$[Bi_2O_2]^{2+}$ Layers in $Bi_2O_2(OH)(NO_3)$: Synthesis and Structure Determination

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Dedicated to Professor Kurt O. Klepp on the occasion of his 60th birthday

$Bi_2O_2(OH)(NO_3)$ is the first bismuth oxynitrate containing $[Bi_2O_2]^{2+}$ layers for which the crystal structure has been determined. The current study presents its synthesis, formula determination using powder XRD, thermogravimetric analysis and nitrate assay, and finally, crystal structure refinement from twinned crystals. $Bi_2O_2(OH)(NO_3)$ crystallizes in the orthorhombic system, $a = 5.3878(11)$, $b = 5.3984(10)$ and $c = 17.136(2)$ Å, with the space group $Cmc2_1$. The structure refinement based on 1257 independent reflections converged to R_I (obs) $= 0.0321$ and R_{Iw} (obs) $= 0.0765$. The $Bi_2O_2(OH)(NO_3)$ structure is based on $[Bi_2O_2]^{2+}$ sheets in the *(ab)* plane. The interlayer space is composed of two slices containing OH^- and $(NO_3)^-$ groups, respectively. Within the nitrate layers, the disorder over two possible NO_3^- orientations (related by a four fold axis) involves half occupied positions for two of the oxygen atoms. An attempt to lower the symmetry and/or enlarge the unit cell, looking for an $(NO_3)^-$ ordering, failed.

Key words: Structure Determination, Bismuth Oxynitrate

Introduction

The earlier investigations on bismuth basic nitrates have shown the existence of numerous phases and no less than fifteen of them have already been described in the literature since the 17th century [1]. Because of the difficulties with chemical analyses and the preparation of isolated pure phases, a great confusion arises in their identification from the older literature. Furthermore, the presence of very loosely bound water molecules and/or rather hydroxyl groups, difficult to pinpoint with standard physical methods, increases the difficulties. As an illustration, the title compound has recently been assigned to the misleading $[Bi_6O_6(OH)_3](NO_3)_3 \cdot 1.5H_2O$ formula [2]. Among the reported compounds so far let us also mention $Bi_2O_3 \cdot BiONO_3 \cdot nH_2O$ [3 – 6], $3Bi_2O_3 \cdot 2N_2O_5 \cdot 4H_2O$ [7], $BiO(OH)_{1/2}(NO_3)_{1/2}$ [8], $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 3H_2O$ [9], $[Bi_6O_4(OH)_4](NO_3)_6 \cdot 4H_2O$ [10], $[Bi_6O_4(OH)_4](NO_3)_5 \cdot H_2O$ [11] and $Bi(NO_3)_5 \cdot 5H_2O$ [12], although not all of them have been fully characterized yet. Among the number of entities formed by the Bi^{3+}/O^{2-} ions in these nitrates (*i. e.*, isolated Bi^{3+}, $[Bi_2O_2]^{2+}$ planes, 1D columns…) one predominant arrangement usually stands out: $[Bi_6O_x(OH)_{8-x}]^{(10-x)+}$, that corresponds to the intramolecular polycondensation of $[Bi_6(OH)_{12}]^{6+}$ ions, present in solutions of basic Bi salts [13 – 14]. Four compounds showing heteropolycations of this kind have been fully characterized: $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 3H_2O$ [9], $[Bi_6O_4(OH)_4](NO_3)_6 \cdot 4H_2O$ [10], $[Bi_6O_4(OH)_4](NO_3)_5 \cdot H_2O$ [11] and $[Bi_6O_{4.5}(OH)_{3.5}](NO_3)_{11}$ [15]. Although less common, $[Bi_2O_2]^{2+}$ layers associated with $(NO_3)^-$ anions can also be found, with similar structural details as in the two reference adaptive series of oxides: the Aurivillius phases [16] and the Sillén phases [17]. We report herein the synthesis and the structure determination from twinned crystals of $Bi_2O_2(OH)(NO_3)$, a new phase showing Aurivillius-like $[Bi_2O_2]^{2+}$ layers.

