

The Crystal Structure of a Bismuth Basic Nitrate, $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$

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The bismuth basic nitrate $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 17.152$ (1), $b = 9.181$ (1), $c = 17.752$ (1) Å, $\beta = 127.830$ (7)° and $Z = 4$. The structure was solved by direct methods and Fourier techniques and refined by a least-squares method to $R = 0.063$ for 2554 reflexions [$I > 4\sigma(I)$] measured on a four-circle single-crystal diffractometer and corrected for absorption [$\mu(\text{Mo } K\alpha) = 454.4 \text{ cm}^{-1}$]. The structure consists of polycations, in which pairs of cage-like groups $[\text{Bi}_6\text{O}_5(\text{OH})_3]$ are joined across the symmetry centres through two bridging O atoms, together with nitrate anions and water molecules. In the $[\text{Bi}_6\text{O}_5(\text{OH})_3]$ group the six Bi atoms are located at the corners of an octahedron with the O atoms above the centres of the octahedral faces. The three OH groups and the bridging O atom have three Bi neighbours arranged pyramidally at longer distances, while the remaining four O atoms are linked to three more nearly coplanar Bi neighbours by shorter distances. Bi–Bi interactions were not observed.

Introduction

About fifteen bismuth basic nitrates have been described in the literature since the 17th century (Pascal, 1958). Only a few of them have been confirmed unequivocally by more up to date investigations. The main reasons for such a great variety of compounds and for some confusion arising from the older literature are: difficulties in chemical analysis and in isolating pure chemical substances, the fact that water is very loosely bound in these compounds and the lack of powerful physical methods (spectroscopic or diffraction) for identification. The most adequately characterized bismuth basic nitrates are $\text{Bi}_2\text{O}_3 \cdot \text{N}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ (= $\text{BiONO}_3 \cdot \text{H}_2\text{O}$); $\text{Bi}_2\text{O}_3 \cdot \text{N}_2\text{O}_5 \cdot \text{H}_2\text{O}$ (= $2\text{BiONO}_3 \cdot \text{H}_2\text{O}$); the title compound $6\text{Bi}_2\text{O}_3 \cdot 5\text{N}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$; $3\text{Bi}_2\text{O}_3 \cdot 2\text{N}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$; and $2\text{Bi}_2\text{O}_3 \cdot \text{N}_2\text{O}_5 \cdot \text{H}_2\text{O}$ (= $\text{BiONO}_3 \cdot \text{BiOOH}$) (only simple stoichiometric formulae are given) (Ozols, 1950*a,b,c*; Gattow & Schott, 1963; Kiel, 1967; Brčić, Kolar, Lazarini & Malešič, 1973). For the first three of these compounds it is possible to grow crystals with dimensions suitable for X-ray experiments. The title compound can be obtained in the pH range 1.2 to 2.4 by adding large quantities of water to an acid solution of $\text{Bi}(\text{NO}_3)_3$ or from a solution of $\text{BiONO}_3 \cdot \text{H}_2\text{O}$, which is the first hydrolysis product of $\text{Bi}(\text{NO}_3)_3$ at pH values below 1.2. The title compound appears to be more stable than $\text{BiONO}_3 \cdot \text{H}_2\text{O}$. Further details of the chemical relationships between different bismuth basic nitrates will be published elsewhere.

Solutions of perchlorate salts contain $[\text{Bi}_6(\text{OH})_{12}]^{6+}$ polycations which are stable over a wide range of pH, as shown by diffraction methods (Levy, Danford &

Agron, 1959) as well as by spectroscopic methods (Maroni & Spiro, 1968). It seems likely that such polycations or products of their intra- and intermolecular condensation have an important role in crystal structures of bismuth basic salts. Unfortunately, no crystal structure containing such polycations has yet been found. Attempts to carry out the complete structural analysis have failed (Gattow & Kiel, 1968; Sundvall, 1974), probably because of the very high scattering power of Bi in comparison to O and N, or because of very high absorption effects. The crystal structure of $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ appears to be the first example which confirms unequivocally the presence of polycations in solid bismuth basic salts.

