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Hydrolysis Studies on Bismuth Nitrate: Synthesis and Crystallization of Four Novel Polynuclear Basic Bismuth Nitrates

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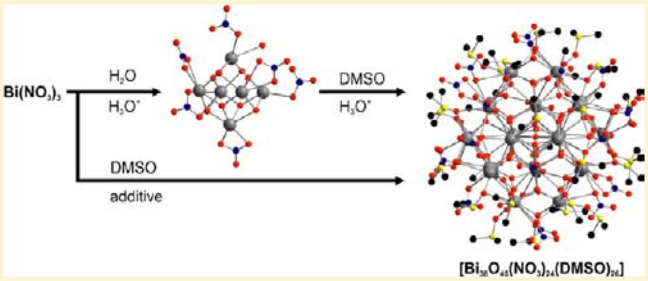
Ⓢ *Supporting Information*

ABSTRACT: Hydrolysis of $Bi(NO_3)_3$ in aqueous solution gave crystals of the novel compounds $[Bi_6O_4(OH)_4(NO_3)_5(H_2O)](NO_3)$ (**1**) and $[Bi_6O_4(OH)_4(NO_3)_6(H_2O)_2]\cdot H_2O$ (**2**) among the series of hexanuclear bismuth oxido nitrates. Compounds **1** and **2** both crystallize in the monoclinic space group $P2_1/n$ but show significant differences in their lattice parameters: **1**, a = 9.2516(6) Å, b = 13.4298(9) Å, c = 17.8471(14) Å, β = 94.531(6)°, V = 2210.5(3) Å^3; **2**, a = 9.0149(3) Å, b = 16.9298(4) Å, c = 15.6864(4) Å, β = 90.129(3)°, V = 2394.06(12) Å^3. Variation of the conditions for partial hydrolysis of $Bi(NO_3)_3$ gave bismuth oxido nitrates of even higher nuclearity, $[\{Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{26}\}\cdot 4DMSO]$-$[\{Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{24}\}\cdot 4DMSO]$ (**3**) and $[\{Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{26}\}\cdot 2DMSO]$-$[\{Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{24}\}\cdot 0.5DMSO]$ (**5**), upon crystallization from DMSO. Bismuth oxido clusters **3** and **5** crystallize in the triclinic space group $P\bar{1}$ both with two crystallographically independent molecules in the asymmetric unit. The following lattice parameters are observed: **3**, a = 20.3804(10) Å, b = 20.3871(9) Å, c = 34.9715(15) Å, α = 76.657(4)°, β = 73.479(4)°, γ = 60.228(5)°, V = 12021.7(9) Å^3; **5**, a = 20.0329(4) Å, b = 20.0601(4) Å, c = 34.3532(6) Å, α = 90.196(1)°, β = 91.344(2)°, γ = 119.370(2)°, V = 12025.8(4) Å^3. Differences in the number of DMSO molecules (coordinated and noncoordinated) and ligand (nitrate, DMSO) coordination modes are observed.



■ INTRODUCTION

Medicinal usage of basic bismuth nitrate can be traced back to the Middle Ages. Its first drug application was reported in 1786 by *Odier* administered as *magisterium bismuti* and *bismutum subnitricum* for treatment of dyspepsia.[1−3] Absorption of so-called bismuth subnitrate by the skin and in the stomach and upper intestine is very low due its poor solubility, but it reacts with the hydrochloric acid of the stomach.[4,5] Additionally, bismuth subnitrate is suggested to cover the gastric mucosa and thereby protect it.[4] In the 19th century bismuth subnitrate was also found to be useful for wound healing, and in the 20th century it was launched as reliable antisyphilitic.[1,5] Today bismuth subnitrate is used as a pharmaceutical ingredient for eradication of *Heliobacter pylori* in the bismuth-based triple and quadruple therapy, especially in developing countries.[6] So-called bismuth subnitrate was suggested to be a mixture of $BiONO_3$, $Bi(NO_3)(OH)_2$, and $BiOOH$ obtained by hydrolysis of aqueous bismuth(III) nitrate solution.[4,7,8] Under controlled reaction conditions defined compounds composed of polynuclear, mainly hexanuclear, bismuth oxido nitrates were obtained. Thus far single-crystal X-ray diffraction studies have been reported for four of these compounds (Table 1).[9−12]

These crystal structure investigations demonstrated that formation of complex ions $[Bi_6O_4(OH)_4]^{6+}$ and $[Bi_6O_5(OH)_3]^{5+}$ is preferred and depends on the pH value.[13] Additionally, several compounds of similar composition were identified based on X-ray diffraction, synchrotron X-ray, and neutron scattering data.[13−17] These complexes result from hydrolysis of aqueous bismuth nitrate solution, and their formation is assumed to result from intramolecular condensation of hydrated Bi^{3+} ions.[18]

We are interested in the basic principles of hydrolysis, nucleation, and particle growth of basic bismuth nitrates in order to get ideas for a controlled approach toward different bismuth oxide polymorphs. In former studies we already provided insight into a possible nucleation process for polynuclear bismuth oxido compounds based on ESI mass spectrometry.[19] Herein, we focus on the crystallization conditions and report the structural characterization of four novel polynuclear basic bismuth nitrates. Among these are $[Bi_6O_4(OH)_4(NO_3)_5(H_2O)](NO_3)$ (**1**) and $[Bi_6O_4(OH)_4(NO_3)_6(H_2O)_2]\cdot H_2O$ (**2**), which were obtained after hydrolysis of $Bi(NO_3)_3$ from aqueous solution. Partial hydrolysis of $[Bi_6O_4(OH)_4(NO_3)_6]\cdot H_2O$ (**1a**) in DMSO gave crystals of $[\{Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{26}\}\cdot 4DMSO]$-$[\{Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{24}\}\cdot 4DMSO]$ (**3**). A compound of similar composition, $[\{Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{26}\}\cdot 2DMSO]$-

