Crystal and Molecular Structure of Tetraoxotetrahydroxo-bismuth(III) Nitrate Monohydrate, $Bi_6O_4(HO)_4(NO_3)_6.H_2O$

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The compound $Bi_6O_4(HO)_4(NO_3)_6.H_2O$ crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with $a=9.289(2)$, $b=13.462(4)$, $c=19.527(5)$ Å, $\beta=114.13(2)°$ and $Z=4$. The structure was solved from three-dimensional X-ray diffractometer data by using direct (MULTAN type) and Fourier methods. The structural parameters were refined by least-squares methods to a residual $R=0.075$. The structure contains discrete hexanuclear complexes $Bi_6O_4(HO)_4^{6+}$, similar to those found previously in a structure determination of a basic Bi(III) perchlorate. The coordination polyhedron around Bi within the complex is trigonal bipyramidal with the lone $6s^2$ electron pair occupying the place of a fifth ligand. Every bismuth interacts weakly with four or five nitrate or water oxygens outside the complex. The nitrate groups, when acting as ligands, are uni- or unsymmetrical bidentately coordinated. All the hydrogen atoms are participating in hydrogen bonds.

Several investigations[1] have shown that in fairly acidic solutions the main hydrolysis product of bismuth(III) is a hexanuclear species. Discrete hexanuclear complexes $Bi_6O_4(HO)_4^{6+}$ have been found in the crystal structure of a basic bismuth(III) perchlorate,[2] where the bismuth atoms form an octahedron with triply bridged oxygen atoms above the octahedral faces.

In a preliminary report[3] on the structure of the basic nitrate $BiONO_3.\frac{1}{2}H_2O$ a hexanuclear bismuth unit with a trigonal prismatic arrangement of the Bi atoms has been suggested. Through a center of symmetry two such units were united to a twelve-nuclear complex. The positions of the metal atoms were derived by Patterson and Fourier methods. However, no refinement of the Bi parameters seems

to have been performed and the locations of the light atoms were not determined.

In order to get complete and accurate structure data it was decided to reinvestigate the structure of the basic nitrate.

EXPERIMENTAL

Colourless crystals of the basic nitrate were obtained by treating $Bi(NO_3)_3.5H_2O$ with 0.05 M HNO_3, and recrystallizing the microcrystalline precipitate at 100 °C.

A stout prismatic crystal was cut from a crystal agglomerate. A preliminary X-ray investigation showed the compound to be identical with that previously investigated.[3] The stoichiometric formula $BiONO_3.\frac{1}{2}H_2O$ was confirmed in the following structure determination and no analysis or density measurements were made.

The intensity data were collected on a SYNTEX $P2_1$ four-circle, computer controlled diffractometer. The orientation of the crystal and the cell parameters were determined as described elsewhere.[4] A quadrant of the reflexion sphere was investigated. Computation of intensities and estimated standard deviations was carried out as previously described.[4] Cell data, information regarding the intensity data collection and least-squares refinement are given in Table 1.

Three check reflexions were monitored each 50th reflexion. The intensities increased about 15 % during the first half of the data collection, which implies that the structure became more mosaic. During the second part of the data collection the intensities of the check reflexions were constant within 5 %. No measures to correct for the increase in intensity were undertaken, i.e. all data were scaled uniformly.

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Table 1. Crystal data, conditions for data collection and refinement.