Encouraged by the successful crystal structure analysis of the title compound, we intend to perform the structural analysis of some other bismuth basic nitrates in order to elucidate the chemistry as well as the stereochemistry of these compounds.

Experimental

A solution of 10 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 10 ml of 65% HNO_3 was diluted with water to 1000 ml. By adding 4% NaOH the pH of the solution was increased to 1.5 and a very fine crystalline precipitate of the title compound was obtained. After a few months some crystals of suitable dimensions for X-ray experiments were grown from this suspension at room temperature. The crystals were dried on filter paper. Chemical analysis: calculated for $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$: Bi 71.69%, NO_3 17.73%; found: Bi 71.2%, NO_3 17.5%. The chemical composition differs from that quoted in

the literature, because Gattow & Schott (1963) dried the crystals at 120°C, while in one of our earlier investigations on bismuth basic nitrates (Brčić, Kolar, Lazarini & Malešič, 1973) the crystals were dried by means of acetone and petroleum ether. The density of the title compound was measured pycnometrically using dry toluene.

A well-developed crystal, selected for diffraction measurements, was characterized by the following planes (the distances from the crystal faces to an arbitrary origin inside the crystal are in parentheses): $\pm\{100\}$ (0.045 mm), $\pm\{110\}$ (0.158 mm), $\pm\{1\bar{1}0\}$ (0.158 mm) and $\pm\{10\bar{1}\}$ (0.035 mm).

The unit-cell parameters were calculated from Al-calibrated zero-layer $hk0$ and $h0l$ Weissenberg photographs [$\lambda(\text{Cu } K\alpha_1) = 1.54051 \text{ \AA}$, $t = 20^\circ\text{C}$] by the least-squares treatment of 45 high-order reflexions. The space group $P2_1/c$ was determined from systematic absences ($h0l: l = 2n + 1$, $0k0: k = 2n + 1$). The crystal data are listed in Table 1. The unit-cell parameters are in agreement with those found by Gattow & Schott (1963) [$a = 17.58$ (4), $b = 9.15$ (3), $c = 27.20$ (5) \AA , $\beta = 83.2$ (3)°] considering the fact that they chose a non-primitive unit cell with the corresponding space group $B2_1/a$ but quoted it as $P2_1/c$ by mistake. The following transformation matrix should be applied to transform the conventional primitive unit cell to the non-primitive, chosen by Gattow & Schott (1963):

$$\begin{pmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ 2 & 0 & 1 \end{pmatrix}$$

The intensity data were collected at 20 (1)°C with an Enraf-Nonius CAD-4 diffractometer. The experimental conditions were: graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$), $\omega-2\theta$ scan, $\theta_{\min} = 1^\circ$, $\theta_{\max} = 25^\circ$, 2θ scan width (°) $0.7 + 0.2 \tan \theta$, aperture (mm) $2.5 + 0.9 \tan \theta$, maximum scan time 40 s, background: $\frac{1}{4}$ of the scan time at each of the scan limits. A set of 3880 independent reflexions was recorded. During the refinement procedure, it became apparent that the weaker reflexions were badly measured. Therefore all reflexions with $I < 4\sigma(I)$ (calculations based on counting statistics) were rejected and only 2554 reflexions were used in the refinement. The usual corrections were applied for Lorentz and polarization effects. Great attention was paid to absorption

Table 1. *Crystal data*

$[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$	$F(000) = 3000$
FW = 1749.02	$V = 2208.18 \text{ \AA}^3$
$a = 17.152$ (1) \AA	$D_o = 5.19$ (6) g cm^{-3}
$b = 9.181$ (1)	$D_c = 5.260$
$c = 17.752$ (1)	$Z = 4$
$\beta = 127.830$ (7)°	$\mu(\text{Mo } K\alpha) = 454.4 \text{ cm}^{-1}$
Space group $P2_1/c$	

corrections [$\mu(\text{Mo } K\alpha) = 454.4 \text{ cm}^{-1}$]. The corrections A^* , calculated from the measured crystal dimensions (Gaussian-grid method, 1680 sampling points, crystal volume 0.00265 mm^3), range from 9.6 to 63.9.