Experimental Section

Powder synthesis

A mixture of 0.7 g of $Bi(NO_3)_3 \cdot 5H_2O$ (Aldrich, 99.99%) and 0.1 g of KOH was placed into a 23 ml Teflon-lined stain-

less steel autoclave with 14 ml of water and heated to 180 °C for one day. The resulting product (white powder) was filtered, washed with water and dried at room temperature. A more diluted starting mixture (18 ml of water) with the same experimental conditions led to the precipitation of crystals.

Determination of the composition

In an earlier stage, before crystals of proper size could be obtained, several investigations were carried out from powdered material to characterize the compound [18] as follows:

Powder diffraction data

Powder diffraction data were collected with an INEL curved position sensitive detector in a transmission setup and a D5000 diffractometer in a reflection setup. The powder patterns could be indexed using the TREOR program [19], in a primitive tetragonal unit cell with parameters $a = 3.816(2)$ and $c = 17.143(8)$ Å which corresponds to the announced lattice parameters in previous work [2]. It is worth noting that the *a* parameter is characteristic of the $[Bi_2O_2]^{2+}$ layer. All attempts to solve the structure from the powder diffraction data failed. Initially it was thought that this was due to bad quality data set. Indeed, for a compound such as $Bi_2O_2(OH)(NO_3)$, the two selected diffractometer geometries have two disadvantages: absorption in the transmission setup (INEL) because of the presence of Bi and huge preferred orientation effects in the reflection setup because of the platelet shape of the crystals. In fact, the presence of a pseudo symmetry was later confirmed by single crystal investigations. With this additional information, the cell metric was finally refined as $a = 5.387(5)$, $b = 5.398(4)$ and $c = 17.136(8)$ Å using the powder diffraction module of the Jana2000 program [20]. Such an orthogonal distortion of the tetragonal symmetry is quite common for Aurivillius and Sillén related phases [21].

Thermogravimetric analysis

The molar mass has been obtained by a thermogravimetry analysis (TGA) coupled to a differential thermal analysis (DTA) (Fig. 1), collected on a TGA 92 SETARAM apparatus in air and under a 5 °C min^{-1} heating rate between room temperature and 630 °C. The compound shows a total weight loss of 12.2% and a final product identified as α-Bi_2O_3 by XRD measurements, leading to the calculation of a molar weight of 530 g mol^{-1}. At 530 °C an intermediate is formed, which was identified as $Bi_5O_7NO_3$ [22] by means of a high-temperature XRD study with a Guinier-Lenné camera. It is worthwhile to note that the weight loss between 530 and 630 °C (4.3%) agrees perfectly with the equation: $Bi_5O_7NO_3 \rightarrow 5/2\ Bi_2O_3 + 1\ NO + 3/4\ O_2$. From the calculated molar mass and the measured density, 7.04(1) g cm^{-3}, the number of formula units per cell should be $Z = 2$ for the subcell and $Z = 4$ for the supercell.

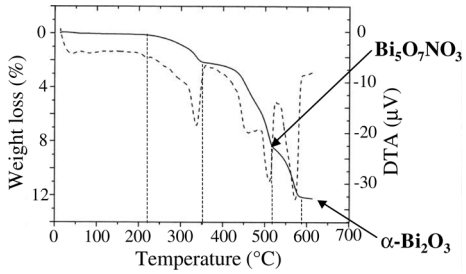

Fig. 1. Thermogravimetry analysis coupled to differential thermal analysis of $Bi_2O_2(OH)(NO_3)$. The total weight loss is equal to 12.2% and the final product is α-Bi_2O_3.

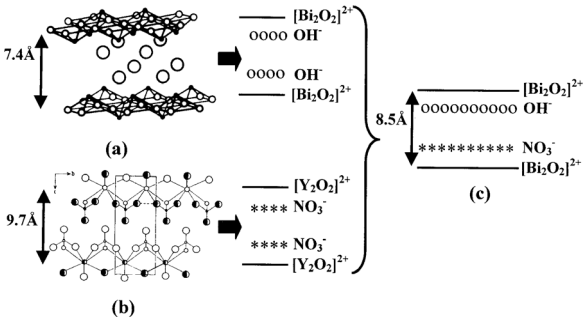

Fig. 2. Comparison of the $[Bi_2O_2]^{2+}$ or $[Y_2O_2]^{2+}$ interlayer space of (a) BiO(Cl, OH) [21], (b) $YONO_3$ [23] and (c) $Bi_2O_2(OH)(NO_3)$.