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Table 1. Crystallographic Parameters of Reported Basic Bismuth Nitrates from X-ray Single-Crystal Structure Analyses.[a]

compound	a [Å]	b [Å]	c [Å]	β [deg]	V [Å^3]	space group
$[Bi_6O_4(OH)_4(NO_3)_6]\cdot H_2O$ (**1a**)[9]	9.313(2)	13.514(7)	19.575(5)	114.12(1)	2258.5	$P2_1/c$
$[Bi_6O_4(OH)_4(NO_3)_6(H_2O)_2]\cdot 2H_2O$[10]	9.059(4)	17.050(2)	18.269(2)	120.00(1)	2443.7	$P2_1/c$
$[Bi_6O_5(OH)_3(NO_3)_3]_2(NO_3)_4\cdot 6H_2O$[11] [b]	17.152(1)	9.181(1)	17.752(1)	127.830(7)	2208.2	$P2_1/c$
$[Bi_6O_5(OH)_3(NO_3)_4(H_2O)]_2(NO_3)_2\cdot 4H_2O$[12]	15.348(3)	9.1739(17)	17.142(3)	114.050(2)	2204.2	$P2_1/n$
$[Bi_6O_4(OH)_4(NO_3)_5(H_2O)](NO_3)$ (**1**)	9.2516(6)	13.4298(9)	17.8471(14)	94.531(6)	2210.5	$P2_1/n$
$[Bi_6O_4(OH)_4(NO_3)_6(H_2O)_2]\cdot H_2O$ (**2**)	9.0149(3)	16.9298(4)	15.6864(4)	90.129(3)	2394.1	$P2_1/n$

[a] A Bi−O distance in the range of 1.44−3.15 Å was assigned to coordinating nitrate ions. Formulas are given based on this assignment. [b] In the literature $[Bi_6O_5(OH)_3(NO_3)_3]_2(NO_3)_4\cdot 6H_2O$ often is declared as "$[Bi_6O_5(OH)_3](NO_3)_5\cdot 3H_2O$". However, in the solid state dimers are formed by establishing two Bi−O bonds (Bi−O = 2.55 Å) between the cluster cores of the crystallographic independent molecule and the next symmetry generated one.

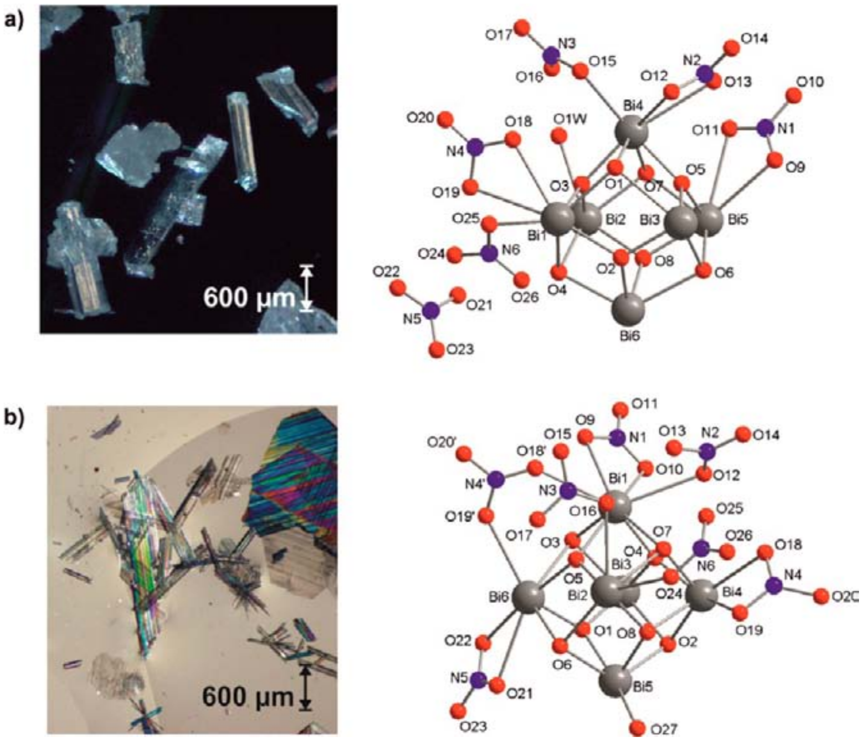

Figure 1. (Left) Photographs showing isolated crystals of the basic bismuth nitrates **1** (a) and **2** (b). (Right) Asymmetric units of $[Bi_6O_4(OH)_4(NO_3)_5(H_2O)](NO_3)$ (**1**) (a) and $[Bi_6O_4(OH)_4(NO_3)_6(H_2O)_2]\cdot H_2O$ (**2**) (b). For **2** two disordered nitrate groups are displayed with occupancies of 0.5 (N4, O18−O20 and N4′, O18′−O20′). Disordered water molecules (O29 and O29′) are not shown.

$[\{Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{24}\}\cdot 0.5DMSO]$ (**5**), was obtained after slow evaporation of the solvent from a DMSO solution of $Bi(NO_3)_3$ in the presence of sodium methacrylate.

■ RESULTS AND DISCUSSION

Previously we demonstrated that the basic nitrate $[Bi_6O_4(OH)_4(NO_3)_6]\cdot H_2O$ (**1a**)[9] serves as potential starting material for synthesis of several bismuth oxido clusters, e.g., $[Bi_6O_4(OH)_4(OTf)_6(CH_3CN)_6]\cdot 2CH_3CN$, $[Bi_{38}O_{45}(NO_3)_{20}(DMSO)_{28}](NO_3)_4\cdot 4DMSO$, $[Bi_{38}O_{45}(OH)_2(pTsO)_8(NO_3)_{12}(DMSO)_{24}](NO_3)_2\cdot 4DMSO\cdot 2H_2O$, $[Bi_{38}O_{45}(HSal)_{22}(OH)_2(DMSO)_{16.5}]\cdot DMSO\cdot H_2O$ (H_2Sal = salicylic acid), and $[Bi_{38}O_{45}(OMc)_{24}(DMSO)_9]\cdot 2DMSO\cdot 7H_2O$ (OMc = methacrylate).[19−22] However, small deviations from the original synthesis protocol gave $[Bi_6O_4(OH)_4(NO_3)_5(H_2O)](NO_3)$ (**1**), a constitution isomer of $[Bi_6O_4(OH)_4(NO_3)_6]\cdot H_2O$ (**1a**).[9] Both compounds were obtained from a concentrated suspension of $Bi(NO_3)_3\cdot 5H_2O$ in nitric acid solution (pH = 1.5). Crystals of compound **1a** were prepared by heating an aqueous suspension of $[Bi_6O_4(OH)_4(NO_3)_6(H_2O)_2]\cdot 2H_2O$[10] at 50 °C for several days.[9] Compound **1** was isolated by filtration of the aqueous suspension and storage of a small amount of the wet precipitate for approximately 2 months without removal of the residual water. Thus, a more stable polymorph (**1**) recrystallizes under ambient conditions following Ostwald's rule. Addition of a 0.5 M sodium hydroxide solution to a 0.1 M solution of $Bi(NO_3)_3$ in 1.0 M nitric acid (pH = 0.9) and subsequent slow diffusion of acetone into the reaction mixture gave colorless single crystals of another yet unknown basic bismuth nitrate, $[Bi_6O_4(OH)_4(NO_3)_6(H_2O)_2]\cdot H_2O$ (**2**). Similar to compound **1**, $[Bi_6O_4(OH)_4(NO_3)_6(H_2O)]\cdot H_2O$ (**2**) crystallizes in the monoclinic space group $P2_1/n$ (Table 1) and both show a similar crystal habit (Figure 1).