Structure determination and refinement

The positions of six Bi atoms of the asymmetric unit were determined by direct methods using *MULTAN* (Declercq, Germain, Main & Woolfson, 1973). 32 sets of phases were calculated with 120 normalized structure factors and 2000 unique phase relationships. After

Table 2. *Final positional parameters ($\times 10^4$) for Bi atoms with standard deviations in parentheses*

	x	y	z
Bi(1)	445 (1)	8280 (2)	4473 (1)
Bi(2)	2338 (1)	8155 (2)	4092 (1)
Bi(3)	3098 (1)	8485 (2)	6554 (1)
Bi(4)	878 (1)	4944 (2)	3736 (1)
Bi(5)	3494 (1)	5090 (2)	5813 (1)
Bi(6)	1403 (1)	5257 (2)	6014 (1)

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

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

	x	y	z	U (\AA^2)
O(1)	996 (20)	7298 (31)	3809 (20)	13 (6)
O(2)	3252 (22)	7392 (33)	5539 (21)	18 (7)
O(3)	1657 (24)	7583 (35)	5868 (23)	21 (7)
O(4)	2025 (22)	4701 (36)	5270 (22)	11 (7)
O(5)	221 (23)	5871 (34)	4518 (22)	9 (7)
O(6)	2342 (24)	5536 (35)	4039 (23)	21 (7)
O(7)	1955 (21)	9497 (32)	4934 (20)	16 (6)
O(8)	3414 (23)	6026 (35)	6919 (22)	22 (7)
O(11)	1694 (25)	2173 (38)	3975 (24)	30 (8)
O(12)	1241 (27)	603 (40)	2841 (26)	34 (9)
O(13)	1142 (23)	2909 (35)	2558 (22)	20 (7)
O(21)	873 (26)	7837 (39)	2014 (25)	33 (8)
O(22)	453 (26)	5724 (40)	2004 (25)	31 (9)
O(23)	-130 (36)	6681 (60)	668 (35)	61 (13)
O(31)	2845 (30)	2028 (48)	2383 (29)	47 (11)
O(32)	2457 (30)	4350 (46)	2149 (29)	47 (11)
O(33)	1475 (27)	2782 (41)	1056 (26)	34 (9)
O(41)	4624 (34)	4064 (52)	2683 (33)	56 (12)
O(42)	3592 (29)	3181 (47)	1262 (28)	45 (10)
O(43)	4686 (24)	1716 (40)	2429 (24)	30 (8)
O(51)	4551 (32)	6717 (52)	3683 (30)	53 (11)
O(52)	4164 (27)	7167 (41)	4603 (26)	35 (9)
O(53)	3058 (24)	7308 (36)	3044 (23)	22 (8)
O(W1)	4549 (26)	214 (43)	3724 (25)	37 (9)
O(W2)	3603 (28)	498 (43)	4591 (27)	41 (10)
O(W3)	3714 (34)	3547 (54)	4249 (33)	61 (12)
N(1)	1366 (31)	1893 (50)	3115 (30)	31 (10)
N(2)	436 (28)	6726 (46)	1591 (27)	20 (9)
N(3)	2261 (27)	3068 (44)	1838 (26)	22 (8)
N(4)	4323 (30)	3000 (48)	2133 (29)	28 (10)
N(5)	3946 (32)	7055 (49)	3754 (30)	31 (10)

