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# $[\text{Bi}_6\text{O}_{4.5}(\text{OH})_{3.5}]_2(\text{NO}_3)_{11}$ : a new anhydrous bismuth basic nitrate. Synthesis and structure determination from twinned crystals

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## Abstract

The bismuth basic nitrate  $[\text{Bi}_6\text{O}_{4.5}(\text{OH})_{3.5}]_2(\text{NO}_3)_{11}$  crystallizes in the monoclinic space group  $P2_1$  with  $a = 15.850(3)$  Å,  $b = 14.986(3)$  Å,  $c = 18.230(4)$  Å,  $\beta = 107.329(17)^\circ$  and  $V = 4133.7(14)$  Å<sup>3</sup> ( $Z = 4$ ). Its structure has been determined from 120 K, twinned crystal X-ray data (16 781 reflections, 683 parameters,  $R = 0.0703$ ). It is built upon  $[\text{Bi}_6\text{O}_x(\text{OH})_{8-x}]^{(10-x)+}$ ,  $x = 4$  and  $x = 5$  hexanuclear complexes and nitrate groups. The polycationic entities are linked to the nitrate anions either by hydrogen bonds or through bismuth–oxygen coordination. Even at 120 K, the  $[\text{Bi}_6\text{O}_4(\text{OH})_4]^{6+}$  and  $[\text{Bi}_6\text{O}_5(\text{OH})_3]^{5+}$  polycations could not be observed as such, the crystal structure refinement only detecting an average  $[\text{Bi}_6\text{O}_{4.5}(\text{OH})_{3.5}]^{5.5+}$  polycation. To prove the presence of both hexanuclear complexes in the structure, we report the existence of a correlation between the bismuth-linked oxygen bond-valence parameters and the presence, or not, of hydroxyl groups. Moreover, the Raman spectrum of the new anhydrous bismuth basic nitrate is compared to those of  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ ,  $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot 4\text{H}_2\text{O}$ , and two yet uncharacterized bismuth nitrates.

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**Keywords:** Anhydrous bismuth basic nitrate; Twinned crystal; Structure determination

## 1. Introduction

In the course of prospecting for new bismuth cuprates, hydrothermal syntheses under autogeneous pressure were considered as a potentially efficient method [1]. Different bismuth precursors and various media were thus tested under those conditions with the hope of obtaining mixed valence compounds. Several attempts starting with bismuth oxide in acidic solutions almost exclusively led to bismuth acid salts, for instance  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  in  $\text{HNO}_3$  solution. With bismuth nitrate as a precursor and in aqueous or basic solutions, three uncharacterized bismuth basic nitrates:  $[\text{Bi}_6\text{O}_{4.5}(\text{OH})_{3.5}]_2(\text{NO}_3)_{11}$ ,  $\text{Bi}_2\text{O}_2(\text{OH})(\text{NO}_3)$  and a still undefined compound (labeled **X** in this work [2]) were obtained. We therefore punctually focussed our attention on the  $[\text{Bi}_6\text{O}_{4.5}(\text{OH})_{3.5}]_2(\text{NO}_3)_{11}$  new compound.

About 15 bismuth basic nitrates have already been described in the literature since the 17th century [3]. Only a few have been unequivocally confirmed by recent

investigations. The main reasons for such a great variety of compounds and for the possible confusion arising from the older literature are the difficulties encountered in their chemical analyses and in isolating pure phases. Other reasons are the presence of very loosely bounded water molecules or hydroxyl groups and the lack of powerful physical identification methods. For further information in that field, it is rather interesting to report a non-exhaustive list of identified compounds such as  $\text{Bi}_2\text{O}_3$ ,  $\text{BiONO}_3 \cdot n\text{H}_2\text{O}$  [4–7],  $3\text{Bi}_2\text{O}_3$ ,  $2\text{N}_2\text{O}_5$ ,  $4\text{H}_2\text{O}$  [8],  $\text{BiO}(\text{OH})_{1/2}(\text{NO}_3)_{1/2}$  [9],  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  [10],  $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot 4\text{H}_2\text{O}$  [11],  $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_5 \cdot \text{H}_2\text{O}$  [12] and  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  [13]. All these compounds have not yet been fully characterized. In general, among the number of entities formed by the  $\text{Bi}^{3+}/\text{O}^{2-}$  ions in these nitrates (i.e., isolated  $\text{Bi}^{3+}$ ,  $[\text{Bi}_2\text{O}_2]^{2+}$  Aurivillius-type planes, 1D columns, etc.), one predominant arrangement stands out,  $[\text{Bi}_6\text{O}_x(\text{OH})_{8-x}]^{(10-x)+}$ : the intramolecular polycondensation of  $[\text{Bi}_6(\text{OH})_{12}]^{6+}$  ions, present in solutions of Bi basic salts [14,15]. In his systematic study of bismuth basic nitrates, Lazarini determined the crystal structures of three compounds,  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  [10],

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$[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot 4\text{H}_2\text{O}$  [11], and  $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_5 \cdot \text{H}_2\text{O}$  [12], showing heteropolycations of this kind. In the present study, we report the synthesis, the structure determination and the Raman spectroscopy analysis of a new, water-free bismuth basic nitrate:  $[\text{Bi}_6\text{O}_{4.5}(\text{OH})_{3.5}]_2(\text{NO}_3)_{11}$ . Both polycations ( $x = 5$  and 4) are present in this compound. In fact, our study shows that the two  $[\text{Bi}_6\text{O}_x(\text{OH})_{8-x}]^{(10-x)+}$  polycations cannot be isolated as such, the crystal structure refinement only giving an average  $[\text{Bi}_6\text{O}_{4.5}(\text{OH})_{3.5}]^{5.5+}$  polycation. To prove the presence of both polycations in the structure, we report the existence of a correlation between the oxygen to bismuth bond-valence parameters [16] and the presence, or not, of hydroxyl groups.

## 2. Experimental

### 2.1. Synthesis

$[\text{Bi}_6\text{O}_{4.5}(\text{OH})_{3.5}]_2(\text{NO}_3)_{11}$ : Colorless crystals of the title compound have been obtained through a slow evaporation of a bismuth basic nitrate (Prolabo, corresponding to  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  solution ( $1 \text{ g L}^{-1}$ )) at room temperature in air.

$\text{Bi}_2\text{O}_2(\text{OH})(\text{NO}_3)$ : A mixture of 0.7 g  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (Aldrich, 99.99%) and 0.1 g KOH was placed in a 23 mL Teflon-lined stainless steel autoclave with 14 mL of water and then heated at  $180^\circ\text{C}$  for 1 day. The resulting product (white powder) was filtered, water washed and dried at room temperature. The crystal structure determination is not fully completed yet, but the formula has been ascertained and we can announce a pseudo-tetragonal unit cell with parameters  $a \approx 5.39 \text{ \AA}$ ,  $c \approx 17.14 \text{ \AA}$ .

**X**: 0.5 g  $\text{Bi}_2\text{O}_3$  (Aldrich, 99.99%) was dissolved in 2 mL nitric acid solution (70%, sds). This solution was added dropwise in 200 mL of a 50/50 water/ethanol solution. The precipitate was filtered, water washed and dried at room temperature. Tentatively, we can propose that the phase crystallizes in a rhombohedral unit cell with  $a = 15.184(2) \text{ \AA}$ ,  $c = 15.833(2) \text{ \AA}$ ,  $F(20) = 48(0.0078, 53)$ .

