3892 (17)	32 (7)
O(32)	2520 (42)	904 (24)	4178 (19)	40 (8)
O(33)	3565 (32)	1036 (19)	3390 (14)	18 (6)
O(41)	10091 (46)	309 (22)	2547 (20)	37 (7)
O(42)	7545 (41)	197 (26)	2257 (19)	44 (8)
O(43)	8370 (36)	1255 (22)	1662 (17)	31 (7)
O(51)	9825 (39)	4054 (23)	3876 (17)	34 (8)
O(52)	7609 (37)	4239 (23)	2971 (17)	33 (7)
O(53)	9287 (38)	3082 (23)	2930 (17)	34 (8)
O(61)	9333 (42)	1011 (24)	4020 (18)	36 (8)
O(62)	7972 (31)	2321 (21)	3999 (14)	25 (6)
O(63)	6782 (38)	961 (22)	3428 (16)	30 (7)
O(W)	8838 (36)	887 (21)	120 (16)	29 (7)
N(1)	5023 (40)	3918 (25)	4569 (18)	22 (7)
N(2)	7452 (38)	3902 (24)	508 (17)	18 (7)
N(3)	3038 (40)	1406 (22)	3809 (19)	15 (7)
N(4)	8664 (37)	569 (22)	2166 (17)	13 (7)
N(5)	8906 (39)	3819 (25)	3236 (18)	21 (7)
N(6)	7982 (43)	1436 (24)	3804 (20)	22 (8)

Table 3. *Interatomic distances (Å) and angles (°) with standard deviations in parentheses*

O(1)—Bi(1)	2.14 (3)	Bi(1)—O(1)—Bi(2)	119 (1)
O(1)—Bi(2)	2.23 (3)	Bi(1)—O(1)—Bi(3)	119 (1)
O(1)—Bi(3)	2.15 (3)	Bi(2)—O(1)—Bi(3)	114 (1)
O(2)—Bi(1)	2.21 (3)	Bi(1)—O(2)—Bi(4)	117 (1)
O(2)—Bi(4)	2.10 (2)	Bi(1)—O(2)—Bi(6)	112 (1)
O(2)—Bi(6)	2.24 (4)	Bi(4)—O(2)—Bi(6)	121 (1)
O(3)—Bi(2)	2.17 (3)	Bi(2)—O(3)—Bi(4)	116 (2)
O(3)—Bi(4)	2.19 (3)	Bi(2)—O(3)—Bi(5)	119 (1)
O(3)—Bi(5)	2.14 (4)	Bi(4)—O(3)—Bi(5)	117 (2)
O(4)—Bi(3)	2.12 (2)	Bi(3)—O(4)—Bi(5)	119 (1)
O(4)—Bi(5)	2.15 (2)	Bi(3)—O(4)—Bi(6)	120 (1)
O(4)—Bi(6)	2.19 (2)	Bi(5)—O(4)—Bi(6)	113.5 (8)
O(5)—Bi(4)	2.58 (3)	Bi(4)—O(5)—Bi(5)	98 (1)
O(5)—Bi(5)	2.30 (3)	Bi(4)—O(5)—Bi(6)	98.1 (9)
O(5)—Bi(6)	2.41 (2)	Bi(5)—O(5)—Bi(6)	100.7 (7)
O(6)—Bi(1)	2.58 (3)	Bi(1)—O(6)—Bi(2)	99.0 (9)
O(6)—Bi(2)	2.38 (3)	Bi(1)—O(6)—Bi(4)	95 (1)
O(6)—Bi(4)	2.37 (2)	Bi(2)—O(6)—Bi(4)	102 (1)
O(7)—Bi(2)	2.37 (4)	Bi(2)—O(7)—Bi(3)	105 (1)
O(7)—Bi(3)	2.25 (3)	Bi(2)—O(7)—Bi(5)	97 (1)
O(7)—Bi(5)	2.56 (3)	Bi(3)—O(7)—Bi(5)	100 (1)
O(8)—Bi(1)	2.27 (3)	Bi(1)—O(8)—Bi(3)	98 (1)
O(8)—Bi(3)	2.63 (2)	Bi(1)—O(8)—Bi(6)	104.7 (9)
O(8)—Bi(6)	2.38 (3)	Bi(3)—O(8)—Bi(6)	95.9 (9)
O(33)—Bi(4)	2.62 (3)	O(33)—Bi(4)—O(2)	75 (1)
O(W <sup>1</sup> )—Bi(1)	2.64 (3)	O(33)—Bi(4)—O(3)	143 (1)
O(22 <sup>1</sup> )—Bi(2)	2.70 (2)	O(33)—Bi(4)—O(5)	132.1 (9)
O(32 <sup>11</sup> )—Bi(3)	2.71 (4)	O(33)—Bi(4)—O(6)	73.0 (9)
O(61 <sup>111</sup> )—Bi(3)	2.73 (3)	O(W <sup>1</sup> )—Bi(1)—O(1)	76.3 (8)
O(W <sup>1</sup> )—O(1 <sup>11</sup> )	2.74 (6)	O(W <sup>1</sup> )—Bi(1)—O(2)	146 (1)
O(5)—O(53)	2.72 (4)	O(W <sup>1</sup> )—Bi(1)—O(6)	130.6 (8)
O(7)—O(22 <sup>1v</sup> )	2.73 (4)	O(W <sup>1</sup> )—Bi(1)—O(8)	73 (1)