partial refinement by the least-squares method the O and N atoms were found from two successive difference Fourier maps. 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 the anomalous-dispersion correction for Bi. The function minimized in the least-squares procedure was $\Sigma w(F_o - F_c)^2$. The weighting scheme applied was as follows: for $|F_o| < 120$, $w_F = (|F_o|/120)^{2.5}$; for $120 \leq |F_o| \leq 700$, $w_F = 1.0$; for $|F_o| > 700$, $w_F = (700/|F_o|)^{2.9}$; for $\sin \theta < 0.15$, $w_S = (\sin \theta/0.15)^{1.8}$; for $0.15 \leq \sin \theta \leq 0.30$, $w_S = 1.0$; for $\sin \theta > 0.30$, $w_S = (0.30/\sin \theta)^{2.2}$; $w = 0.1 w_F w_S$. An isotropic extinction parameter (Zachariasen, 1963; Larson, 1967) was also included in the final stage of the refinement [$g = 1.58(9) \times 10^{-3}$]. An attempt to locate H atoms turned out to be over-optimistic. The final R values are: $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.063$ and $R_w = [\Sigma w(F_o - F_c)^2 / \Sigma w F_o^2]^{1/2} = 0.071$ for 2554 reflexions and 180 parameters. The average parameter shift-to-error ratio was 0.26 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) adapted by Professor L. Golič, 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 the anomalous-dispersion correction tabulated by Cromer & Liberman (1970).

The positional and thermal parameters of the Bi atoms are listed in Table 2 and those of the O and N atoms in Table 3.*

Results and discussion

The structure in the projection along b and the atom-numbering system used are shown in Fig. 1. Some important interatomic distances and angles are given in Table 4.

The crystal structure consists of polycations, in which pairs of $[\text{Bi}_6\text{O}_5(\text{OH})_3]$ groups are joined across the symmetry centres through two bridging O atoms, together with nitrate anions and water molecules. In the $[\text{Bi}_6\text{O}_5(\text{OH})_3]$ group, shown in the stereoscopic view (Johnson, 1965) (Fig. 2), the six Bi atoms are located at the corners of a nearly regular octahedron with the O atoms above the centres of the octahedral faces. The three O atoms of the OH groups [O(6), O(7) and O(8)]

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33694 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

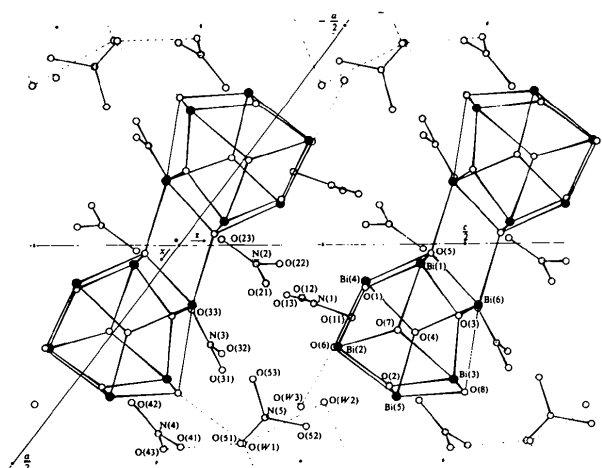


Fig. 1. A projection of the structure along the b axis.

Table 4. Interatomic distances (Å) and angles (°) with standard deviations in parentheses