In compound **2** the hydrogen atoms of the bismuth oxido core were placed at observed positions, whereas in **1** the hydrogen atoms were not located. The molecular structures of **1** and **2** contain the typical central $[Bi_6O_4(OH)_4]^{6+}$ core,[9,10,23]

Table 2. Bi–O Bond Lengths and Angles of $[Bi_6O_4(OH)_4(NO_3)_5(H_2O)](NO_3)$ (**1**) and $[Bi_6O_4(OH)_4(NO_3)_6(H_2O)_2]\cdot H_2O$ (**2**)

$[Bi_6O_4(OH)_4(NO_3)_5(H_2O)](NO_3)$ (**1**)				$[Bi_6O_4(OH)_4(NO_3)_6(H_2O)_2]\cdot H_2O$ (**2**)			
bond lengths [Angstroms]							
Bi(1)–O(2)	2.191(9)	Bi(2)–O(4)	2.555(8)	Bi(1)–O(4)	2.150(7)	Bi(2)–O(7)	2.278(7)
Bi(2)–O(3)	2.146(8)	Bi(3)–O(6)	2.280(8)	Bi(1)–O(5)	2.162(7)	Bi(3)–O(2)	2.377(8)
Bi(2)–O(8)	2.186(8)	Bi(3)–O(1)	2.533(9)	Bi(2)–O(5)	2.116(7)	Bi(3)–O(3)	2.378(7)
Bi(3)–O(2)	2.122(8)	Bi(4)–O(1)	2.302(8)	Bi(2)–O(8)	2.197(7)	Bi(4)–O(2)	2.431(7)
Bi(3)–O(5)	2.136(8)	Bi(4)–O(7)	2.600(8)	Bi(3)–O(1)	2.137(7)	Bi(4)–O(7)	2.301(7)
Bi(4)–O(5)	2.139(9)	Bi(5)–O(6)	2.371(8)	Bi(3)–O(4)	2.171(7)	Bi(5)–O(2)	2.358(7)
Bi(4)–O(3)	2.168(8)	Bi(5)–O(7)	2.393(9)	Bi(4)–O(4)	2.141(7)	Bi(5)–O(6)	2.379(7)
Bi(5)–O(5)	2.171(9)	Bi(6)–O(4)	2.350(9)	Bi(4)–O(8)	2.169(7)	Bi(6)–O(3)	2.576(7)
Bi(5)–O(8)	2.189(7)	Bi(6)–O(6)	2.549(9)	Bi(5)–O(1)	2.193(8)	Bi(6)–O(6)	2.310(8)
Bi(6)–O(2)	2.184(9)	Bi(1)–O(18)	2.698(9)	Bi(5)–O(8)	2.153(7)	Bi(1)–O(10)	2.718(8)
Bi(6)–O(8)	2.136(8)	Bi(2)–O(1W)	2.670(9)	Bi(6)–O(1)	2.141(7)	Bi(1)–O(18′)	2.67(3)
Bi(1)–O(1)	2.351(8)	Bi(4)–O(12)	2.681(9)	Bi(6)–O(5)	2.168(7)	Bi(2)–O(16)	2.724(8)
Bi(1)–O(4)	2.379(8)	Bi(4)–O(15)	2.741(9)	Bi(1)–O(3)	2.284(7)	Bi(4)–O(19)	2.724(18)
Bi(2)–O(7)	2.250(8)	Bi(6)–O(14)a	2.596(8)	Bi(1)–O(7)	2.559(7)	Bi(5)–O(27)	2.717(11)
				Bi(2)–O(6)	2.521(7)		
angles [degrees]							
O(1)–Bi(1)–O(4)	127.1(3)	O(3)–Bi(2)–O(8)	90.1(3)	O(3)–Bi(1)–O(7)	124.4(3)	O(7)–Bi(2)–O(6)	125.7(3)
O(2)–Bi(1)–O(1)	73.2(3)	O(1)–Bi(1)–O(18)	78.9(3)	O(4)–Bi(1)–O(3)	72.4(3)	O(3)–Bi(1)–O(18′)	84.0(8)
O(2)–Bi(1)–O(4)	70.6(3)	O(2)–Bi(1)–O(18)	150.7(3)	O(4)–Bi(1)–O(5)	88.1(3)	O(4)–Bi(1)–O(18′)	153.4(8)
O(3)–Bi(1)–O(1)	70.3(3)	O(4)–Bi(1)–O(18)	122.6(3)	O(5)–Bi(1)–O(3)	71.5(3)	O(5)–Bi(1)–O(18′)	72.5(7)
O(3)–Bi(1)–O(2)	89.1(3)	O(3)–Bi(2)–O(1W)	77.4(3)	O(5)–Bi(1)–O(7)	70.4(2)	O(7)–Bi(1)–O(18′)	120.0(5)
O(3)–Bi(1)–O(4)	71.8(3)	O(4)–Bi(2)–O(1W)	131.8(3)	O(5)–Bi(2)–O(6)	70.0(3)	O(10)–Bi(1)–O(18′)	111.5(6)
O(3)–Bi(2)–O(4)	68.7(3)	O(7)–Bi(2)–O(1W)	71.3(3)	O(5)–Bi(2)–O(7)	77.1(3)	O(5)–Bi(2)–O(16)	75.1(3)
O(3)–Bi(2)–O(7)	75.5(3)			O(5)–Bi(2)–O(8)	90.4(3)		

[a] Symmetry transformations used to generate equivalent atoms. *a*: $x + 1/2, -y + 3/2, z + 1/2$.