CRYSTAL DATA

$Bi_6O_4(HO)_4(NO_3)_6 \cdot H_2O$
Monoclinic, $P2_1/c$ (No. 14)
$a = 9.289(2)$ Å
$b = 13.462(4)$ Å
$c = 19.527(5)$ Å
$\beta = 114.13(2)°$
$V = 2228.5$ Å^3
$Z = 4$
$F(000) = 3048$ electrons
$D_m = 5.31$ g cm^{-3} [a]
$D_x = 5.29$ g cm^{-3}
$\mu(MoK\alpha) = 450.4$ cm^{-1}

DATA COLLECTION

Crystal size $= 0.11 \times 0.15 \times 0.18$ mm
Temperature 25 ± 1 °C
$\lambda = 0.71073$ Å (graphite monochromatized MoKα)
2θ interval: $0 - 45°$
ω-scan, $\Delta\omega = 1.00°$
Scan rate: intensity dependent variable, lowest speed 1° min^{-1}

LEAST-SQUARES REFINEMENT

Number of
  reflexions used in refinement, $m = 1953$
  zero weight reflexions $[|F_o| < 3.92\sigma(F_o)] = 955$
  parameters refined, $n = 187$
Function minimized $= \sum w_i \||F_o| - k|F_c\||^2$
Weight $w_i = [\sigma_i^2(F_o) + (0.04F_o)^2]^{-1}$
$R = \sum |F_o - kF_c| / \sum |F_o| = 0.075 \ (0.112^b)$
$R_w = (\sum w_i |F_o - kF_c|^2 / \sum w_i F_o^2)^{1/2} = 0.087 \ (0.096^b)$
$S = [\sum w_i |F_o - kF_c|^2/(n-m)]^{1/2} = 1.53$

[a] From Ref. 3.   [b] Including zero weight data.

A very few of the innermost strong reflexions (measured in the beginning of the data collection) could be suspected of being slightly affected by extinction. The most serious case was 100, for which the ratio of F_c to F_o was 1.20. No correction for the extinction effects was made.

Corrections for Lorentz and polarization effects were applied. Correction for absorption effects will be discussed later on.

STRUCTURE DETERMINATION AND REFINEMENT

A full-matrix least squares refinement of the previously reported[3] positional parameters of the Bi atoms led to a conventional R-value of 0.46 and unreasonable (negative or very high) values of the isotropic temperature factors. This indicates that the proposed trigonal prismatic geometry of the hexanuclear Bi-units is in error.

A starting model for the structure was obtained by direct methods. The MULTAN program set in the XTL computer program system gave four possible solutions based on the 249 strongest reflexions. The electron density map of one asymmetric unit, calculated from the solution with the second largest combined figure of merit, showed six large peaks in general positions. All of these had about the same magnitude, and were at least twice as large as the remaining peaks. As there are 24 formula units $BiONO_3.\frac{1}{2}H_2O$ in the unit cell, the six peaks were assigned to six Bi atoms. The resulting geometrical arrangement of the Bi atoms in the asymmetric unit was octahedral, as in the perchlorate. A Patterson vector map confirmed the model chosen.

From successive difference Fourier syntheses and least-squares refinements six nitrate groups, eight oxygens belonging to the Bi_6 complex, and one water oxygen could be located. In the difference syntheses all data including zero weight reflexions were used.

Scattering factors including anomalous dispersion for Bi were calculated from analytical expressions for the neutral atoms.[5] The final refinement was performed with Bi anisotropic and the rest of the atoms isotropic.

Correction for absorption by using the Gaussian integration method was not possible due to the irregular shape of the crystal, hence a semi-empirical method[4,6] was tried. The largest relative variation of the intensity was as $1:0.39$. A least-squares refinement based on the absorption corrected data gave no final convergence, not even for the metal atoms. The residual achieved ($R = 0.083$) was higher than that obtained without absorption correction, and in addition several of the light atoms obtained negative temperature factors. The absorption correction procedure apparently introduced larger errors than those that should be corrected for.

The approximations used in the semi-empirical absorption correction method are better the lower the absorption coefficient and the smaller the crystal.[6] The present compound has the very large absorption coefficient of 450.4 cm^{-1}, and a rather large crystal was used. Besides, the systematic error due to the initial increase in intensity may have

Table 2a. Fractional atomic positional and isotropic thermal parameters with estimated standard deviations in parentheses.