O(1)—Bi(1)	2.11 (4)	O(5)—Bi(1)	2.26 (3)
O(1)—Bi(2)	2.18 (4)	O(5)—Bi(4)	2.42 (5)
O(1)—Bi(4)	2.17 (3)	O(5)—Bi(6)	2.21 (3)
O(2)—Bi(2)	2.15 (3)	O(5)—Bi(6 ⁱ)	2.55 (4)
O(2)—Bi(3)	2.22 (4)	O(6)—Bi(2)	2.41 (3)
O(2)—Bi(5)	2.15 (3)	O(6)—Bi(4)	2.29 (4)
O(3)—Bi(1)	2.13 (3)	O(6)—Bi(5)	2.52 (3)
O(3)—Bi(3)	2.14 (4)	O(7)—Bi(1)	2.45 (3)
O(3)—Bi(6)	2.23 (3)	O(7)—Bi(2)	2.32 (4)
O(4)—Bi(4)	2.18 (3)	O(7)—Bi(3)	2.46 (3)
O(4)—Bi(5)	2.10 (4)	O(8)—Bi(3)	2.32 (3)
O(4)—Bi(6)	2.21 (5)	O(8)—Bi(5)	2.22 (4)
N(1)—O(11)	1.29 (7)	N(3)—O(32)	1.26 (6)
N(1)—O(12)	1.25 (6)	N(3)—O(33)	1.23 (4)
N(1)—O(13)	1.24 (6)	N(4)—O(41)	1.25 (7)
N(2)—O(21)	1.21 (5)	N(4)—O(42)	1.27 (5)
N(2)—O(22)	1.17 (6)	N(4)—O(43)	1.29 (6)
N(2)—O(23)	1.29 (6)	N(5)—O(51)	1.16 (9)
N(3)—O(31)	1.29 (5)	N(5)—O(52)	1.31 (8)
		N(5)—O(53)	1.27 (5)
O(W1)—O(8 ⁱⁱ)	2.78 (5)	O(W1)—O(W2)	2.85 (8)
O(W1)—O(43)	2.81 (7)	O(W1)—O(W2 ⁱⁱⁱ)	2.79 (4)
		O(W3)—O(6)	2.82 (7)
Bi(1)—O(1)—Bi(2)	119 (1)	Bi(1)—O(5)—Bi(4)	100 (2)
Bi(1)—O(1)—Bi(4)	114 (2)	Bi(1)—O(5)—Bi(6)	104 (1)
Bi(2)—O(1)—Bi(4)	115 (2)	Bi(4)—O(5)—Bi(6)	101 (1)
Bi(2)—O(2)—Bi(3)	117 (1)	Bi(6 ⁱ)—O(5)—Bi(1)	124 (1)
Bi(2)—O(2)—Bi(5)	119 (1)	Bi(6 ⁱ)—O(5)—Bi(4)	116 (1)
Bi(3)—O(2)—Bi(5)	111 (2)	Bi(6 ⁱ)—O(5)—Bi(6)	109 (2)
Bi(1)—O(3)—Bi(3)	120 (2)	Bi(2)—O(6)—Bi(4)	103 (2)
Bi(1)—O(3)—Bi(6)	108 (1)	Bi(2)—O(6)—Bi(5)	98 (1)
Bi(3)—O(3)—Bi(6)	123 (1)	Bi(4)—O(6)—Bi(5)	99 (2)
Bi(4)—O(4)—Bi(5)	118 (2)	Bi(1)—O(7)—Bi(2)	102 (1)
Bi(4)—O(4)—Bi(6)	109 (1)	Bi(1)—O(7)—Bi(3)	98 (1)
Bi(5)—O(4)—Bi(6)	125 (1)	Bi(2)—O(7)—Bi(3)	102 (1)
		Bi(3)—O(8)—Bi(5)	105 (2)
O(5)—Bi(1)—O(1)	75 (2)	O(5)—Bi(4)—O(1)	71 (1)
O(5)—Bi(1)—O(3)	74 (1)	O(5)—Bi(4)—O(4)	73 (1)
O(7)—Bi(1)—O(1)	69 (1)	O(6)—Bi(4)—O(1)	73 (1)
O(7)—Bi(1)—O(3)	71 (1)	O(6)—Bi(4)—O(4)	73 (2)
O(5)—Bi(1)—O(7)	127 (1)	O(5)—Bi(4)—O(6)	128 (1)
O(1)—Bi(1)—O(3)	94 (1)	O(1)—Bi(4)—O(4)	93 (1)
O(6)—Bi(2)—O(1)	70 (1)	O(6)—Bi(5)—O(2)	70 (1)

Table 4 (*cont.*)