in which the bismuth atoms occupy the corners of an octahedron and μ_3-oxygen atoms are placed above each trigonal face (Figure 1). While the positions of the hydroxides within the bismuth oxido core of **2** are assigned based on the X-ray data, in **1** the differentiation of oxide and hydroxide oxygen atoms is based on calculations of the bond-valence parameters.[16] For O2, O3, O5, and O8 bond-valence parameters (υ) varying from 2.42 to 2.56 were calculated. These values are assigned to oxide. The oxygen atoms O1, O4, O6, and O7 were attributed to hydroxide with υ in the range of 1.24–1.36. The Bi–μ_3-OH bond lengths in the range of 2.250(8)–2.600(8) Å in **1** and 2.278(7)–2.576(7) Å in **2**, respectively, are distinguished from the significantly shorter Bi–μ_3-O^{2-} distances (**1** = 2.122(8)–2.191(9) Å, **2** = 2.116(7)–2.197(7) Å) within the $[Bi_6O_4(OH)_4]^{6+}$ core (Table 2). The Bi–Bi distances range from 3.6 to 3.7 Å and are in agreement with the mean nonbonding Bi–Bi distance of 3.7 Å in $[Bi_6O_4(OH)_4(NO_3)_6]\cdot H_2O$ (**1a**).[9,24] Bismuth coordination numbers from five to eight are found both in **1** and **2**. Additionally, a 9-fold coordination for Bi6 is observed in **2**. In general, the coordination polyhedra can be described as square-based pseudo pyramids which are capped by 1–5 oxygen atoms.[25] The coordination polyhedra are composed of short primary and significantly longer secondary bonds as reported previously. The strong distortions of the bismuth coordination spheres might be assigned to the stereochemical activity of the lone pair at the bismuth atom.[25,26]

Compounds **1** and **2** are both built from similar bismuth oxido cores but show differences within their nitrate coordination spheres. In $[Bi_6O_4(OH)_4(NO_3)_5(H_2O)](NO_3)$ (**1**) two nitrate groups coordinate in a monodentate mode (Bi–O = 2.741(9) and 2.874(9) Å) and three nitrate ions in a chelating bridging mode (Bi–O = 2.689(8)–2.998(9) Å), with two of them being asymmetrically and one of them being symmetrically coordinated to the bismuth oxido framework. One nitrate group does not coordinate. Its shortest Bi–O distance amounts to 4.09 Å, which is significantly larger than the sum of the van der Waals radii of bismuth and oxygen ($r_{vdW}(O)$ = 1.52 Å, $r_{vdW}(Bi)$ = 2.07 Å).[27]

The nitrate groups in $[Bi_6O_4(OH)_4(NO_3)_6(H_2O)_2]\cdot H_2O$ (**2**) coordinate monodentate (Bi–O = 2.724(8)–2.848(8) Å) and in a symmetrically chelating bidentate mode (Bi–O = 2.718(8)–2.832(8) Å) to the central $[Bi_6O_8]^{6+}$ core. Furthermore, the nitrate group containing N6 is μ-bridging via O24 to Bi2 (2.783(8) Å) and additionally forms a hydrogen bond from O7 to O25 with a corresponding O···O distance of 2.759(11) Å (O7–H7–O25 = 156.7°). Disordered nitrate groups (N4, O18–O20 and N4′, O18′–O20′) were found each with an occupancy of 0.5 and refined at two positions. Interestingly, one of them coordinates in an symmetrically chelating bidentate mode (Bi–O = 2.836(8) and 2.724(18) Å), and the other shows a symmetrically μ-bridging coordination (Bi–O′ = 2.751(9) and 2.776(8) Å). In the solid state structure of $[Bi_6O_4(OH)_4(NO_3)_5(H_2O)](NO_3)$ (**1**) each molecule is connected to six proximate $[Bi_6O_4(OH)_4]^{6+}$ units via crystallographically independent nitrate groups containing N1–N4 and N6, thus forming a complex 3D network (Figure 2b). The bismuth oxido octahedra are linked via the nitrates O18–N4–O19 and O24–N6–O25 to build 1D polymeric chains along the crystallographic *a* axis. The Bi–O bond lengths amount to 2.789(9) Å for Bi3–O19 and 2.790(9) Å for Bi5–O24. In addition, adjacent chains are linked by coordination from N6–O24 to Bi1 (Bi–O = 2.774(9) Å) of the adverse $[Bi_6O_4(OH)_4]^{6+}$ unit. Furthermore, the resulting layers within the (*a*, *b*) plane are connected by the nitrates containing N1–O10 and N3–O15/O17, each of them being connected with