Nitrate assay

The nitrate weight content of the compound was determined by the Kjeldhal method: NO_3 calcd. 11.72%, found 12.20%. As presumed (vide supra), the new nitrate is composed of $[Bi_2O_2]^{2+}$ layers and should have, therefore, a formulation such as $Bi_2O_2(OH)(NO_3)_x$, yH_2O. To achieve the charge electroneutrality, *x* must be equal to 1. The second parameter, *y*, can be calculated from the total weight loss determined before (12.2% corresponding to 64.7g per formula unit): the weight loss during the decomposition of $Bi_2O_2(OH)(NO_3)$, yH_2O in Bi_2O_3 is equal to $63 + 18y$, then *y* is equal to 0. Consequently, the formulation of the new bismuth basic nitrate is $Bi_2O_2(OH)(NO_3)$. As a confirmation, it is interesting to note that c/2 (*i.e.* 8.54 Å) corresponds to the sum of the $[Bi_2O_2]^{2+} + OH^-$ double layer width in BiO(Cl, OH) [21], *i.e.* 7.4/2 Å and $[Y_2O_2]^{2+} + (NO_3)^-$ double layer in $YONO_3$ [23], *i.e.* 9.7/2 Å (Fig. 2). Thus, the interlayer space contains both the OH^- and $(NO_3)^-$ ions.

Single crystal X-ray data collection

Special attention was paid to obtain large enough single crystals (vide supra). The selection of a suitable crystal for X-ray diffraction data collection was carried out on a Bruker-

Table 1. Crystallographic data for $Bi_2O_2(NO_3)(OH)$.

1) Physical, crystallographic, and analytical data	
Formula	Bi_2NO_6H
Crystal color	colorless
Molecular weight (g.mol^{-1})	528.97
Crystal system	orthorhombic
Space group	$Cmc2_1$
Temperature (K)	173
Cell parameters (from powder, room temperature)	
a (Å)	5.3878(11)
b (Å)	5.3984(10)
c (Å)	17.136(2)
V (Å^3)	498.41(15)
Z	4
Density (calcd.)	7.047(2)
Crystal description	platelet
Crystal size (mm^3)	$\sim 0.001 \times 0.08 \times 0.09$
2) Data collection	
Diffractometer	Bruker-Nonius Kappa CCD
Monochromator	oriented graphite (002)
Radiation	MoK-$L_{2,3}$ ($\lambda = 0.71073$ Å)
Scan mode	φ and ω
No. of measured reflections	7484
hkl Range	$-8 \le h \le 8$ $-8 \le k \le 8$ $-25 \le l \le 26$
Sin(θ)/λ range (Å)	$0.071 - 0.806$
Twin matrices	$\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}, \begin{pmatrix}-1&0&0\\0&-1&0\\0&0&-1\end{pmatrix}, \begin{pmatrix}0&1&0\\1&0&0\\0&0&1\end{pmatrix}, \begin{pmatrix}0&-1&0\\-1&0&0\\0&0&-1\end{pmatrix}$
Twin fractions	0.29(7), 0,29(4), 0.20(4), 0.22(4)
3) Data reduction	
Linear absorption coeff. (mm^{-1})	75.0
Absorption correction	analytical (Gaussian integration)
T_{min}/T_{max}	0.018/0.470
Number of reflections	7484
No. of independent reflections	1257
Criterions for observed reflections	$I > 2\sigma(I)$
R_{int} (obs)	0.081
Average redundancy	6.0
No. of observed reflections	1232
4 – Refinement	
Refinement	F^2
No. of reflections used in the refinement	1257
$R^{\dagger}$ (obs)	0.0301
$R_w{}^{\dagger}$ (obs)	0.0715
S (obs)	1.37
No. of refined parameters	37
Weighting scheme	$w = 1/(\sigma^2(\lvert F_o\rvert^2) + 0.002\lvert F_o\rvert^2)$
Secondary extinction coeff.	0.078(14)
Difference Fourier residues	$[-3.8, +4.3]$ e$^-$/ Å^3

† $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. $R_w = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|^4)]^{1/2}$.