O(6)—Bi(2)—O(2)	73 (1)	O(6)—Bi(5)—O(4)	70 (1)
O(7)—Bi(2)—O(1)	70 (1)	O(8)—Bi(5)—O(2)	73 (1)
O(7)—Bi(2)—O(2)	72 (1)	O(8)—Bi(5)—O(4)	76 (1)
O(6)—Bi(2)—O(7)	124 (2)	O(6)—Bi(5)—O(8)	128 (1)
O(1)—Bi(2)—O(2)	93 (1)	O(2)—Bi(5)—O(4)	93 (1)
O(7)—Bi(3)—O(2)	68 (1)	O(3)—Bi(6)—O(4)	87 (2)
O(7)—Bi(3)—O(3)	71 (1)	O(3)—Bi(6)—O(5)	73 (1)
O(8)—Bi(3)—O(2)	70 (1)	O(5')—Bi(6)—O(4)	120 (1)
O(8)—Bi(3)—O(3)	77 (1)	O(5')—Bi(6)—O(5)	71 (1)
O(7)—Bi(3)—O(8)	125 (1)	O(3)—Bi(6)—O(5')	126 (1)
O(2)—Bi(3)—O(3)	92 (1)	O(4)—Bi(6)—O(5)	76 (1)
O(11)—N(1)—O(12)	120 (5)	O(31)—N(3)—O(33)	120 (4)
O(11)—N(1)—O(13)	120 (4)	O(32)—N(3)—O(33)	121 (4)
O(12)—N(1)—O(13)	121 (5)	O(41)—N(4)—O(42)	118 (4)
O(21)—N(2)—O(22)	120 (4)	O(41)—N(4)—O(43)	122 (4)
O(21)—N(2)—O(23)	120 (5)	O(42)—N(4)—O(43)	119 (4)
O(22)—N(2)—O(23)	119 (4)	O(51)—N(5)—O(52)	120 (4)
O(31)—N(3)—O(32)	119 (3)	O(51)—N(5)—O(53)	123 (6)
		O(52)—N(5)—O(53)	117 (6)

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

and the bridging O atom [O(5)] have three Bi neighbours arranged pyramidally at longer distances, while the remaining four O atoms [O(1), O(2), O(3) and O(4)] are linked to three more nearly coplanar Bi neighbours by shorter distances. The four atoms of each kind [O(1) to O(4) and O(5) to O(8)] are located at the corners of a slightly distorted tetrahedron (see Fig. 2). The shortest distance between two O atoms in the polycation is O(1)—O(7), 2.60 (4) Å.

The association of H atoms with the O(6), O(7) and O(8) atoms is compatible with the fact that the H atoms are farther from the positive Bi ions in this case, than they would be if they were associated with O(1), O(2), O(3) or O(4). A similar bonding scheme involving H atoms was found in the α -diaspore structure determined by neutron diffraction (Busing & Levy, 1958). In the present investigation, it was not possible to locate H atoms and to distinguish directly

between OH⁻, O²⁻ or H₂O oxygens. The proposed arrangement of H atoms was therefore checked indirectly by NMR broad-line spectroscopic measurements (carried out by Mr J. Slak at the Jožef Stefan Institute, Ljubljana). The first derivative of the proton magnetic resonance absorption line shows undoubtedly an OH⁻:H₂O ratio 1:1. These results are in contrast to any other arrangement and number of H atoms in the polycation, which would demand the replacement of H₂O molecules by OH⁻ ions.

The [Bi₆O₅(OH)₃] groups are linked in pairs by bonding between Bi(6) and the O(5) atom of the other group. The Bi(6)—O(8) distance, 2.86 (4) Å, cannot be considered to be a bonding contact, but a relatively strong hydrogen bond [2.78 (5) Å] can be observed between the O(8) atom of the OH group and the O(W1) atom of a water molecule. The Bi—O bond lengths are in agreement with those found in related compounds. Metal—metal interactions are not observed in the polycations. The shortest distance, Bi(1)—Bi(6), 3.518 (2) Å, is 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 appears to be a distorted pseudo-trigonal bipyramid with the electron lone pair at one of the equatorial corners (Table 4). The deviations from the regular trigonal-bipyramidal geometry are much larger than for example in PdBi₂O₄ (Conflant, Boivin & Thomas, 1977), probably because each of the O atoms is bonded strongly to two more Bi atoms forming the cage-like polycation.