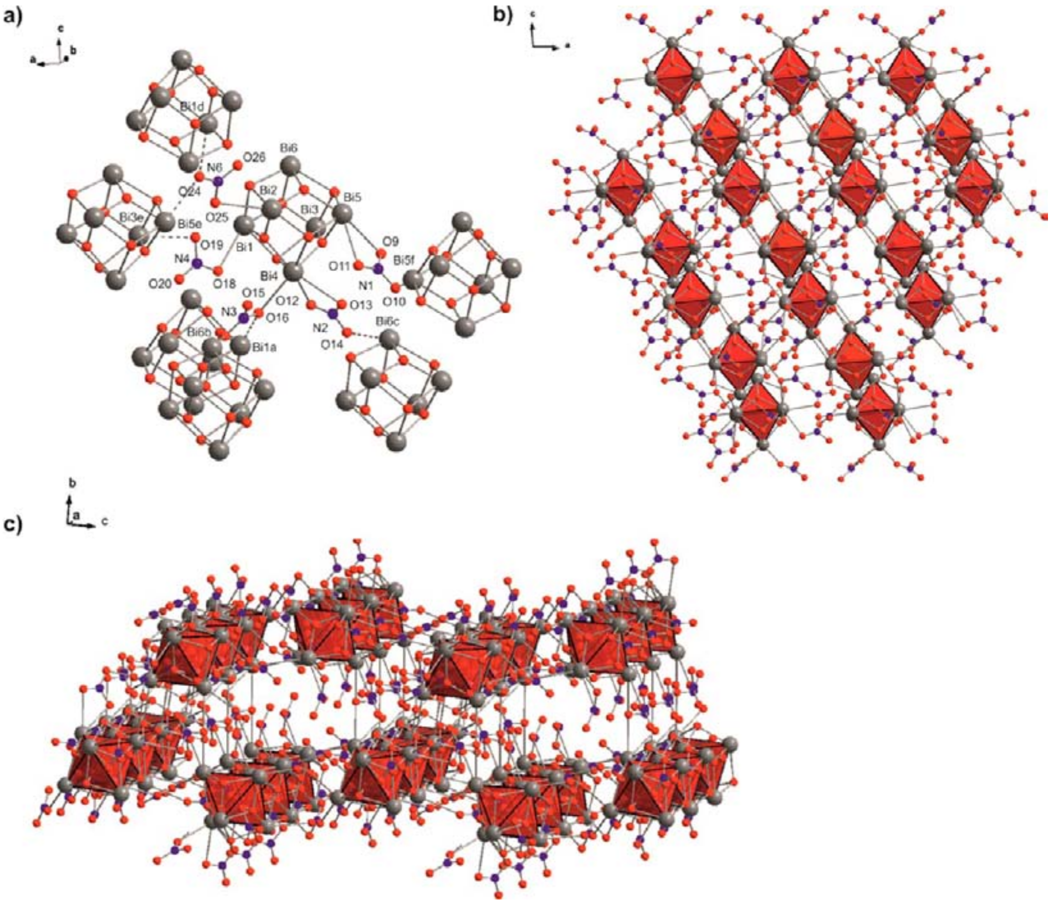

Figure 2. (a) In $[Bi_6O_4(OH)_4(NO_3)_5(H_2O)](NO_3)$ (**1**) each bismuth oxido cluster is connected via its crystallographically independent nitrate groups N1−N4 and N6, respectively, with six proximate $[Bi_6O_4(OH)_4]^{6+}$ units. Residual nitrate groups are omitted for clarity. Symmetry transformations used to generate equivalent atoms: $a = -x, -y + 1, -z$; $b = x + 1/2, -y + 3/2, z - 1/2$; $c = x - 1/2, -y + 3/2, z - 1/2$; $d = -x + 1/2, y + 1/2, -z + 1/2$; $e = x + 1, y, z$; $f = -x - 1, -y + 2, -z$. (b) View along the crystallographic *b* axis in the solid state structure of **1**. (c) View on the 3D connectivity pattern in the solid state of $[Bi_6O_4(OH)_4(NO_3)_6(H_2O)_2]\cdot H_2O$ (**2**). Connection of the $[Bi_6O_4(OH)_4]^{6+}$ octahedra between the layers occurs by the bridging nitrate groups containing N1 and N5.

two bismuth oxido units to form a layer in the (*b*, *c*) plane. The Bi−O bond lengths of the intermolecular connection are in the range 2.763(9)−2.872(9) Å. In $[Bi_6O_4(OH)_4(NO_3)_6(H_2O)]\cdot H_2O$ (**2**) the bismuth oxido clusters also form a 3D network (Figure 2c).

The intermolecular connection of the $[Bi_6O_4(OH)_4]^{6+}$ units, which implicates formation of a 1D polymeric chain along the crystallographic *a* axis, occurs via the nitrate groups containing N2 and N5. Therefore, the nitrate group containing N2 coordinates with O12 and O14 in a chelating bidentate mode to Bi6′ (Bi−O = 2.862(8) and 2.880(8) Å) of the next bismuth oxido core. Additionally, this nitrate group establishes a linkage via O13 to Bi5′ (Bi−O = 2.860(8) Å) and thus to the neighboring cluster within the parallel polymeric chains. The linkage via O21−N5−O23 to Bi4′ and Bi3′ completes the connection of the bismuth oxido units along the *a* axis. Apart from the bridging nitrate group containing N2 the connection of the polymeric chains within the (*a*, *c*) plane occurs via O11−N1−O9 to Bi3′ and Bi2′ (Bi−O = 2.881(8) and 2.786(8) Å), N3−O17 to Bi4′ (Bi−O = 2.936(8) Å), and N6−O26 to Bi3′ (Bi−O = 2.761(8) Å). Additionally, the resulting layers are connected via the oxygen atoms of the nitrates containing O9−N1−O11 and N5−O22 along the crystallographic *b* axis to form a 3D network. The Bi−O bond lengths resulting from intermolecular connection are in the range 2.786(8)−2.987(8) Å.

Compounds **1** and **2** are stable under helium atmosphere up to 150 and 110 °C, respectively, until release of water is observed. Decomposition of both compounds gave α-Bi_2O_3 (ICDD 01-070-8243) as the final material at 600 °C.

The octahedral bismuth oxido unit $[Bi_6O_8]^{2+}$as observed in compounds **1** and **2** is found in the solid state of a variety of large polynuclear bismuth oxido clusters as structural building motif. The bismuth oxido cores of $[Bi_{20}O_{18}(OSiMe_3)_{24}]$, $[Bi_{22}O_{26}(OSiMe_2{}^tBu)_{14}]$, and the nanoscaled bismuth oxido clusters such as $[Bi_{38}O_{45}(NO_3)_{20}(DMSO)_{28}](NO_3)_4\cdot 4DMSO$, $[Bi_{38}O_{45}(OH)_2(pTsO)_8(NO_3)_{12}(DMSO)_{24}](NO_3)_2\cdot 4DMSO\cdot 2H_2O$, $[Bi_{38}O_{45}(HSal)_{22}(OH)_2(DMSO)_{16.5}]\cdot DMSO\cdot H_2O$ (H_2Sal = salicylic acid), and $[Bi_{38}O_{45}(OMc)_{24}(DMSO)_9]\cdot 2DMSO\cdot 7H_2O$ (OMc = methacrylate) are built from an assembly of octahedral edge-sharing $[Bi_6O_{8-x}]^{2(1+x)+}$ units.[19,21,22,28,29] As a result, a nearly fcc packing of the bismuth atoms is formed similar to tetragonal β-Bi_2O_3 and cubic δ-Bi_2O_3, respectively.[25,28]

Dissolution of $[Bi_6O_4(OH)_4(NO_3)_6]\cdot H_2O$ (**1a**) in DMSO at approximately 80 °C, slowly cooling down to room temperature, and subsequent diffusion of THF into the reaction solution gave a mixture composed of colorless hexagonal crystals of the novel cluster $[\{Bi_{38}O_{45}(NO_3)_{24}$-

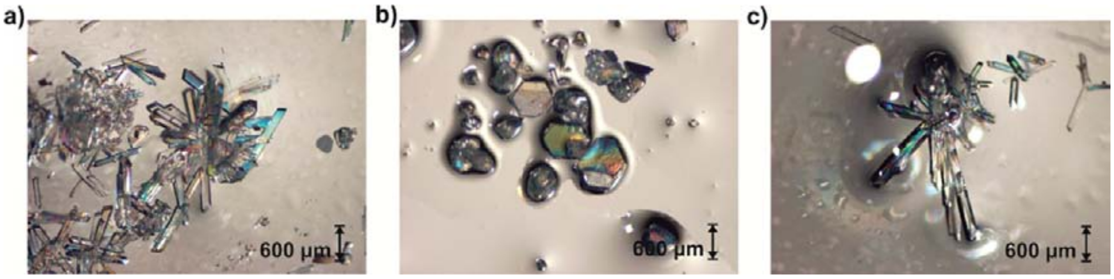

Figure 3. Photograph of the crystal mixture (a) isolated after diffusion of THF into a solution of $[Bi_6O_4(OH)_4(NO_3)_6]\cdot H_2O$ (**1a**) in DMSO. Under the microscope manually separated crystals of **3** and **4** are shown in the photographs of b and c, respectively.