Nonius Kappa CCD diffractometer at *ca.* 173 K. The low temperature needed to improve the diffracted intensity of weak intensity reflections was achieved by means of an Oxford cryostream cooler. Crystals showed diffraction patterns with apparent tetragonal symmetry (primitive cell, $a = 3.82$, $c = 17.15$ Å), but with a slight splitting of the spots suggesting twinning within an orthorhombic distortion. One suitable crystal was mounted at the tip of Lindeman glass capillary using silicon grease. The data collection was carried out at 173 K on the Kappa CCD diffractometer, with a 90 second exposure time per frame. Data collection details are gathered in Table 1.

Table 2. Fractional atomic coordinates, equivalent isotropic displacement parameters (Å^2, Bi), isotropic displacement parameters (Å^2, N and O), and s. u.'s for $Bi_2O_2(OH)(NO_3)$. The occupancy of O4 and O5 atoms have been fixed to 0.5.

Atom	x	y	z	$U_{eq}{}^{\dagger}$
Bi1	0	0.04156(11)	1/4	0.00818(12)
Bi2	1/2	0.07943(14)	0.09873(4)	0.01518(19)
O1	0.2544(17)	0.2843(13)	0.1820(3)	0.0077(11)
O2	1/2	0.490(3)	0.0548(11)	0.037(4)
O3	1/2	0.033(2)	0.3143(5)	0.0142(18)
O4	0.631(4)	-0.129(4)	0.4181(9)	0.021(3)
O5	0.375(6)	0.167(6)	0.4248(13)	0.046(6)
N1	1/2	0.020(3)	0.3884(8)	0.012(3)

† $U_{eq} = \frac{1}{3}(\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i a_j)$.

Table 3. Anisotropic displacement parameters U^{ij} † (Å^2) and s. u.'s for $Bi_2O_2(OH)(NO_3)$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}
Bi1	0.0097(3)	0.00646(18)	0.00833(17)	−0.00049(19)
Bi2	0.0221(5)	0.0109(3)	0.0125(2)	−0.0032(2)

† $U = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$, $U_{12} = U_{13} = 0$.

Data processing and structure determination

Intensity integration and standard Lorentz-polarization correction were performed with the Bruker-Nonius Eval-CCD program package. Except for the direct methods tests carried out with the SHELXTL software [24], and for the structure drawings realized with the Diamond program [25], all calculations were conducted with the Jana2000 program suite [20]. The set of reflections was corrected for absorption *via* a Gaussian analytical method, after a face indexing and a careful measurement of the crystal dimensions ($T_{min}/T_{max} = 0.018/0.470$). No particular systematic extinctions were observed, allowing several possible space groups. All structure determination attempts failed and it was soon clear from a thorough analysis of the tested solutions that the cell had to be extended and the symmetry lowered. The cell was doubled through the $(110, -110, 001)$ transformation with twinning possibilities, as suggested by the doubling of spots. Many trials involving various structure / space group combinations were tested and a solution was finally found in the orthorhombic crystalline system, space group $Cmc2_1$ and a mirror as a twin element. With this symmetry, the merging of data according to the mm2 point group led to the internal R value $R_{int} = 0.081$. This rather high value is

Table 4. Distances (Å) and bond valence calculation for $Bi_2O_2(OH)(NO_3)$.