Atom [a]	x	y	z	B, Å^2
Bi(1)	0.5442(2)	0.2491(1)	0.2166(1)	
Bi(2)	0.4921(3)	0.1080(1)	0.3664(1)	
Bi(3)	0.8743(3)	0.1013(1)	0.3498(1)	
Bi(4)	0.8770(2)	0.3797(1)	0.3584(1)	
Bi(5)	0.5014(2)	0.3760(1)	0.3790(1)	
Bi(6)	0.8411(2)	0.2286(1)	0.5081(1)	
O(123)	0.6278(43)	0.1305(25)	0.3029(19)	1.2(7)
O(145)	0.6211(39)	0.3574(22)	0.3029(18)	0.5(6)
O(256)	0.5968(41)	0.2400(25)	0.4327(20)	1.5(7)
O(346)	0.9127(41)	0.2355(25)	0.4142(19)	1.3(7)
O(125)	0.3772(37)	0.2421(23)	0.2945(18)	0.7(6)
O(134)	0.8205(37)	0.2342(22)	0.2647(17)	0.6(5)
O(236)	0.7804(50)	0.0791(28)	0.4456(22)	2.2(8)
O(456)	0.7830(39)	0.4065(22)	0.4472(17)	0.4(6)
N(1)	0.7002(49)	0.3617(29)	0.1202(23)	0.9(8)
O(11)	0.7541(45)	0.4105(26)	0.0827(20)	1.5(7)
O(12)	0.6432(49)	0.3992(28)	0.1624(22)	2.1(8)
O(13)	0.6919(42)	0.2659(26)	0.1121(20)	1.6(7)
N(2)	0.4978(51)	0.1076(28)	0.0447(23)	0.7(8)
O(21)	0.6118(44)	0.0754(26)	0.0385(20)	1.5(7)
O(22)	0.4668(42)	0.0844(25)	0.1017(19)	1.2(7)
O(23)	0.3939(51)	0.1598(30)	−0.0077(23)	2.6(9)
N(3)	0.2047(47)	0.3532(28)	0.1196(21)	0.5(7)
O(31)	0.2048(39)	0.2658(25)	0.0993(18)	1.2(7)
O(32)	0.3330(51)	0.4026(29)	0.1618(23)	2.4(8)
O(33)	0.0677(43)	0.3992(24)	0.0952(19)	1.2(7)
N(4)	0.1131(53)	0.1201(31)	0.1772(24)	1.1(8)
O(41)	0.2313(46)	0.0713(28)	0.2045(21)	1.9(8)
O(42)	0.0158(45)	0.0901(26)	0.1115(21)	1.6(7)
O(43)	0.0836(54)	0.1900(33)	0.2085(25)	3.3(9)
N(5)	0.1249(44)	0.4348(26)	0.2832(20)	−0.2(7)
O(51)	0.1603(47)	0.3713(28)	0.3301(21)	1.9(8)
O(52)	−0.0047(55)	0.4759(29)	0.2457(24)	2.4(8)
O(53)	0.2439(57)	0.4799(34)	0.2740(26)	3.5(10)
N(6)	0.2556(57)	0.1150(32)	0.4461(26)	1.6(9)
O(61)	0.1450(46)	0.0870(26)	0.4697(20)	1.6(7)
O(62)	0.3985(45)	0.0986(26)	0.4932(20)	1.4(7)
O(63)	0.2150(46)	0.1501(28)	0.3839(22)	1.9(8)
O(W)	0.1208(46)	0.4123(27)	0.4912(21)	1.8(8)

[a] Numbering of atoms: the oxygen atom O(*pqr*) is the one bonded to the bismuth atoms Bi(*p*), Bi(*q*) and Bi(*r*); the oxygen atom O(*st*) is the *t*:th one bonded to the nitrogen atom N(*s*); O(W) is the water oxygen.