Table 3. Crystallization Conditions and Crystal Data of the Polynuclear Bismuth Oxido Nitrates 3−5

	crystallization conditions	crystallographic data	
$[\{Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{26}\}\cdot 4DMSO][\{Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{24}\}\cdot 4DMSO]$ (**3**)	a crystal mixture of **3** and **4** was obtained after diffusion of THF into a solution of $[Bi_6O_4(OH)_4(NO_3)_6]\cdot H_2O$ (**1a**) (0.02 M, 2 mL) and nitric acid (65%) in DMSO; by applying a 0.03 M acidic DMSO solution crystal growth of **4** will be partially suppressed	triclinic, $P\bar{1}$	α = 76.657(4)°
		a = 20.3804(10) Å	β = 73.479(4)°
		b = 20.3871(9) Å	γ = 60.228(5)°
		c = 34.9715(15) Å	V = 12021.7(9) Å^3
$[Bi_{38}O_{45}(NO_3)_{20}(DMSO)_{28}](NO_3)_4\cdot 4DMSO$[19] (**4**)	in analogy to **3** diffusion of THF into a solution of **1a** and nitric acid in DMSO gave a crystal mixture composed of **3** and **4**; from a 0.2 M acidic DMSO solution formation of **4** after THF diffusion is favored; noteworthy, slow evaporation of DMSO from the reaction solution without diffusion of THF gave exclusively crystals of **4**	monoclinic, $C2/c$	β = 92.67(10)°
		a = 29.656(2) Å	V = 23957.6(3) Å^3
		b = 27.765(2) Å	
		c = 29.127(3) Å	
$[\{Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{26}\}\cdot 2DMSO][\{Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{24}\}\cdot 0.5DMSO]$ (**5**)	crystals of **5** were obtained after slow evaporation of the solvent from a filtered solution of $Bi(NO_3)_3$ and sodium methacrylate in DMSO	triclinic, $P\bar{1}$	α = 90.196(1)°
		a = 20.0329(4) Å	β = 91.344(2)°
		b = 20.0601(4) Å	γ = 119.370(2)°
		c = 34.3532(6) Å	V = 12025.8(4) Å^3

$(DMSO)_{26}\}\cdot 4DMSO][\{Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{24}\}\cdot 4DMSO]$ (**3**) (Figure 3) and the previously reported bismuth oxido nitrate $[Bi_{38}O_{45}(NO_3)_{20}(DMSO)_{28}](NO_3)_4\cdot 4DMSO$[19] (**4**) with rhombohedral morphology (Table 3).

To favor crystal growth of either **3** or **4**, the concentration of both $[Bi_6O_4(OH)_4(NO_3)_6]\cdot H_2O$ (**1a**) and nitric acid, reaction temperature, and reaction time were varied over a wide range. By comparing the number and morphology of the isolated crystals we noticed that mainly the concentration of the nitric acid influences the composition. With increasing acid concentration growth of **4** was favored, and finally, after addition of 2.9 mmol nitric acid (65%, 0.2 mL) to a solution of **1a** (0.3 mmol) in 15 mL of DMSO formation of compound **3** was suppressed. In contrast, at nitric acid concentrations in the range 0.03−0.11 M (65%, 0.02−0.12 mL) crystal growth of **4** is partially inhibited but it is not possible to obtain crystals of **3** exclusively. Thus, separation of crystals of compound **3** from the crystal mixture was carried out manually under the microscope. Compounds **3** and **4** crystallize in different space groups, and in contrast to the crystal structure of **4**, compound **3** contains two crystallographically independent molecules in the asymmetric unit (Table 3). Both bismuth oxido clusters consist of a $[Bi_{38}O_{45}]^{24+}$ core but show differences in their ligand periphery, namely, in the coordination behavior of coordinating nitrate ions and DMSO molecules.

In order to get more information on the hydrolysis process of the bismuth oxido clusters in DMSO we changed the hexanuclear starting material to mononuclear $Bi(NO_3)_3$. Previously, we reported that reaction of $[Bi_6O_4(OH)_4(NO_3)_6]\cdot H_2O$ (**1a**) and sodium methacrylate in DMSO gave crystals of $[Bi_{38}O_{45}(OMc)_{24}(DMSO)_9]\cdot 2DMSO\cdot 7H_2O$ (OMc = methacrylate).[22] Thus, sodium methacrylate was added to check its influence on the crystallization behavior of a $Bi(NO_3)_3$ solution in DMSO. As a result, we obtained crystals of the novel bismuth oxido nitrate $[\{Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{26}\}\cdot 2DMSO][\{Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{24}\}\cdot 0.5DMSO]$ (**5**) after filtration and subsequent partial evaporation of the solvent. The sodium methacrylate is not incorporated and acts as an additive which modulates the crystallization behavior. Noteworthy, in the absence of sodium methacrylate colorless crystals of $Bi(NO_3)_3\cdot 3DMSO$ were formed.[30]

Both compounds, **3** and **5**, crystallize in the triclinic space group $P\bar{1}$ with two crystallographically independent and centrosymmetric molecules in the unit cell as shown in Figure 4 for compound **3**. The independent cluster molecules of **3** and **5** show differences in their nitrate coordination modes and in the number of coordinating DMSO molecules. In analogy to other bismuth oxido clusters consisting of a $[Bi_{38}O_{45}]^{24+}$ core the molecules of **3** and **5** are assembled within the solid state in a nearly hexagonal close packing. In contrast to the hexanuclear basic bismuth nitrates **1** and **2** no linkage via nitrate groups is found between the bismuth oxido clusters. As shown by superposition of the bismuth−oxygen core structures of **3** and **5** no significant differences in their atom positions were determined. Maximum deviations of 0.14 and 0.23 Å were