Environments of bismuth				Environments of oxygen			
Atom	Atom	Dist. (Å)	s	Atom	Atom	Dist. (Å)	s
Bi1	O1	2.226(8)	0.71	O1	Bi1	2.226(8)	0.71
	$O1^{i}$	2.226(8)	0.71		$Bi1^{iii}$	2.244(8)	0.67
	$O1^{ii}$	2.244(8)	0.67		Bi2	2.239(8)	0.67
	$O1^{iii}$	2.244(8)	0.67		$Bi2^{iii}$	2.540(8)	0.29
	$O3^{iii}$	2.873(11)	0.12				**2.35**
	$O3^{i}$	2.911(4)	0.11				
	O3	2.911(4)	0.11	O2	Bi2	2.341(17)	0.51
	$O3^{iii}$	2.957(11)	0.10		$Bi2^{iii}$	2.839(6)	0.13
			3.20		$Bi2^{iii}$	2.839(6)	0.13
							0.78
Bi2	O1	2.239(7)	0.67				
	$O1^{i}$	2.239(7)	0.67	O3	N	1.273(17)	1.50
	O2	2.341(17)	0.51		$Bi1^{iii}$	2.873(11)	0.12
	$O1^{ii}$	2.540(8)	0.29		Bi1	2.911(4)	0.11
	$O1^{iii}$	2.540(8)	0.29		Bi1	2.911(4)	0.11
	$O2^{iii}$	2.839(6)	0.13		$Bi1^{iii}$	2.957(11)	0.10
	$O2^{iii}$	2.839(6)	0.13				**1.94**
			2.71				
				O4	N	1.19(2)	**2.01**
				O5	N	1.21(3)	**1.82**

easily explained if one considers the very high linear absorption coefficient (75 mm^{-1}) and the crystal twinning because of which no proper absorption correction can be made. After locating the bismuth and oxygen atoms of the $[Bi_2O_2]^{2+}$ layers, the oxygen atom of the hydroxyl group and the oxygen and nitrogen atoms of the nitrate groups were found through difference Fourier synthesis maps. Within the *C*mc2_1 space group, the $(NO_3)^-$ anions are disordered over two possible orientations. Attempts to further lower the symmetry and/or search for supercell spots to order those anions failed. However, a further twinning (inversion twin) was evidenced by refining Flack enantiopole parameters using Friedel pairs. With a secondary extinction coefficient and anisotropic displacement parameters for bismuth atoms only, the residual factor smoothly converged to the $R = 0.0301$ value for 1232 observed reflections $(I > 2\sigma(I))$ and 37 parameters. Final refinement details are given in Table 1. Atomic parameters are gathered in Tables 2 and 3.

Structure Description and Discussion

The $Bi_2O_2(OH)(NO_3)$ structure is based on cationic $[Bi_2O_2]^{2+}$ layers in the (*a*,*b*) plane. In the interlayer space, two layers of anions are inserted, one is composed of $(OH)^-$ (bound to Bi^{3+} cations with Bi2-OH bonds of 2.341(17) and the other of $(NO_3)^-$ with Bi1-O3NO_2 bonds of ~ 2.9 Å, confirming prior hypotheses (Fig. 3).

Hydrogen bonding. The bond valence [26] results are presented in Table 4. The O2 bond valence value

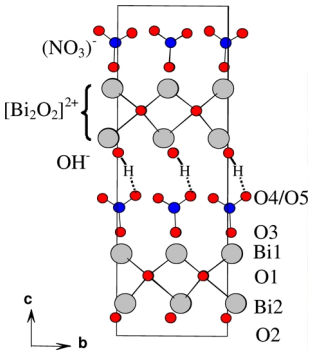

Fig. 3. Crystal structure of $Bi_2O_2(OH)(NO_3)$ (the figure is limited to the nitrate groups that stand at right angle to each).

is equal to 0.78 without using the OH bond for the calculation, a little inferior to the oxygen value for a hydroxyl group (*i.e.* 1). A low value (s = 1.82 instead of 2) is also observed for the O5 of the $(NO_3)^-$ groups. This could be explained by O5–H-O2 hydrogen bonds to make the cohesion between the two negative layers and then the cohesion of the structure. According to Sundvall [27], the O-O distances within a O–H-O group in the tetraoxotetrahydroxohexabismuth perchlorate heptahydrate range from 2.72(2) to 3.10(2) Å, in good agreement with the shortest distance between the O2 and the $(NO_3)^-$ groups (d(O5-O2) = 2.97(3) Å).