$[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  and  $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot 4\text{H}_2\text{O}$ : Syntheses have been carried out according to Refs. [10] and [11], respectively.

### 2.2. Data collection

Several sphere-like crystals of  $[\text{Bi}_6\text{O}_{4.5}(\text{OH})_{3.5}]_2(\text{NO}_3)_{11}$  were tested on a Bruker–Nonius Kappa CCD diffractometer at 120 K. The low temperature, needed to improve the diffracted intensity, was achieved using an Oxford cryostream cooler. All crystals showed complicated diffraction patterns that, although easily indexed with a large monoclinic cell (*ca.*  $a = 36.3 \text{ \AA}$ ,  $b =$

$60.4 \text{ \AA}$ ,  $c = 15.9 \text{ \AA}$ ,  $\beta = 106.6^\circ$ ), presented an unusual set of extinctions, clearly hinting at a probable twinning. In addition to the twinning, the structure appeared as a twofold weak superstructure along the *a*-axis. A thorough analysis of the diffraction patterns suggested a monoclinic cell as the possible true supercell ( $a = 15.85 \text{ \AA}$ ,  $b = 15.00 \text{ \AA}$ ,  $c = 18.23 \text{ \AA}$ ,  $\beta = 107.3^\circ$ , i.e., height times smaller than the original one), the larger apparent cell being recovered by threefold rotations around the new *a*-axis. The topological reasons for such a twin arrangement will be explained thereafter. The domains appeared as approximately equally sized for each tested crystal. Several data collections were carried out on different crystals but all attempts to solve the structure using different space groups failed. To ease both the choice of the space group and the structure determination, a crystal was cut, hoping a splitting into crystals with different domain sizes in case of a macrotwinning. A twin ratio change upon cutting the crystal was indeed observed, reflecting the prospected macrotwinning, and a crystal with domains approximately 70:12:18 in ratio was selected and used in subsequent measurements.

The crystal was mounted onto a glass fiber on a goniometer head using silicone grease. The data collection was carried out at 120 K on the Kappa CCD diffractometer, using two different exposure times (192 and 38 s) to collect enough weak-intensity satellites and at the same time overcome main reflection overflow scans. The lattice parameters were least-squares refined [17] from the positions of 680 reflections of the main twin domain:  $a = 15.850(3) \text{ \AA}$ ,  $b = 14.986(3) \text{ \AA}$ ,  $c = 18.230(4) \text{ \AA}$ ,  $\beta = 107.329(17)^\circ$  and  $V = 4133.7(14) \text{ \AA}^3$  ( $Z = 4$ ). Data collection details are gathered in Table 1.

### 2.3. Data processing and structure determination

The intensity integration was carried out with the Bruker–Nonius EvalCCD program package for the main domain only, nevertheless taking into account the two other domains to reject partially overlapping reflections and model peak shapes. The set of reflection intensities was then corrected for absorption via a Gaussian analytical method, using an approximate face indexing due to the absence of well-defined faces. All calculations, but the direct methods achieved with the Shelxs program [18], have been carried out with the Jana2000 suite program [19]. Taking into account the twinning and the space group selection (*vide infra*) the initial set of 150 565 reflections was merged according to the 2-point group. A rather high internal *R* value of 0.12 for observed reflections ( $I \geq 3\sigma(I)$  cutoff, redundancy of 3.5) was calculated, inherent to the macrotwinning for which no proper correction can be realized and to the very high linear absorption coefficient ( $54.52 \text{ mm}^{-1}$ ). A set of 16 781 independent

Table 1  
Crystallographic data for  $[\text{Bi}_6\text{O}_{4.5}(\text{OH})_{3.5}]_2(\text{NO}_3)_{11}$

<b>1. Physical, crystallographic, and analytical data</b>	
Formula	$\text{Bi}_{12}\text{N}_{11}\text{O}_{49}\text{H}_7$
Crystal color	Colorless
Molecular weight ( $\text{g mol}^{-1}$ )	3452.84
Crystal system	Monoclinic
Space group	$P2_1$
Temperature (K)	120
Cell parameters (from 680 reflections collected on CCD)	
$a$ (Å)	15.850(3)
$b$ (Å)	14.986(3)
$c$ (Å)	18.230(4)
$\beta$ (deg)	107.329(17)
$V$ (Å <sup>3</sup> )	4133.7(14)
$Z$	4
Density (calc.)	5.5463
Crystal description	Block
Crystal size ( $\text{mm}^3$ )	$\sim 0.06 \times 0.07 \times 0.1$
<b>2. Data collection</b>	
Diffractometer	Brüker–Nonius Kappa CCD
Monochromator	Oriented graphite (002)
Radiation	MoK-L <sub>2,3</sub> ( $\lambda = 0.71073$ Å)
Scan mode	$\varphi$ and $\omega$
No. of measured reflections	150 565
$hkl$ range	$-23 \leq h \leq 25$ $-24 \leq k \leq 24$ $-29 \leq l \leq 29$
$\sin(\theta)/\lambda$ range	0.12–0.81
Twin matrices/twin fractions	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} // 0.422(16), 0.264(16)$ $\begin{pmatrix} -1 & 0 & 0 \\ 1/4 & -1/2 & 3/4 \\ 1/2 & 1 & 1/2 \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ -1/4 & 1/2 & -3/4 \\ -1/2 & -1 & -1/2 \end{pmatrix} // 0.0659(13), 0.0659$ $\begin{pmatrix} -1 & 0 & 0 \\ -1/4 & -1/2 & -3/4 \\ 1/2 & -1 & 1/2 \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 1/4 & 1/2 & 3/4 \\ -1/2 & 1 & -1/2 \end{pmatrix} // 0.0913(13), 0.0913$
<b>3. Data reduction</b>	
Linear absorption coeff. ( $\text{mm}^{-1}$ )	54.52
Absorption correction	Analytical (Gaussian integration)
$T_{\min}/T_{\max}$	0.050/0.350
Number of reflections	150 656
No. of independent reflections	42 965
Criteria for observed reflections	$I > 3\sigma(I)$
$R_{\text{int}}$ (obs)	0.12
Average redundancy	3.5
No. of observed reflections	17 159
<b>4. Refinement</b>	
Refinement	$F^2$
No. of reflections used in the refinement	16 781
$\sin(\theta)/\lambda$ cutoff	0.75
$R^a$ (obs)	0.0703
$R_w^b$ (obs)	0.144
$S$ (obs)	1.48
No. of refined parameters	683
Weighting scheme	$w = 1/(\sigma^2( F_o ^2) + 0.0025 F_o ^2)$
Secondary extinction coeff.	None
Difference Fourier residues	$[-4.5 + 11.3] \text{ e}^- \text{ \AA}^{-3}$

<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ .

<sup>b</sup>  $R_w = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(|F_o|^4)]^{1/2}$ .

observed reflections ( $\sin(\theta)/\lambda < 0.75 \text{ \AA}^{-1}$ ) were then available for refinement. See Table 1 for additional information.