Table 2b. Anisotropic thermal parameters [a] (Å^2) with estimated standard deviations in parentheses.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Bi(1)	1.14(9)	0.48(8)	0.25(8)	0.08(7)	−0.26(7)	−0.05(6)
Bi(2)	1.51(11)	0.42(8)	1.04(9)	−0.58(7)	0.63(8)	−0.32(6)
Bi(3)	0.99(10)	0.32(8)	0.51(8)	0.23(6)	0.12(7)	−0.11(6)
Bi(4)	0.78(10)	0.26(8)	0.51(8)	−0.11(6)	0.20(7)	0.09(6)
Bi(5)	0.80(10)	0.46(8)	0.69(8)	0.29(6)	0.25(7)	−0.03(6)
Bi(6)	0.90(9)	0.63(8)	0.18(8)	0.04(7)	−0.01(7)	0.07(6)

[a] The anisotropic temperature factors are of the form $\exp[-1/4(B_{11}h^2a^{*2} + \dots + 2B_{12}hka^*b^* + \dots)]$. They must be regarded with caution due to the absence of absorption correction.

affected the correction. However, whether the errors in the corrected data set were in fact due to the correction method being inadequate, as might be inferred, was not further investigated.

Hence the final refinement was carried out with a data set uncorrected for absorption. In the last cycle the ratio of parameter shifts to e.s.d.'s was less than 0.01. The final agreement factors are given in Table 1 and the atomic parameters are listed in Tables 2a and 2b.

Systematic errors from the absorption effects are probably the main cause of the small values of some of the temperature factors of the light atoms. A final difference electron density map contained several rather large peaks (heights up to 4.6 electrons/Å^3) around the metal atoms. These may also be due to the systematic errors.

Computer programs. XTL crystal determination program system, version 2,[7] for a NOVA 32 K computer with a disk memory unit; ORTEP-II, a thermal-ellipsoid plot program for crystal structure illustrations;[8] LONE, a BASIC program, written by the author, calculates position of a lone electron pair and distances to atoms.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The basic bismuth(III) nitrate contains discrete hexanuclear complexes $Bi_6O_4(HO)_4^{6+}$, very similar to those previously found in the basic bismuth(III) perchlorate.[2] A view of the complex is given in Fig. 1, and selected interatomic distances in the
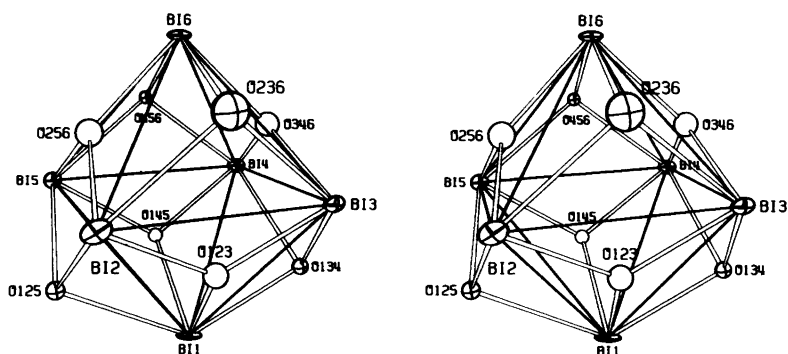

Fig. 1. A stereoview of the complex $Bi_6O_4(HO)_4^{6+}$. Ellipsoids are scaled to include 50 % probability. Hydroxide oxygens are denoted by having the principal ellipsoids drawn in addition to the enveloping ones. Numbering of atoms: See footnote in Table 2a. Solid lines between Bi atoms do not indicate bonding.
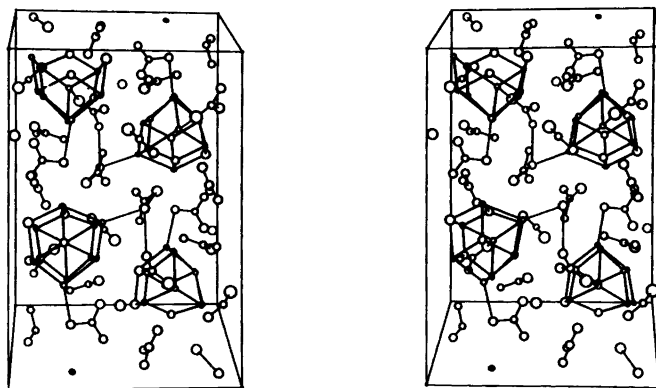

Fig. 2. A stereoview of the unit cell contents of $Bi_6O_4(HO)_4(NO_3)_6 \cdot H_2O$. Ellipsoids are scaled to include 50 % probability. Isotropic temperature factors having values less than 1 have, for the sake of clarity, been given the value $B = 1.0$.