$[Bi_2O_2]^{2+}$ layers. Most $[Bi_2O_2]^{2+}$ layers have been observed in two different adaptive series: the Aurivillius phases [16] and the Sillén phases [17]. In the Aurivillius phases, the $[Bi_2O_2]^{2+}$ layers are

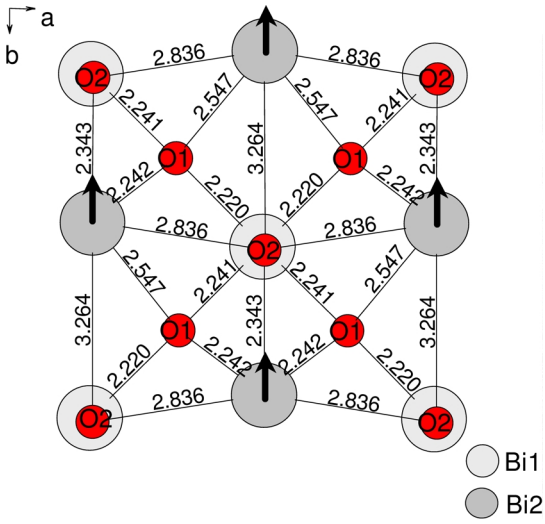

Fig. 4. Representation of the $[Bi_2O_2]^{2+}$ layers in the *(ab)* plane. The Bi2 displacement along the *b* axis is emphasized by arrows.

found between perovskite-like layers of formula $[A_{n-1}M_nO_{3n+1}]^{2-}$. In the Sillén phases, $[Bi_2O_2]^{2+}$ layers are around halide or alkali-halide layers of formula [X] or $[AX]_2$, respectively. In $Bi_2O_2(OH)(NO_3)$, these layers are deformed which induces the orthorhombic distortion (see Fig. 4). This in-plane deformation is shown by the Bi2 environment with two short Bi2-O1 bonds (2.239(7) Å) and two ones of 2.540(8) Å. The distortion thus occurs from a cooperative Bi2 shift along b represented by the arrows in the Fig. 4. This Bi2 displacement can result from competing repulsions between the central Bi^{3+} lone pair (= E) which is commonly located at the top of an EO_4Bi square pyramid, and the four surrounding $(OH)^-$ hydroxyl groups. As a consequence, a cooperative alignment of the E/OH^- pairs along b can be envisaged.

Nitrate distribution. The structure contains two possible orientations of the nitrate groups due to the disorder of O4 and O5. The occupancy of these sites has been fixed to 0.5. Attempts to further lower the symmetry to order those anions was not successful and no supercell spots were detected on single crystal and powder diffraction data. Fig. 5 shows the two alternative orientations. The $(NO_3)^-$ groups stand at right angles

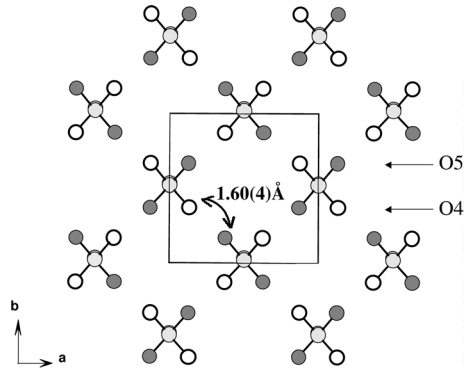

Fig. 5. The two alternative orientations (white and gray) of the nitrate groups due to the disorder of O4 and O5.

to each other and, in this case, the shortest O-O distance between two different nitrate groups has the reasonable value of 2.89(4) Å. A similar nitrate disorder has already been observed for $YONO_3$ [23] and $RBi_2O_4NO_3$ (R=Y, Sm, Eu, Gd, Tb, Dy, Er, Yb) [28] layer compounds. The O-O distances for the nitrate groups standing at right angle to each other are 2.94(4) and 2.99(3) Å, respectively.