From the systematic absences,  $P2_1/m$  and  $P2_1$  were identified as possible space groups, but other space groups could also be possible since the twin-related Bragg reflection overlap could invalidate systematic absences. Several tests in  $P2_1/m$  failed and  $P2_1$  was in turn considered. As it is usually the case for weak superstructure, the structure determination was initiated from the main reflections ( $a/2$ ,  $b$ ,  $c$  subcell) only. Given the small proportion of the two additional domains of the twinned crystal, a solution was finally found for the Bi atoms in the direct methods output, yielding octahedral Bi entities similar to those observed in related compounds [10–12]. No further progress could be done in the subcell. The solution was thus transposed into the supercell and the translationally pseudo-equivalent Bi positions decorrelated through many refinement cycles with a small dampening factor (0.01), yielding a residual factor of  $R = 0.11$ . Some oxygen atoms of the  $[\text{Bi}_6\text{O}_{4.5}(\text{OH})_{3.5}]^{5.5+}$  entities were found in difference Fourier synthesis maps and introduced in the structural model. The missing oxygen atoms of those entities were then positioned following the pseudo- $a/2$  symmetry translation. Because of strong correlations between the  $a/2$  related oxygen atoms, constraints were introduced on the isotropic displacement parameters (two related atoms being given the same isotropic parameter). To reduce the difference Fourier synthesis residues around the Bi atoms and find the missing part of the structure, anisotropic tensors were introduced for the bismuth atoms. The residual factor slightly improved with  $R = 0.091$  for 330 parameters.

From that stage, each atom of the 22  $[\text{NO}_3]^-$  groups was successively found in the difference Fourier syntheses, looking in the empty spaces left in between the  $[\text{Bi}_6\text{O}_{4.5}(\text{OH})_{3.5}]^{5.5+}$  entities. It was quickly realized that those  $[\text{NO}_3]^-$  groups were not related by the pseudo- $a/2$  translation and were thus at the origin of the superstructure. To stabilize the refinement and get realistic  $[\text{NO}_3]^-$  anions, soft restrains were introduced on both the N–O distance (1.25(2) Å) and the O–N–O angles ( $120(1)^\circ$ ). When all the space between the  $[\text{Bi}_6\text{O}_{4.5}(\text{OH})_{3.5}]^{5.5+}$  entities had been filled by the  $[\text{NO}_3]^-$  groups, the soft restrains on the angles were removed but those on the distances were kept. Indeed, the  $[\text{NO}_3]^-$  groups are poorly defined because of both their weak diffracting power as compared to that of Bi and their rather high atomic displacement parameters. With 352 additional parameters, the residual value dropped to  $R = 0.071$ . The presence of water molecule was ruled out by means of a search for extra empty space with the Platon program [20]. Given the non-centrosymmetry of the space group, additional twinning matrices were introduced to account for the possible

Table 2

Fractional atomic coordinates, equivalent isotropic displacement parameters ( $\text{\AA}^2$ , Bi), isotropic displacement parameters ( $\text{\AA}^2$ , N and O), and s.u.'s for  $[\text{Bi}_6\text{O}_{4.5}(\text{OH})_{3.5}]_2(\text{NO}_3)_{11}$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	
Bi11	0.01001(11)	0.376	0.11413(10)	0.0145(5)
Bi12	0.22206(11)	0.10732(15)	0.13624(12)	0.0205(6)
Bi13	0.16594(11)	0.30191(17)	0.00902(11)	0.0193(6)
Bi14	−0.01190(11)	0.15682(17)	0.03831(10)	0.0189(6)
Bi15	0.06588(11)	0.18948(16)	0.23920(10)	0.0168(6)
Bi16	0.24657(10)	0.33329(16)	0.21698(11)	0.0154(6)
Bi21	0.53426(11)	0.38463(17)	0.10255(12)	0.0245(6)
Bi22	0.72855(12)	0.10114(16)	0.13454(11)	0.0202(6)
Bi23	0.70208(11)	0.29469(17)	0.01613(11)	0.0211(6)
Bi24	0.50232(11)	0.16419(17)	0.01696(11)	0.0216(6)
Bi25	0.56590(10)	0.18687(16)	0.22687(10)	0.0155(5)
Bi26	0.75776(10)	0.32085(16)	0.22031(10)	0.0169(6)
Bi31	0.17876(11)	0.17599(16)	0.52655(10)	0.0153(5)
Bi32	−0.02025(10)	0.30700(16)	0.51902(10)	0.0143(5)
Bi33	0.03948(11)	0.30758(16)	0.72845(10)	0.0159(5)
Bi34	0.20437(11)	0.38099(16)	0.63605(11)	0.0170(6)
Bi35	0.01623(11)	0.09513(16)	0.62193(11)	0.0165(6)
Bi36	0.23655(11)	0.16835(16)	0.73419(10)	0.0179(6)
Bi41	0.64644(11)	0.18898(16)	0.50704(10)	0.0165(6)
Bi42	0.45680(11)	0.31971(16)	0.53284(10)	0.0168(6)
Bi43	0.54217(12)	0.30415(18)	0.73142(11)	0.0239(6)
Bi44	0.69393(11)	0.38857(16)	0.62479(11)	0.0167(6)
Bi45	0.73171(11)	0.16871(17)	0.71813(11)	0.0199(6)
Bi46	0.49840(11)	0.10794(14)	0.61898(11)	0.0180(6)
O11	0.0411(19)	0.287(2)	0.0402(19)	0.029(6)
O12	0.0812(16)	0.1275(17)	0.1376(16)	0.012(4)
O13	0.1084(17)	0.309(2)	0.2082(17)	0.019(5)
O14	0.2400(14)	0.2481(16)	0.1220(15)	0.003(3)
O15	−0.0435(16)	0.2393(18)	0.1285(17)	0.012(4)
O16	0.1567(17)	0.4070(19)	0.1029(17)	0.017(4)
O17	0.132(2)	0.145(2)	0.0092(19)	0.029(5)
O18	0.2424(17)	0.180(2)	0.2529(17)	0.022(5)
O21	0.6679(17)	0.3548(19)	0.1142(16)	0.017
O22	0.6362(19)	0.177(2)	0.0372(18)	0.029
O23	0.6929(18)	0.192(2)	0.2148(17)	0.022
O24	0.5030(16)	0.2437(18)	0.1143(17)	0.012
O25	0.7987(15)	0.2355(16)	0.1229(15)	0.003
O26	0.5348(19)	0.315(2)	−0.0081(19)	0.029
O27	0.5628(16)	0.0850(18)	0.1278(16)	0.012
O28	0.6045(17)	0.332(2)	0.2351(17)	0.019
O31	0.145(2)	0.126(2)	0.625(2)	0.031(6)
O32	0.1195(16)	0.3020(19)	0.5482(15)	0.013(4)
O33	0.1672(15)	0.2977(17)	0.7169(15)	0.011(4)
O34	−0.0161(17)	0.2353(19)	0.6224(18)	0.016(4)
O35	0.2694(16)	0.2433(18)	0.6326(17)	0.014(4)
O36	0.0791(17)	0.155(2)	0.7399(17)	0.018(5)
O37	0.0388(16)	0.4036(18)	0.6238(16)	0.011(4)
O38	0.0096(17)	0.1615(19)	0.4957(17)	0.016(4)
O41	0.5503(16)	0.3592(18)	0.6247(16)	0.011
O42	0.5958(17)	0.182(2)	0.7102(17)	0.018
O43	0.5145(16)	0.1912(19)	0.5335(16)	0.016
O44	0.7178(16)	0.2458(19)	0.6143(17)	0.014
O45	0.4365(17)	0.2402(19)	0.6269(19)	0.016
O46	0.6093(16)	0.3365(18)	0.5009(16)	0.013
O47	0.6991(16)	0.3170(17)	0.7460(15)	0.011
O48	0.668(2)	0.078(2)	0.616(2)	0.031
N1	0.4229(18)	0.031(2)	0.231(3)	0.051(13)
O1a	0.5020(16)	0.0107(17)	0.2650(16)	0.014(6)
O1b	0.403(2)	0.110(2)	0.210(2)	0.038(9)
O1c	0.3661(18)	−0.0297(18)	0.2131(18)	0.023(7)