Table 3. Selected interatomic distances in Å in the complex $Bi_6O_4(HO)_4^{6+}$ with estimated standard deviations in parentheses.

Distances Bi – Bi		Distances O – Bi			
		Oxide oxygens		Hydroxide oxygens	
Bi(1) – Bi(2)	3.682(3)	O(123) – Bi(1)	2.22(3)	O(125) – Bi(1)	2.58(4)
Bi(1) – Bi(3)	3.689(3)	– Bi(2)	2.12(4)	– Bi(2)	2.27(3)
Bi(1) – Bi(4)	3.649(3)	– Bi(3)	2.13(4)	– Bi(5)	2.40(3)
Bi(1) – Bi(5)	3.763(3)	O(145) – Bi(1)	2.12(3)	O(134) – Bi(1)	2.35(4)
Bi(2) – Bi(3)	3.696(4)	– Bi(4)	2.19(4)	– Bi(3)	2.35(3)
Bi(2) – Bi(5)	3.616(3)	– Bi(5)	2.21(4)	– Bi(4)	2.59(3)
Bi(2) – Bi(6)	3.670(3)	O(256) – Bi(2)	2.18(3)	O(236) – Bi(2)	2.52(5)
Bi(3) – Bi(4)	3.752(3)	– Bi(5)	2.12(4)	– Bi(3)	2.38(4)
Bi(3) – Bi(6)	3.656(3)	– Bi(6)	2.15(4)	– Bi(6)	2.30(4)
Bi(4) – Bi(5)	3.672(3)	O(346) – Bi(3)	2.15(3)	O(456) – Bi(4)	2.27(4)
Bi(4) – Bi(6)	3.685(3)	– Bi(4)	2.18(3)	– Bi(5)	2.44(4)
Bi(5) – Bi(6)	3.707(3)	– Bi(6)	2.19(4)	– Bi(6)	2.63(3)

complex are listed in Table 3. The complete structure is shown in Fig. 2.

The mean values of the Bi – Bi (3.69 Å), Bi – O^{2-} (2.16 Å), and Bi – HO^- (2.42 Å) distances in the present structure agree very well with those found in the perchlorate (3.68, 2.17, and 2.41 Å from the X-ray, 3.68, 2.15, and 2.40 Å, respectively, from the neutron diffraction determination). The slight distortions from the ideal T_d symmetry in the complex are different in the perchlorate and the nitrate, hence they are probably due to packing effects.

The occurrence of the $Bi_6O_4(HO)_4^{6+}$ ion in two different basic bismuth(III) salts gives a strong indication that this complex is present also in hydrolyzed solutions, at least at high Bi(III) concentrations. This point will be the subject of a forthcoming X-ray study of concentrated Bi(III) perchlorate solutions.[9]

The coordination around each Bi within the complex is the commonly occurring trigonal bipyramidal configuration, with the lone $6s^2$ electron pair (E) of the metal atom taking the place of a fifth ligand in the equatorial plane of the bipyramid. The oxide oxygens are the equatorial ligands and the hydroxide oxygens are the axial ones. Each oxygen in the complex is thus shared between three coordination polyhedra. The lone pairs are pointing radially out from the Bi_6 octahedron.