Conclusion

$Bi_2O_2(OH)(NO_3)$ contains $[Bi_2O_2]^{2+}$ layers. In the interlayer space, two layers are inserted, one is composed of $(OH)^-$ and the other of $(NO_3)^-$ anions linked by hydrogen bonds. $[Bi_2O_2]^{2+}$ layers conserve the main structural features of Aurivillius [16] and Sillén phases [17]. $BiONO_3$ described in the literature since the 17th century [1] is the most simple bismuth oxynitrate probably containing these layers, but its crystal structure has not yet been determined. Recently a new yttrium oxynitrate, $YONO_3$ [23], was prepared by thermal decomposition of $Y(NO_3)\cdot 5H_2O$, and its crystal structure was reported to be similar to that of BiOCl [21].

On the other hand, the last product of the thermal decomposition of $Bi(NO_3)\cdot 5H_2O$ [18] is not $BiONO_3$ but $Bi_5O_7NO_3$ [22]. So, the title compound $Bi_2O_2(OH)(NO_3)$ is the first bismuth oxynitrate containing $[Bi_2O_2]^{2+}$ layers for which the crystal structure has been solved.

[1] P. Pascal, Nouveau Traité de Chimie Minérale, Paris: Masson, Vol. XI, 795 (1958).
[2] A. N. Christensen, M. A. Chevalier, J. Skibsted, B. B. Iversen, J. Chem. Soc, Dalton Trans. **3**, 2265 (2000).
[3] J. Ozols, Latv. PSR Zinat. Akad. Vestis **4**, 87 (1950a).
[4] J. Ozols, Latv. PSR Zinat. Akad. Vestis **5**, 83 (1950a).
[5] J. Ozols, Latv. PSR Zinat. Akad. Vestis **6**, 49 (1950a).
[6] G. Gattow and D. Scott, Z. Anorg. Allg. Chem. **324**, 31 (1963).
[7] G. Kiel, Untersuchungen über Wismuth(III)-nitrate. Thesis, Georg-August-Univ. Göttingen (1967).
[8] B. S. Breic, D. Kolar, F. Lazarini, M. Malesic, Monatsh. Chem. **104**, 365 (1973).
[9] F. Lazarini, Acta Crystallogr. B **34**, 3169 (1978).
[10] F. Lazarini, Crystal Struct. Commun. **8**, 69 (1979).
[11] F. Lazarini, Acta Crystallogr. B **35**, 448 (1979).
[12] F. Lazarini, Acta Crystallogr. C **41**, 1144 (1985).
[13] H. A. Levy, M. D. Danford, P. A. Agron, J. Chem. Phys. **31**, 1458 (1979).
[14] V. A. Maroni, T. G. Spiro, Inorg. Chem. **7**, 183 (1968).
[15] N. Henry, M. Evain, P. Deniard, S. Jobic, O. Mentré, F. Abraham, J. Solid State Chem. **176**, 127 (2003).
[16] L. G. Sillén, Naturwissenschaften **30**, 318 (1942).
[17] B. Aurivillius, Arki. Kemi. **1**, 463 (1949).
[18] N. Henry, Thesis, University of Lille (France) (2000).
[19] TREOR, Version January (1990).
[20] V. Petricek, M. Dusek: JANA2000, a crystallographic computing system, Institute of Physics, Academy of Sciences of the Czech Republic, Prague (2000).
[21] J. F. Ackerman, J. Solid State Chem. **62**, 92 (1986).
[22] H. Kodama, J. Solid State Chem. **112**, 27 (1994).
[23] D. Pelloquin, M. Louer, D. Louer, J. Solid State Chem. **112**, 182 (1994).
[24] G. M. Sheldrick, SHELXTL^{TM} version 5, Siemens Analytical X-ray Instruments, Inc. Madison, WI.
[25] K. Brandenburg, Diamond version 3-1, Crystal Impact GbR (2001).
[26] N. E. Brese, M. O'Keeffe, Acta Crystallogr. B **47**, 192 (1991).
[27] B. Sundvall, Inorg. Chem. **22**, 1906 (1983).
[28] N. Kumada, N. Takahashi, N. Kinomura, A. W. Sleight, J. Solid State Chem. **139**, 321 (1998).