Table 2 (continued)

Atom	x	y	z	
N2	0.893(2)	0.089(3)	0.3035(18)	0.037(11)
O2a	0.822(2)	0.050(3)	0.301(2)	0.053(11)
O2b	0.8925(16)	0.1407(18)	0.2500(16)	0.014(6)
O2c	0.9641(17)	0.083(2)	0.3572(17)	0.021(7)
N3	0.4548(18)	0.271(2)	0.3354(17)	0.014(7)
O3a	0.5241(17)	0.228(2)	0.3638(18)	0.025(7)
O3b	0.407(2)	0.308(2)	0.370(2)	0.042(9)
O3c	0.438(3)	0.291(3)	0.2664(19)	0.058(12)
N4	0.3018(18)	0.246(3)	0.908(2)	0.045(13)
O4a	0.2231(16)	0.2270(17)	0.8837(15)	0.010(6)
O4b	0.358(2)	0.229(2)	0.875(2)	0.033(8)
O4c	0.327(3)	0.267(3)	0.978(2)	0.084(16)
N5	0.675(2)	0.4939(18)	0.3561(18)	0.016(8)
O5a	0.717(2)	0.484(2)	0.3084(17)	0.029(8)
O5b	0.6218(17)	0.4358(18)	0.3609(17)	0.020(7)
O5c	0.679(2)	0.567(2)	0.390(2)	0.042(9)
N6	0.945(2)	0.212(3)	0.8389(17)	0.031(10)
O6a	1.0228(18)	0.232(2)	0.868(2)	0.032(8)
O6b	0.898(3)	0.192(3)	0.881(2)	0.064(12)
O6c	0.9194(18)	0.212(2)	0.7671(16)	0.021(7)
N7	0.866(2)	0.401(2)	0.9493(18)	0.024(9)
O7a	0.8688(17)	0.3372(18)	0.9941(16)	0.020(7)
O7b	0.914(3)	0.467(2)	0.972(3)	0.062(12)
O7c	0.812(2)	0.408(3)	0.884(2)	0.059(12)
N8	0.365(2)	0.092(2)	0.4407(17)	0.031(10)
O8a	0.4067(16)	0.0264(15)	0.4773(15)	0.007(5)
O8b	0.345(2)	0.157(2)	0.4739(19)	0.034(8)
O8c	0.347(2)	0.086(2)	0.3701(18)	0.038(9)
N9	0.8773(17)	0.019(2)	0.7169(18)	0.028(9)
O9a	0.9568(16)	−0.0035(18)	0.7383(16)	0.017(6)
O9b	0.8243(17)	0.0080(19)	0.7546(16)	0.020(7)
O9c	0.8568(18)	0.0720(19)	0.6616(16)	0.024(7)
N10	0.3454(18)	0.026(2)	0.025(2)	0.020(8)
O10a	0.4127(18)	0.000(2)	0.0085(19)	0.023(7)
O10b	0.2758(19)	−0.018(2)	0.013(2)	0.034(8)
O10c	0.345(2)	0.102(2)	0.051(2)	0.057(11)
N11	0.7918(17)	0.236(2)	0.4098(16)	0.014(7)
O11a	0.7128(17)	0.246(2)	0.3780(19)	0.025(7)
O11b	0.8163(17)	0.2020(18)	0.4750(15)	0.019(6)
O11c	0.844(2)	0.257(2)	0.374(2)	0.036(9)
N12	0.8377(19)	0.4940(17)	0.147(2)	0.017(8)
O12a	0.8865(18)	0.5477(19)	0.1261(18)	0.023(7)
O12b	0.852(2)	0.4123(17)	0.143(2)	0.030(8)
O12c	0.7750(17)	0.5199(19)	0.1690(17)	0.019(7)
N13	0.374(2)	0.4934(17)	0.589(2)	0.024(9)
O13a	0.3694(17)	0.4129(16)	0.6063(16)	0.013(6)
O13b	0.324(2)	0.546(2)	0.609(2)	0.033(8)
O13c	0.4189(19)	0.517(2)	0.5461(18)	0.028(8)
N14	0.2223(19)	0.316(2)	0.4097(16)	0.019(8)
O14a	0.261(2)	0.310(3)	0.4806(17)	0.042(9)
O14b	0.237(2)	0.369(2)	0.3628(18)	0.039(9)
O14c	0.1656(19)	0.2547(19)	0.3859(19)	0.028(8)
N15	0.3370(19)	0.448(2)	0.0180(19)	0.014(7)
O15a	0.3929(18)	0.4834(19)	−0.0067(17)	0.021(7)
O15b	0.259(2)	0.471(4)	−0.010(3)	0.094(17)
O15c	0.360(3)	0.409(3)	0.081(2)	0.072(14)
N16	0.8871(17)	0.4601(19)	0.726(2)	0.021(8)
O16a	0.9594(18)	0.499(2)	0.745(2)	0.030(8)
O16b	0.8216(18)	0.5016(19)	0.7341(19)	0.027(8)
O16c	0.8731(18)	0.3845(18)	0.6955(17)	0.025(7)
N17	0.964(2)	0.381(2)	0.3241(19)	0.047(12)
O17a	1.019(2)	0.377(2)	0.3896(18)	0.038(9)
O17b	0.9581(16)	0.3161(17)	0.2787(15)	0.014(6)
O17c	0.9048(19)	0.441(2)	0.3168(19)	0.030(8)

Table 2 (continued)

Atom	x	y	z	
N18	0.096(2)	0.4769(18)	0.8819(19)	0.021(8)
O18a	0.1001(18)	0.5601(17)	0.8838(18)	0.022(7)
O18b	0.140(2)	0.444(3)	0.843(2)	0.048(10)
O18c	0.062(2)	0.443(3)	0.929(2)	0.049(11)
N19	0.3798(19)	0.393(2)	0.8008(18)	0.027(9)
O19a	0.4505(17)	0.405(2)	0.8532(16)	0.022(7)
O19b	0.314(2)	0.442(2)	0.793(2)	0.039(9)
O19c	0.3686(19)	0.335(2)	0.7491(18)	0.030(8)
N20	0.832(2)	0.4658(17)	0.528(2)	0.022(9)
O20a	0.8182(17)	0.3847(16)	0.5330(16)	0.019(6)
O20b	0.7994(17)	0.5207(17)	0.5643(16)	0.019(6)
O20c	0.8934(19)	0.492(2)	0.5039(19)	0.027(8)
N21	0.746(2)	0.145(2)	0.9096(18)	0.037(11)
O21a	0.750(2)	0.078(2)	0.872(2)	0.047(10)
O21b	0.7884(19)	0.156(2)	0.9785(17)	0.030(8)
O21c	0.701(2)	0.208(2)	0.873(2)	0.039(9)
N22	0.465(3)	0.127(3)	0.823(2)	0.048(13)
O22a	0.433(2)	0.151(2)	0.7554(19)	0.033(8)
O22b	0.528(2)	0.169(3)	0.865(2)	0.067(12)
O22c	0.419(4)	0.073(4)	0.847(3)	0.11(2)

presence of enantiomorphic domains. Out of the three initial domains, only the main domain was refined as enantiomorphic, the two other minor components being doubled by an inversion matrix but with restrained, equal ratios (see Table 1). A secondary extinction coefficient could not be refined with a meaningful positive value, it was therefore not considered in the final refinement. The H atoms were not introduced in the calculation, their presence being later on deduced from the overall charge equilibrium and bond-valence sum calculations. At the end of the refinement, high residues (positive and negative) were still observed in the vicinity of the Bi atoms, indicating a bad intrinsic absorption correction (vide supra). Final residual factors are given in Table 1. Atomic parameters are gathered in Tables 2 and 3.