The distances and angles within the five NO₃⁻ anions of the asymmetric unit are in reasonable agreement with the values found in other nitrates. The water molecules are loosely bound. The hydrogen bonds are shown in Fig. 1 by dashed lines. The water molecule with O(W1) is linked by four hydrogen bonds to four nearly tetrahedrally-arranged O atoms, while O(W2) has only two and O(W3) only one contact to O neighbours of less than 2.9 Å.

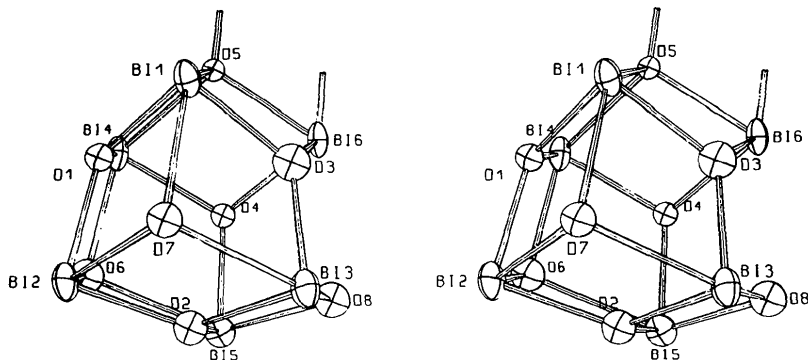


Fig. 2. A stereoscopic drawing of the [Bi₆O₅(OH)₃] group of the polycation. The atoms O(6), O(7) and O(8) are those of the OH groups. The atoms are represented by thermal ellipsoids drawn at the 75% probability level.

The results of this investigation, taken alone, are insufficient to explain unambiguously the mechanism of the hydrolysis of bismuth(III) nitrate, the possible ways of condensation of the $[\text{Bi}_6(\text{OH})_{12}]^{6+}$ species and the existence of various bismuth basic nitrates. More structural and chemical information is needed for the solution of this problem. It is hoped that the structural analysis of the first hydrolysis product $\text{BiONO}_3 \cdot \text{H}_2\text{O}$, which is in progress, as well as that of $2\text{BiONO}_3 \cdot \text{H}_2\text{O}$, will give more decisive answers concerning the hydrolysis of bismuth salts.

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Sc_3Co , a New Structure Type Related to Fe_3C and Re_3B by Periodic Unit-Cell Twinning

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Sc_3Co , orthorhombic, *Pnma*, $a = 13.102$ (9), $b = 8.624$ (6), $c = 5.829$ (3) Å, $Z = 8$, $D_x = 3.91_3$ g cm $^{-3}$, $\mu(\text{Mo } K\alpha) = 107$ cm $^{-1}$. Least-squares refinement gave $R = 0.048$ for 535 independent diffractometer data which were corrected for absorption. The structure is characterized by trigonal prisms of Sc atoms which are centred by Co atoms. Centred trigonal prisms are also found in the Fe_3C and Re_3B structure types. Using the concept of periodic unit-cell twinning, the point positions of all three structure types can be derived. Fe_3C is based on a hexagonal, and Re_3B on a cubic close-packed base structure, while Sc_3Co derives from a close-packed base structure with mixed stackings corresponding to the atom arrangement in the Nd structure type.

Introduction

The compound Sc_3Co was prepared by the arc-melting technique from elements of high purity (Sc 99.95%, Co 99.99%). A single trigonal prismatic crystal (base: $0.14 \times 0.12 \times 0.12$ mm, height: 0.14 mm) was

isolated from the crushed melt. Systematic absences in precession photographs showed the space group to be either *Pn* 2_1 *a* or *Pnma* (*Ok* l with $k + l = 2n + 1$ and $hk0$ with $h = 2n + 1$). Intensities of 588 independent reflexions out to a limit of $\sin \theta/\lambda = 0.702$ Å $^{-1}$ were measured with graphite-monochromated Mo $K\alpha$