## Symmetry code

- (i)  $-1 + x, y, z$   
 (ii)  $x, \frac{1}{2} - y, -\frac{1}{2} + z$   
 (iii)  $-1 + x, \frac{1}{2} - y, -\frac{1}{2} + z$   
 (iv)  $1 - x, 1 - y, -z$

[Bi<sub>6</sub>O<sub>5</sub>(OH)<sub>3</sub>]<sup>5+</sup> group found in other Bi basic nitrates (Lazarini, 1978, 1979). The six Bi atoms are located at the corners of an octahedron, with the O atoms above the centres of the octahedral faces. The four O atoms of the OH groups [O(5) to O(8)], forming a tetrahedron, have three Bi neighbours arranged pyramidally at longer distances, while the remaining four O atoms [O(1) to O(4)], forming a tetrahedron as well, are linked to three more nearly coplanar Bi atoms at shorter distances. The association of H atoms with those O atoms linked to the Bi atoms at longer distances is discussed in detail in a previous paper (Lazarini, 1978). The shortest distance between two O atoms in the polycation is O(1)—O(7), 2.61 (4) Å. The shortest distance between two Bi atoms, Bi(5)—Bi(6), 3.631 (3) Å, is considerably longer than the distances in metallic Bi, 3.111 and 3.481 Å (*International Tables for X-ray Crystallography*, 1962). The coordination polyhedron around Bi atoms, considering only the Bi<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> part, appears to be a distorted pseudo-trigonal-bipyramid with the

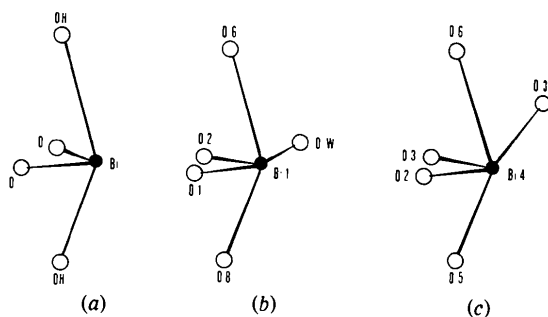


Fig. 2. A schematic representation of the coordination geometry: (a) around Bi(2), Bi(3), Bi(5) and Bi(6), (b) around Bi(1) and (c) around Bi(4).

electron lone pair at one of the equatorial corners (Fig. 2a). The angles O(equat.)—Bi—O(equat.) range from 88.6 (9) to 91.2 (9)°, O(apic.)—Bi—O(apic.) from 125.5 (9) to 127.9 (9)°, and O(equat.)—Bi—O(apic.) from 67.1 (9) to 76 (1)°. Although two additional atoms O(W) and O(33) are bound to Bi(1) and Bi(4) respectively, enough space is left for the electron lone pair (Fig. 2b and c). Within the NO<sub>3</sub><sup>-</sup> groups the N—O bond distances range from 1.19 (6) to 1.30 (4) Å and the O—N—O angles from 116 (4) to 125 (3)°. The differences in NO<sub>3</sub><sup>-</sup> dimensions are not statistically significant.

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