#### 2.4. Raman spectroscopy

Raman scattering spectra were recorded with a multichannel Jobin–Yvon T64000 spectrophotometer connected to a CCD detector using the 514 nm excitation line. The resolution was equal to 3 cm<sup>−1</sup> in the 35–600 cm<sup>−1</sup> spectra range. [Bi<sub>6</sub>O<sub>4.5</sub>(OH)<sub>3.5</sub>]<sub>2</sub>(NO<sub>3</sub>)<sub>11</sub>, Bi<sub>2</sub>O<sub>2</sub>(OH)(NO<sub>3</sub>), and the still undefined compound X [2] were analyzed and compared to [Bi<sub>6</sub>O<sub>5</sub>(OH)<sub>3</sub>](NO<sub>3</sub>)<sub>5</sub> · 3H<sub>2</sub>O [10] and [Bi<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>](NO<sub>3</sub>)<sub>6</sub> · 4H<sub>2</sub>O [11].

### 3. Structure description

The structure of [Bi<sub>6</sub>O<sub>4.5</sub>(OH)<sub>3.5</sub>]<sub>2</sub>(NO<sub>3</sub>)<sub>11</sub> is built from four crystallographically independent [Bi<sub>6</sub>O<sub>4.5</sub>(OH)<sub>3.5</sub>]<sup>5.5+</sup> hexanuclear complexes (the atoms

Table 3  
Anisotropic displacement parameters  $U^{ij}$  ( $\text{\AA}^2$ ) and s.u.'s for  $[\text{Bi}_6\text{O}_{4.5}(\text{OH})_{3.5}]_2(\text{NO}_3)_{11}$

Atom	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Bi11	0.0132(8)	0.0157(8)	0.0154(9)	0.0028(7)	0.0057(7)	0.0031(7)
Bi12	0.0164(9)	0.0146(9)	0.0353(12)	0.0058(7)	0.0152(9)	0.0034(8)
Bi13	0.0222(9)	0.0221(9)	0.0178(10)	0.0020(8)	0.0123(8)	0.0038(8)
Bi14	0.0185(8)	0.0231(9)	0.0131(9)	-0.0025(7)	0.0018(7)	-0.0025(7)
Bi15	0.0234(9)	0.0160(9)	0.0130(9)	-0.0020(7)	0.0087(7)	0.0001(7)
Bi16	0.0104(8)	0.0157(8)	0.0204(10)	-0.0007(7)	0.0050(7)	-0.0004(7)
Bi21	0.0150(9)	0.0180(9)	0.0319(12)	0.0054(7)	-0.0063(8)	-0.0025(9)
Bi22	0.0264(10)	0.0167(9)	0.0232(10)	0.0051(8)	0.0162(9)	0.0055(8)
Bi23	0.0197(9)	0.0221(9)	0.0205(10)	-0.0093(8)	0.0044(8)	0.0065(8)
Bi24	0.0176(9)	0.0254(10)	0.0201(10)	-0.0121(8)	0.0028(7)	-0.0052(8)
Bi25	0.0082(7)	0.0214(9)	0.0174(9)	-0.0013(7)	0.0046(7)	-0.0018(8)
Bi26	0.0098(8)	0.0186(9)	0.0180(9)	-0.0042(7)	-0.0027(7)	0.0013(7)
Bi31	0.0189(8)	0.0142(8)	0.0122(8)	0.0023(7)	0.0038(7)	-0.0010(7)
Bi32	0.0172(8)	0.0122(8)	0.0134(8)	0.0021(7)	0.0043(7)	0.0001(7)
Bi33	0.0172(8)	0.0166(8)	0.0147(9)	-0.0033(7)	0.0060(7)	-0.0018(7)
Bi34	0.0213(9)	0.0148(9)	0.0152(9)	-0.0054(7)	0.0062(7)	-0.0007(7)
Bi35	0.0157(8)	0.0138(8)	0.0186(10)	-0.0012(7)	0.0030(7)	0.0008(7)
Bi36	0.0210(9)	0.0149(8)	0.0133(9)	0.0018(7)	-0.0020(7)	-0.0024(7)
Bi41	0.0209(9)	0.0137(8)	0.0158(9)	0.0006(7)	0.0068(7)	-0.0019(7)
Bi42	0.0223(9)	0.0156(9)	0.0129(8)	0.0036(7)	0.0059(7)	0.0037(7)
Bi43	0.0330(10)	0.0233(10)	0.0185(10)	0.0044(9)	0.0125(8)	-0.0011(9)
Bi44	0.0173(9)	0.0107(8)	0.0224(10)	-0.0015(7)	0.0065(8)	-0.0011(7)
Bi45	0.0174(8)	0.0210(9)	0.0202(10)	0.0008(8)	0.0040(7)	0.0045(8)
Bi46	0.0216(9)	0.0159(9)	0.0156(10)	-0.0037(8)	0.0044(8)	-0.0004(8)

are denoted  $\text{Bi}_{ij}$  and  $\text{O}_{ij}$ , where  $i$  refers to the polycation, i.e., 1, 2, 3 or 4) and from nitrate ions (the atoms are denoted  $\text{N}_k$  and  $\text{O}_{ky}$ , where  $k$  refers to the nitrate group, i.e.,  $k = 1, \dots, 22$  ( $y = a, b$  or  $c$ )) (see Fig. 1). A projection of the crystal structure along the  $a$ -axis enables a good understanding of the twinning type. In fact it appears that the polycations form, perpendicularly to the  $a$ -axis, an hexagonal pavement. This pseudo-threefold symmetry is responsible for the existence of three twin domains, with respect to the  $\text{Bi}_6$  group hexagonal organization, as shown in Fig. 2. Both  $[\text{Bi}_6\text{O}_4(\text{OH})_4]^{6+}$  and  $[\text{Bi}_6\text{O}_5(\text{OH})_3]^{5+}$  polycations already observed in  $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot 4\text{H}_2\text{O}$  [11] and  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  [10] coexist in  $[\text{Bi}_6\text{O}_{4.5}(\text{OH})_{3.5}]_2(\text{NO}_3)_{11}$ . However, the crystal structure refinement only evidences an average  $[\text{Bi}_6\text{O}_{4.5}(\text{OH})_{3.5}]^{5.5+}$  composition for each polycation and the developed formulation can be written as  $[\text{Bi}_6\text{O}_4(\text{OH})_4][\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_{11}$ . This averaging originates from the existence of a random occupancy of some H sites, which suggests a high ionic conductivity by proton hopping. The polycationic entities are linked to the nitrate ions either by hydrogen bonds or through the bismuth–oxygen coordination.