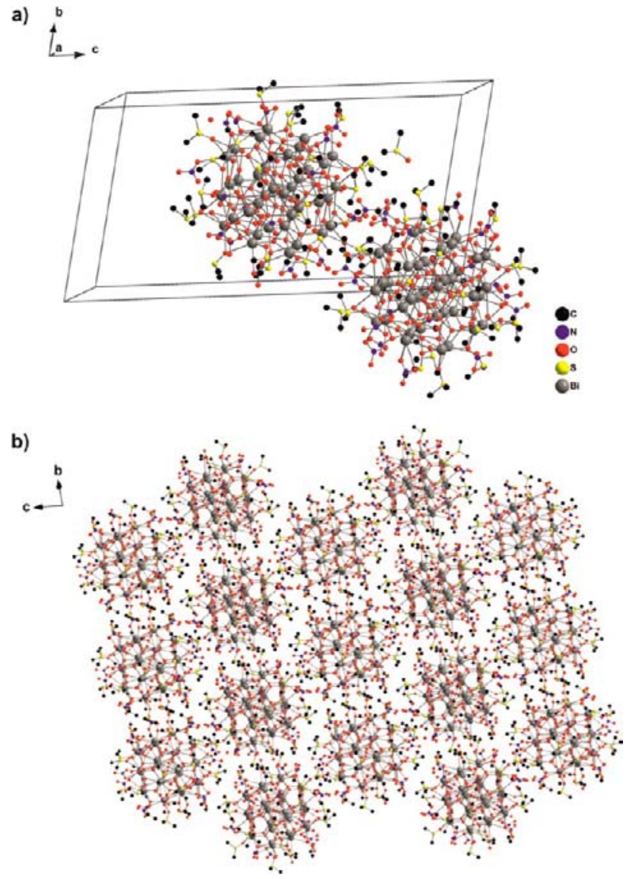

Figure 4. (a) Triclinic unit cell of **3** displaying the two centrosymmetric bismuth oxido clusters $[Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{26}]\cdot 4DMSO$ (**3a**) and $[Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{24}]\cdot 4DMSO$ (**3b**). Hydrogen atoms are omitted for clarity. Symmetry operations used to generate equivalent atoms: $a = -x, -y, -z + 2$; $b = -x + 1, -y + 1, -z + 1$. (b) Packing of the cluster molecules in the solid state.

calculated for the bismuth and oxygen atom positions, respectively.[31]

Similar to previously reported bismuth oxido clusters the bismuth atoms in the $[Bi_{38}O_{45}]^{24+}$ cores of **3** and **5** form approximately a fcc sublattice in which the oxygen atoms mainly occupy the tetrahedral voids.[19,21,22] Unlike the molecular structure of $[Bi_{38}O_{44}(HSal)_{26}(Me_2CO)_{16}(H_2O)_2]$ one oxygen atom is located in the center of the cluster in an octahedral void.[32] The Bi−O framework is best described to be composed of a central $[Bi_6O_9]$ unit in which the bismuth atoms occupy the corners of an octahedron and oxygen atoms are located above a trigonal face similar to **1** and **2** (Figure 5c). A μ_6-oxygen atom with Bi−O bond distances in the range of 2.525(8)−2.615(11) Å for the cluster cores of **3** (**5** = 2.517(8)−2.653(9) Å) is located in the center of the octahedron. The interior $[Bi_6O_9]$ unit is surrounded by 12 edge-sharing octahedral $[Bi_6O_{8-x}]^{2(1+x)+}$ units (Figure 5d). In addition to the μ_6-oxygen atom in the center of the molecule in **3a**, 18 oxygen atoms are coordinated in a μ_3-bridging mode with Bi−O bond lengths varying from 2.050(17) to 2.81(3) Å and 26 oxygen atoms are coordinated in a μ_4-bridging mode with Bi−O bond lengths in the range of 2.062(12)−2.896(17) Å to the bismuth atoms. Bi−μ_3-O−Bi angels vary from 97.2(4)° to 136.1(3)°, and the sums of the bond angles amount to 335.0−357.7°. Thus, 12 of 16 oxygen atoms adopt an almost planar μ_3-coordination.

In contrast to **3a**, the $[Bi_{38}O_{45}]^{24+}$ core of **3b** is built from 16 μ_3-bridging (Bi−O = 2.068(17)−2.450(18) Å) and 28 μ_4-bridging oxygen atoms (Bi−O = 2.073(11)−2.916(17) Å). In analogy to **3b**, the crystallographically independent molecules of **5**, $[Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{26}]\cdot 2DMSO$ (**5a**) and $[Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{24}]\cdot 0.5DMSO$ (**5b**), consist of 16 μ_3-bridging and 28 μ_4-bridging oxygen atoms within the cores with Bi−μ_3-O bonds in the range of 2.088(12)−2.470(12) Å and Bi−μ_4-O bonds in the range of 2.063(13)−2.964(12) Å. The $[Bi_{38}O_{45}]^{24+}$ cores of **3** and **5** are formed by four symmetry related layers (ABB′A′) with 7 and 12 bismuth atoms in one layer, respectively. Basically, the layers can be described by fused $[Bi_3O_{4-x}]^{(2x+1)+}$ units as structural motifs which have also been found in other bismuth oxido core structures.[32−35]

As a consequence of strong distortions within the bismuth−oxygen coordination pattern variable bismuth coordination numbers from five to nine are observed in the molecular structures of **3** and **5**. We propose that primary bonds in **3** exhibit Bi−O distances in the range of 2.05−2.51 Å (**5**, Bi−O = 2.07−2.51 Å) and secondary bonds range from 2.52 to 3.15 Å both in **3** and **5**. Thus, mainly two coordination polyhedra were assigned for the bismuth oxido clusters which can be described as trigonal ($[3 + X]$ ($X = 2−5$) coordinated) and square-based ($[4 + X]$ ($X = 1−5$) coordinated) pseudo pyramids capped by a corresponding number (X) of oxygen atoms. Eight of the bismuth atoms of each cluster in **3** and 12 bismuth atoms of the cluster molecules in **5** coordinate exclusively to oxygen atoms of the $[Bi_{38}O_{45}]^{24+}$ unit. The remaining bismuth atoms additionally are coordinated to nitrate and DMSO in order to complete the bismuth coordination spheres. In general, four coordination modes of nitrate ions are observed in **3** and **5**. In **3** 26 nitrate ions coordinate in a μ-1κO, 2κO mode, whereof 20 are symmetrically and 6 asymmetrically coordinated to bismuth with Bi−O bond lengths in the range of 2.744(15)−2.994(17) Å. Further, eight nitrates are coordinated in an asymmetrically bridging bidentate mode with Bi−O bond lengths varying from 2.67(3) to 3.00(2) Å. Additionally, six nitrate ions show a chelating bidentate coordination with Bi−O bond lengths of 2.67(2) and 2.98(4) Å, indicating asymmetric coordination. The residual nitrate ions coordinate monodentate to bismuth (Bi−O = 2.84(2)−2.95(2) Å). The bismuth oxido clusters of **5** mainly show a μ-1κO, 2κO coordination of the nitrate groups with Bi−O bond lengths in the range 2.393(19)−3.10(3) Å. Twelve nitrates show a chelating bridging mode (Bi−O = 2.628(15)−2.93(6) Å), two nitrates coordinate in a bridging mode (Bi−O = 3.055(16) and 3.063(18) Å) and 10 nitrate groups are monodentate coordinated (Bi−O = 2.42(2)−2.88(2) Å). An overview of the nitrate coordination behavior at the cluster cores of **3a** and **5a** with attention to bidentate coordination modes is given in the Figure 5a and 5b. Additionally, DMSO molecules coordinate to the bismuth−oxygen frameworks of the cluster molecules in **3** as well as **5** via their oxygen atom either in monodentate or in bridging mode with Bi−O bond lengths in the range of 2.56−2.95 Å. In both compounds the same number of coordinating DMSO molecules is found, namely, 24 and 26 DMSO molecules are bound to the bismuth oxido frameworks of the clusters **3a** (**5b**) and **3b** (**5b**), respectively. However, the crystal structures of **3** and **5** display differences in the coordination modes of the ligands as shown for the nitrate ligands in Figure 5 and varying numbers of noncoordinating solvent molecules.