As is expected from the close similarity of the $Bi_6O_4(HO)_4^{6+}$ ion in the perchlorate and the nitrate, the average values of the equatorial – equatorial and the axial – equatorial oxygen dis-

tances, respectively, are practically the same: 3.07 and 2.70 Å in the nitrate, compared to 3.05 and 2.67 Å in the perchlorate (neutron data). The average ratio between those distances is 1.14 in both compounds.

The distances Bi – (E), calculated according to Galy *et al.*,[10] vary between 1.08 and 1.18 Å, *i.e.* virtually the same result as in the perchlorate (1.02 – 1.18 Å).

The main difference between the structures of the basic nitrate and the perchlorate is found in the coordination of outer oxygen atoms from water and nitrate or perchlorate ions to Bi. These bismuth – oxygen bond distances are much longer than those found within the hexanuclear complex. In the perchlorate each Bi is bonded to four outer atoms, the resulting total coordination polyhedra being very distorted dodecahedra. In the nitrate each Bi is weakly coordinating three nitrate groups but for one case, where two NO_3^- groups and a water molecule are coordinated. The maximum number of outer coordinated oxygen atoms was decided according to the following arguments. The van der Waals radius of Bi was estimated as half the average of the short Bi – Bi distances in the complex (these distances being in good agreement[2] with the short Bi – Bi distances in other basic salts), which gives the value 1.8 Å. Hence the upper limit for Bi – O interaction could be taken as $1.8 + 1.4 = 3.2$ Å, 1.4 Å being the generally accepted value of the van der Waals radius of O. Accordingly, each Bi is weakly coordinating four or five outer oxygens by some of the nitrate groups acting as

Table 4. Suggested hydrogen bonds with estimated standard deviations in parentheses.

Atoms	Distance, Å
O(125)···O(43)	2.65(6)
O(134)···O(13)	2.75(5)
O(236)···O(61)	2.70(5)
O(456)···O(W)	2.70(5)
O(W)···O(23)	2.71(7)
O(W)···O(42)	2.89(6)

bidentate ligands (unsymmetrically coordinated). For the different Bi atoms, the shortest of these outer Bi−O interactions lie in the range 2.62(4)−2.81(5) Å. The resulting total coordination polyhedra around Bi, including the oxygen atoms bonded to Bi in the complex, are highly irregular.

In the neutral nitrate hydrate $Bi(NO_3)_3.5H_2O$, bismuth is found[11] to be coordinated to three water oxygens (Bi−O distances 2.61−2.92 Å) and to three unsymmetrically bidentate nitrate groups (average distances Bi−O 2.38 and 2.96 Å). The resulting coordination polyhedron is irregular. The occurrence of bidentate coordination has been further confirmed[12] in a Raman study of aqueous solutions and melts containing Bi(III) and NO_3^-.

The hydrogen bond situation is similar to that in the basic perchlorate. The four hydroxide groups in the complex apparently participate in hydrogen bonds to water or nitrate oxygens. There is no indication of the oxide oxygens being hydrogen bonded. The water molecule is donating two H-bonds to nitrate oxygens and the water oxygen is accepting one H-bond from a hydroxide group. The hydrogen bonds are listed in Table 4. As the hydrogen atoms could not be located the O···O distances had to be used to select the most probable hydrogen bonds.

The nitrate groups are all planar and have, within the significance limits, C_{3v} symmetry. The calculated deviations from planarity are in all cases less than their e.s.d.'s. The N−O distances vary between 1.20(7) and 1.33(7) Å, average value 1.26 Å. Olovsson et al.[13] report an average value of 1.251 Å over 109 N−O distances ranging from 1.20 to 1.32 Å. The O−N−O angle with largest deviation from 120° is 130.5°, but due to the large e.s.d. of 4.4°, the deviation is not significant.

Note added in proof. Very recently another basic bismuth nitrate, $Bi_6O_5(HO)_3(NO_3)_5.3H_2O$,[14] has been shown to contain discrete hexanuclear complexes $Bi_6O_5(HO)_3^{5+}$, having a geometry similar to the complex found in this investigation.

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