In the four crystallographically unequivalent  $[\text{Bi}_6\text{O}_x(\text{OH})_{8-x}]^{(10-x)+}$  groups, Bi atoms are located at the corners of a nearly regular octahedron (see Fig. 3(a)). The Bi–Bi distances ranges from 3.47 to 3.78 Å, in fair agreement with the mean Bi–Bi distance observed in the bismuth basic nitrates [10,11] and in the

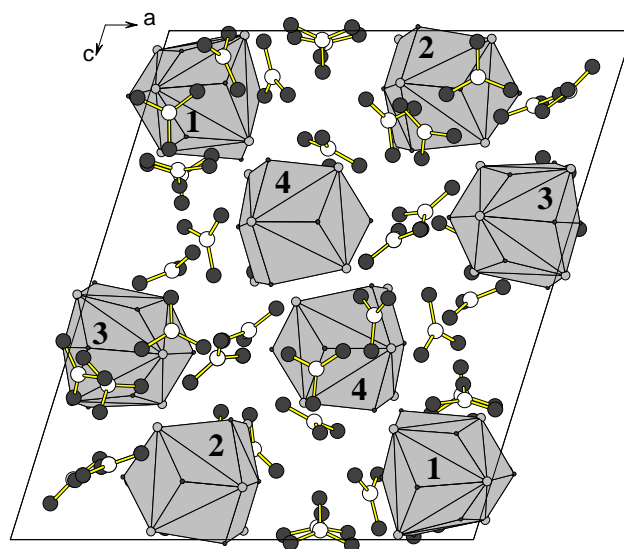


Fig. 1. View along the  $a$ -axis of the  $[\text{Bi}_6\text{O}_{4.5}(\text{OH})_{3.5}]_2(\text{NO}_3)_{11}$  structure.  $[\text{Bi}_6\text{O}_x(\text{OH})_{8-x}]^{(10-x)+}$  hexanuclear polycations are shown as polyhedrons to clarify the figure (white spheres correspond to the nitrogen atoms, dark gray spheres to oxygen atoms and soft gray spheres to the bismuth atoms).

$(\text{BiO}_2)_n$  chain [1] and  $\text{Bi}_2\text{O}_2^{2+}$  layer [21] containing compounds. The shortest Bi–Bi distance (3.475(2) Å) is significantly longer than the shortest one in elemental bismuth (3.072 Å) [22], excluding the possibility of Bi–Bi bonding in the polycations. The  $\text{O}_{ij}$  atoms cap the faces of the bismuth octahedron hence defining  $[\text{OBi}_3]$

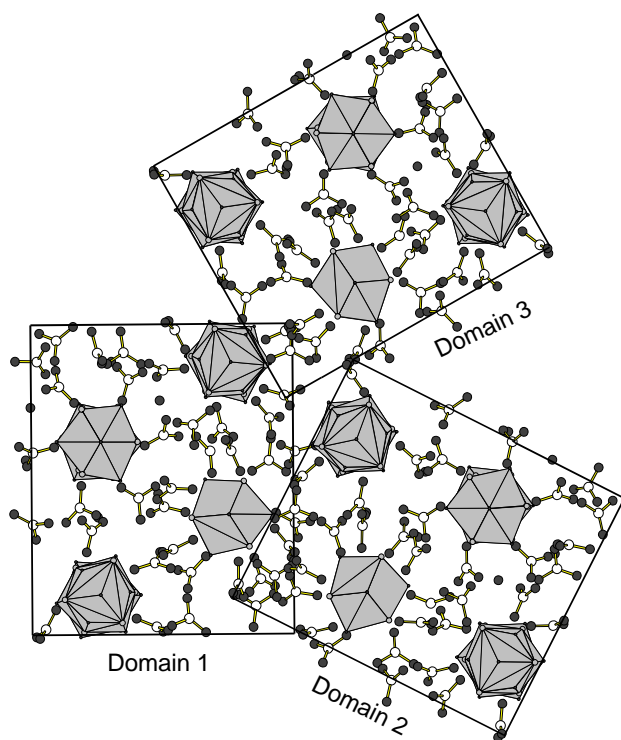


Fig. 2. View along the *a*-axis of the crystal structure showing the correspondence between its pseudo-threefold axis and the threefold axis of the twin law.

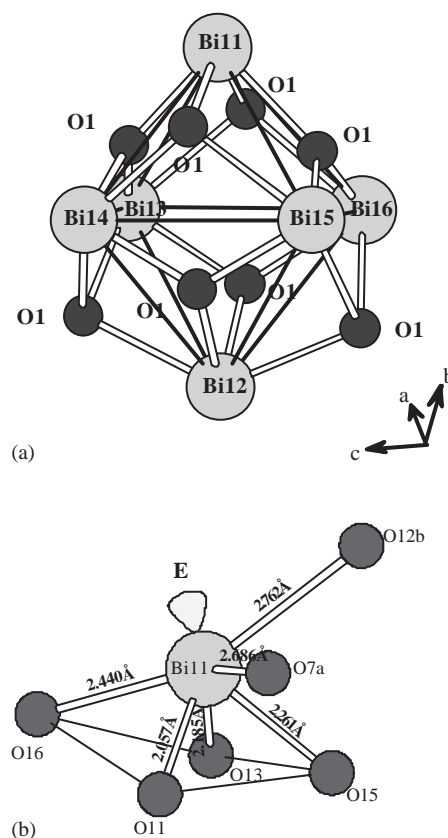


Fig. 3. (a) The  $[\text{Bi}_6\text{O}_x(\text{OH})_{8-x}]^{(10-x)+}$  hexanuclear polycation (arbitrary view). The  $\text{Bi}_6$  octahedron is marked by thick lines, not to be interpreted as indicative of Bi–Bi bonds. (b) Example of Bi coordination (dark gray spheres correspond to oxygen atoms and soft gray spheres to the bismuth atoms).

triangular-based pyramids (Fig. 3(a)). The bismuth electron lone pair (E) is expected to be located at the top of a non-regular  $\text{EO}_4\text{Bi}$  square pyramid [1,13], as displayed in Fig. 3(b). Based upon that assumption, electron lone pairs are pointing towards the bismuth octahedron center. Each bismuth atom is also linked either to one or two  $\text{O}_{ky}$  oxygen atoms of nitrate groups, with an average Bi–O distance of 2.75 Å to ensure the cohesion between the hexanuclear complexes. The average bond-valence sums calculated for Bi atoms over each hexanuclear complex, using  $\text{Bi}^{3+}\text{--O}^{2-}$  data ( $r_0 = 2.094$  and  $B = 0.37$ ) from Brown and Altermatt [23], are very similar (i.e., 3.09, 3.04, 3.12 and 3.09).

As already stated, the localization of the hydrogen atoms is not possible from our X-ray diffraction data set, due to the presence of heavy Bi atoms and twinning. Thus, to discriminate between oxo and hydroxyl groups in the  $[\text{Bi}_6\text{O}_x(\text{OH})_{8-x}]^{(10-x)+}$  complexes, bond-valence parameters  $v$  [16] were calculated for Bi-linked oxygen atoms, not only for the title compound (Table 4) but also for  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  [10] and  $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot 4\text{H}_2\text{O}$  [11] (Table 5).

For  $[\text{Bi}_6\text{O}_5(\text{OH})_3]^{5+}$  [10], the bond-valence parameter calculation yielded five values above and three values below the 2 value limit (with average values of 2.39 and 1.32, respectively), corresponding to oxygen atoms in 5  $\text{O}^{2-}$  oxo and in 3  $\text{HO}^-$  hydroxyl groups, respectively.

For  $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot 4\text{H}_2\text{O}$  [11], we identify four oxo oxygen atoms with an average bond-valence parameter around 2.45 and four hydroxyl oxygen atoms with  $v$  around 1.30 (see Table 5), in good agreement with the  $[\text{Bi}_6\text{O}_4(\text{OH})_4]^{6+}$  polycation formulation.

For the four different polycations of the title compound, the bond-valence parameter calculation lets to discriminate between three types of oxygen atoms (see Table 4):

- (i) bond-valence parameters of *ca.* 2.60 ( $\text{O}i1$ ,  $\text{O}i2$ ,  $\text{O}i3$  and  $\text{O}i4$ ,  $i = 1, \dots, 4$ ) can be assigned to oxo oxygen atoms;
- (ii)  $v$  of *ca.* 1.25 can be attributed to hydroxyl oxygen atoms ( $\text{O}i6$ ,  $\text{O}i7$  and  $\text{O}i8$ ,  $i = 1, \dots, 4$ );
- (iii) intermediate  $v$  value (*ca.* 1.73), found in the four polycations, corresponds to the  $\text{O}i5$  ( $i = 1, \dots, 4$ ) oxygen atoms which are 50% oxo oxygen atoms and 50% hydroxyl oxygen atoms, yielding  $[\text{Bi}_6\text{O}_5(\text{OH})_3]^{5+}$  and  $[\text{Bi}_6\text{O}_4(\text{OH})_4]^{6+}$  polycations, respectively.

Fig. 4 shows the possible location of the H atoms in the polycations. The  $\text{O}15\text{--O}25$  and  $\text{O}35\text{--O}45$  distances

Table 4

Distances (Å) and valence-bond sum parameter for the oxygen atoms of the hexanuclear complexes  $[\text{Bi}_6\text{O}_{4.5}(\text{OH})_{3.5}]^{5.5+}$ 

$O_i$	$\text{Bi}_j$	$d(O_i - \text{Bi}_j)$	$v_i$	$\nu$	$O_i$	$\text{Bi}_j$	$d(O_i - \text{Bi}_j)$	$v_i$	$\nu$
O11	Bi11	2.057(35)	1.09	2.71	O31	Bi35	2.077(33)	1.04	2.66
	Bi14	2.12(3)	0.92			Bi31	2.154(39)	0.84	
	Bi13	2.227(35)	0.69			Bi36	2.179(37)	0.79	
O12	Bi14	2.015(32)	1.22	2.71	O32	Bi34	2.119(30)	0.92	2.59
	Bi15	2.15(3)	0.85			Bi32	2.120(26)	0.92	
	Bi12	2.259(27)	0.63			Bi31	2.198(29)	0.75	
O13	Bi15	2.053(31)	1.11	2.67	O33	Bi33	2.100(26)	0.97	2.57
	Bi16	2.178(28)	0.79			Bi34	2.143(29)	0.87	
	Bi11	2.185(33)	0.77			Bi36	2.206(25)	0.73	
O14	Bi16	2.130(27)	0.90	2.49	O34	Bi32	2.153(32)	0.84	2.49
	Bi12	2.153(24)	0.84			Bi35	2.162(29)	0.82	
	Bi13	2.198(30)	0.75			Bi33	2.164(32)	0.82	
O15	Bi14	2.230(32)	0.68	1.80	O35	Bi31	2.274(32)	0.61	1.64
	Bi11	2.261(28)	0.63			Bi34	2.316(27)	0.54	
	Bi15	2.356(35)	0.49			Bi36	2.352(32)	0.49	
O16	Bi13	2.361(31)	0.48	1.29	O36	Bi35	2.270(32)	0.61	1.39
	Bi16	2.411(33)	0.42			Bi33	2.364(30)	0.48	
	Bi11	2.440(29)	0.39			Bi36	2.537(29)	0.30	
O17	Bi12	2.398(37)	0.43	1.19	O37	Bi32	2.355(29)	0.49	1.19
	Bi13	2.413(30)	0.42			Bi33	2.388(29)	0.45	
	Bi14	2.497(36)	0.33			Bi34	2.590(26)	0.26	
O18	Bi12	2.325(31)	0.53	1.14	O38	Bi32	2.296(29)	0.57	1.19
	Bi16	2.395(30)	0.44			Bi35	2.481(31)	0.35	
	Bi15	2.736(28)	0.17			Bi31	2.579(28)	0.27	
O21	Bi26	2.095(33)	0.99	2.65	O41	Bi42	1.970(31)	1.38	2.77
	Bi21	2.113(28)	0.94			Bi43	2.154(30)	0.84	
	Bi23	2.209(32)	0.72			Bi44	2.316(27)	0.54	
O22	Bi24	2.052(31)	1.11	2.64	O42	Bi43	2.104(31)	0.96	2.61
	Bi23	2.142(32)	0.87			Bi45	2.122(28)	0.92	
	Bi22	2.244(34)	0.66			Bi46	2.204(32)	0.73	
O23	Bi25	2.091(31)	1.00	2.55	O43	Bi46	2.074(30)	1.04	2.54
	Bi26	2.176(30)	0.79			Bi42	2.129(28)	0.90	
	Bi22	2.191(33)	0.76			Bi41	2.282(30)	0.60	
O24	Bi24	2.133(31)	0.89	2.45	O44	Bi41	2.128(32)	0.90	2.48
	Bi25	2.172(32)	0.80			Bi45	2.167(30)	0.81	
	Bi21	2.194(27)	0.75			Bi44	2.191(27)	0.76	
O25	Bi23	2.267(31)	0.62	1.53	O45	Bi42	2.189(34)	0.77	1.96
	Bi22	2.341(25)	0.51			Bi46	2.232(29)	0.68	
	Bi26	2.427(29)	0.40			Bi43	2.338(35)	0.51	
O26	Bi21	2.270(35)	0.61	1.33	O46	Bi41	2.282(27)	0.60	1.26
	Bi24	2.391(31)	0.44			Bi44	2.387(33)	0.45	
	Bi23	2.573(31)	0.27			Bi42	2.661(30)	0.21	
O27	Bi24	2.291(30)	0.58	1.32	O47	Bi45	2.372(26)	0.47	1.26
	Bi25	2.355(29)	0.49			Bi43	2.429(26)	0.40	
	Bi22	2.602(27)	0.25			Bi44	2.437(28)	0.39	
O28	Bi25	2.252(30)	0.65	1.31	O48	Bi45	2.283(34)	0.59	1.07
	Bi21	2.471(33)	0.36			Bi41	2.535(34)	0.30	
	Bi26	2.529(30)	0.31			Bi46	2.742(34)	0.17	



Table 5

Distances (Å) and valence bond sum parameters for the oxygen atoms of the hexanuclear complexes  $[\text{Bi}_6\text{O}_x(\text{OH})_{8-x}]^{(10-x)+}$  for:  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  [10] and  $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot 4\text{H}_2\text{O}$  [11]

$[\text{Bi}_6\text{O}_4(\text{OH})_4]^{6+}$ [5]					$[\text{Bi}_6\text{O}_5(\text{OH})_3]^{5+}$ [4]				
$O_i$	$\text{Bi}_j$	$d(O_i - \text{Bi}_j)$	$v_i$	$\mathbf{v}$	$O_i$	$\text{Bi}_j$	$d(O_i - \text{Bi}_j)$	$v_i$	$\mathbf{v}$
O1	Bi1	2.115(36)	0.93	2.36	O1	Bi1	2.112(42)	0.94	2.54
	Bi2	2.149(50)	0.85			Bi4	2.167(29)	0.81	
	Bi3	2.299(43)	0.57			Bi2	2.180(36)	0.78	
O2	Bi6	2.126(54)	0.91	2.48	O2	Bi2	2.146(31)	0.86	2.42
	Bi4	2.159(58)	0.83			Bi5	2.151(30)	0.85	
	Bi1	2.200(44)	0.74			Bi3	2.215(43)	0.71	
O3	Bi4	2.140(42)	0.87	2.53	O3	Bi1	2.133(30)	0.89	2.45
	Bi5	2.150(49)	0.85			Bi3	2.141(37)	0.87	
	Bi2	2.170(47)	0.81			Bi6	2.226(34)	0.69	
O4	Bi3	2.077(37)	1.04	2.62	O4	Bi5	2.104(37)	0.96	2.47
	Bi5	2.132(44)	0.89			Bi4	2.183(31)	0.78	
	Bi6	2.225(37)	0.69			Bi6	2.207(48)	0.73	
O5	Bi5	2.349(51)	0.50	1.30	O5	Bi6	2.208(30)	0.73	2.07
	Bi4	2.399(62)	0.43			Bi1	2.255(32)	0.64	
	Bi6	2.457(68)	0.37			Bi4	2.417(48)	0.41	
O6	Bi1	2.356(54)	0.49	1.36	O6	Bi4	2.288(44)	0.59	1.32
	Bi2	2.372(38)	0.47			Bi2	2.407(32)	0.42	
	Bi4	2.427(42)	0.40			Bi5	2.521(35)	0.31	
O7	Bi3	2.296(50)	0.57	1.40	O7	Bi2	2.321(41)	0.54	1.27
	Bi2	2.329(43)	0.52			Bi1	2.455(36)	0.37	
	Bi5	2.536(39)	0.30			Bi3	2.462(30)	0.37	
O8	Bi6	2.335(43)	0.52	1.26	O8	Bi5	2.223(45)	0.70	1.36
	Bi1	2.435(55)	0.39			Bi3	2.319(32)	0.54	
	Bi3	2.476(43)	0.35			Bi6	2.860(37)	0.12	

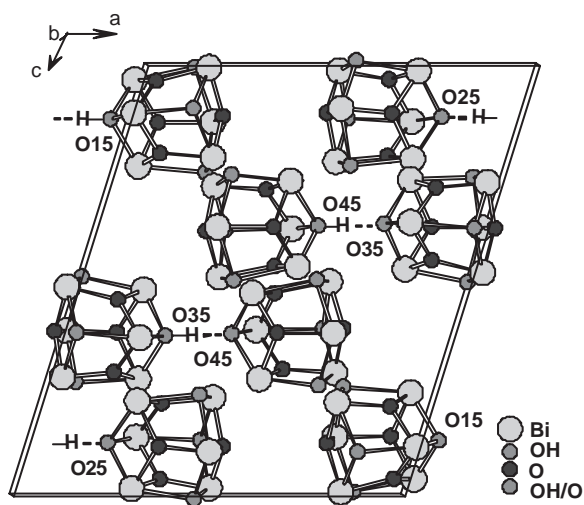


Fig. 4. Projection along the  $b$ -axis of the  $[\text{Bi}_6\text{O}_x(\text{OH})_{8-x}]^{(10-x)+}$  hexanuclear polycations with the possible location of the hydroxyl oxygen atoms.

are equal to 2.47(4) and 2.68(4) Å, respectively, that is too small for an O–H...H–O repulsion but perfectly suitable for an O–H...O hydrogen bonding scheme. An ordering could therefore occur over the H atoms positions. Such a phenomenon is responsible for the ferroelectric transition observed at 123 K in the well-known potassium di-hydrogeno phosphate compound (KDP). In this latter compound, cooperative ordering of hydrogen bonds are responsible for the non-centrosymmetry of the low-temperature form.

The Raman spectra of the title compound and of the  $X$  phase are very similar to the  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  and  $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot 4\text{H}_2\text{O}$  spectra (see Fig. 5). Four prominent vibrational modes at around 87, 105, 151, 185  $\text{cm}^{-1}$  can be observed in the  $[\text{Bi}_6\text{O}_{4.5}(\text{OH})_{3.5}](\text{NO}_3)_{11}$  Raman spectrum, in agreement with the model proposed for the  $[\text{Bi}_6\text{O}_4(\text{OH})_4]^{6+}$  hexanuclear entities of  $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{ClO}_4)_6 \cdot 7\text{H}_2\text{O}$  (i.e., 92, 109, 150 and 186  $\text{cm}^{-1}$  in the solid and 87, 104, 150 and 178  $\text{cm}^{-1}$  in solution) [24]. The peak observed at 419  $\text{cm}^{-1}$  for  $[\text{Bi}_6\text{O}_{4.5}(\text{OH})_{3.5}](\text{NO}_3)_{11}$  seems

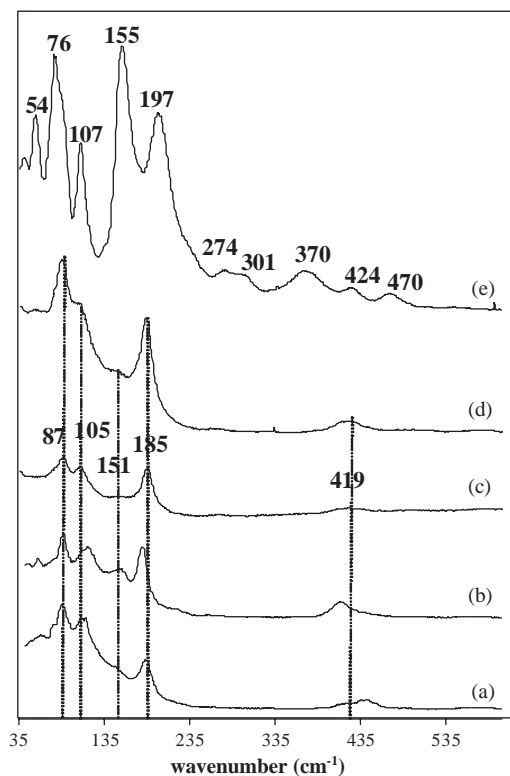


Fig. 5. Raman spectra of (a)  $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot 4\text{H}_2\text{O}$ , (b)  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ , (c)  $[\text{Bi}_6\text{O}_{4.5}(\text{OH})_{3.5}](\text{NO}_3)_{11}$ , (d) the X phase, and (e)  $\text{Bi}_2\text{O}_2(\text{OH})(\text{NO}_3)$ .

to be intermediate to those observed for  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  and  $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot 4\text{H}_2\text{O}$ . However, we cannot unambiguously assign this intermediate position to the presence of both  $[\text{Bi}_6\text{O}_5(\text{OH})_3]^{5+}$  and  $[\text{Bi}_6\text{O}_4(\text{OH})_4]^{6+}$  polycations. It is worth noticing that the  $\text{Bi}_2\text{O}_2(\text{OH})(\text{NO}_3)$  spectrum is totally different from those of the compounds including  $[\text{Bi}_6\text{O}_x(\text{OH})_{8-x}]^{(10-x)+}$  entities, as expected from the

$a$ -cell parameter (vide supra) which is typical of  $\text{Bi}_2\text{O}_2^{2+}$  layers [2,21]. On the contrary, the Raman spectrum of the X phase is similar to those spectra and the X phase should present such entities.

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