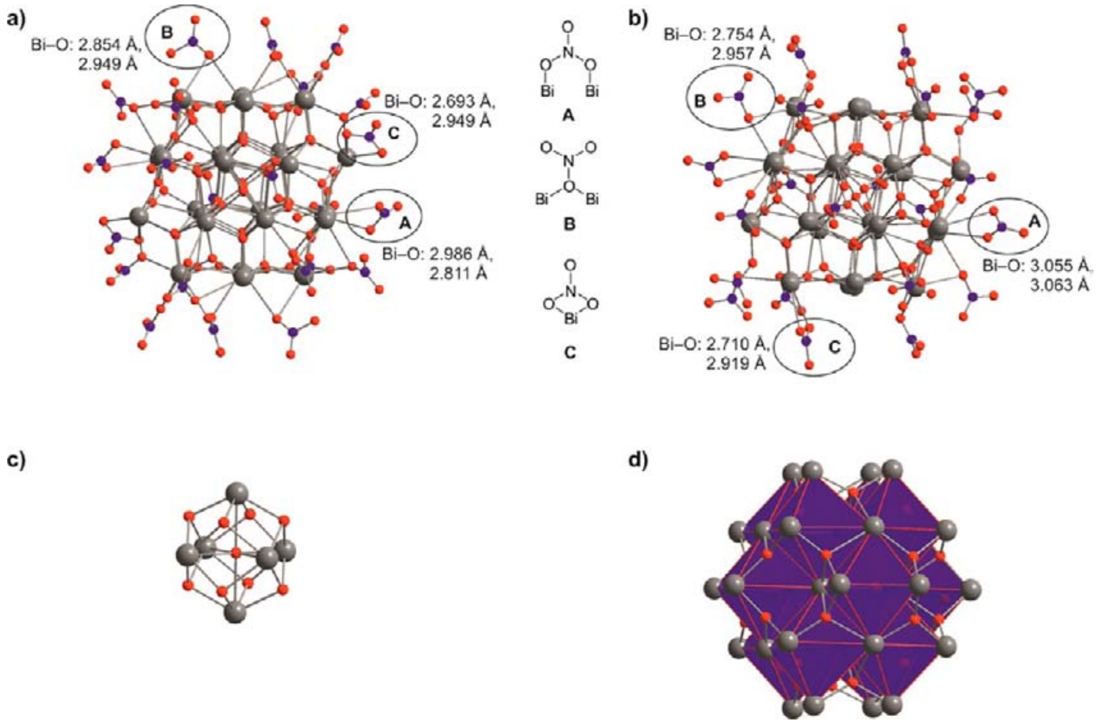

Figure 5. Demonstration of the nitrate coordination behavior at the cluster cores in (a) **3a** and (b) **5a**. DMSO molecules are omitted for clarity. (c) Representation of the $[Bi_6O_9]$ unit as a central structure component of the bismuth−oxygen framework in $[Bi_{38}O_{45}]^{24+}$ clusters. (d) Assembly of the bismuth−oxygen core structure in $[Bi_{38}O_{45}]^{24+}$ by edge-sharing $[Bi_6O_{8-x}]^{2(1+x)+}$ units.

We also determined the thermal stability of the clusters. For both compounds the loss of DMSO is observed up to 200 °C followed by nitrate decomposition. The decomposition residues of the bismuth oxido nitrates **3** and **5** comprise a crystalline fraction of $Bi_{14}O_{20}SO_4$ (ICDD 01-089-0812) along with amorphous material. Thus, DMSO is not completely removed. In addition to $Bi_{14}O_{20}SO_4$ the XRPD pattern of decomposed **5** shows reflexes of low intensity indicating formation of β-Bi_2O_3 (ICDD 00-027-0050) as a second phase.

■ CONCLUSION

We did obtain crystals of the novel basic bismuth nitrate $[Bi_6O_4(OH)_4(NO_3)_5(H_2O)](NO_3)$ (**1**) by hydrolysis of $Bi(NO_3)_3$ in aqueous solution under acidic conditions. Single-crystal X-ray diffraction analysis of **1** revealed formation of a new polymorph of $[Bi_6O_4(OH)_4(NO_3)_6]\cdot H_2O$ (**1a**),[9] which forms a 3D structure in the solid state. Hydrolysis of $Bi(NO_3)_3$ in the presence of aqueous NaOH solution gave crystals of another novel hexanuclear basic bismuth nitrate, $[Bi_6O_4(OH)_4(NO_3)_6(H_2O)_2]\cdot H_2O$ (**2**). In analogy to **1a**, compound **2** forms a 3D network via nitrate bridging in the solid state. Both compounds are built from a central $[Bi_6O_4(OH)_4]^{6+}$ unit, where the bismuth atoms occupy the corners of an octahedron and μ_3-oxygen atoms are situated above each trigonal face. These structural building units also appear in $[\{Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{26}\}\cdot 4DMSO][\{Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{24}\}\cdot 4DMSO]$ (**3**) and $[\{Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{26}\}\cdot 2DMSO][\{Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{24}\}\cdot 0.5DMSO]$ (**5**). Noteworthy, the asymmetric units of both **3** and **5** contain two crystallographically independent and centrosymmetric molecules with different coordination modes of nitrate and DMSO molecules. While **3** was synthesized by partial hydrolysis of **1a** in DMSO and subsequent diffusion of THF into the reaction solution, crystals of **5** were obtained by partial hydrolysis of $Bi(NO_3)_3\cdot 5H_2O$ in DMSO in the presence of sodium methacrylate as additive. It is concluded that $Bi(NO_3)_3$ hydrolyzes first to give a stable hexanuclear basic bismuth nitrate, which then reacts further to give compound **5** with low solubility via highly soluble methacrylate-substituted intermediates. As shown by single-crystal X-ray diffraction analysis both compounds **3** and **5** reveal formation of bismuth oxido clusters consisting of a $[Bi_{38}O_{45}]^{24+}$ core, which is built from an assembly of 13 octahedral edge-sharing $[Bi_6O_{8-x}]^{2(1+x)+}$ units. The central cluster contains a μ_6-oxygen atom that is not found in the hexanuclear units of **1** and **2**. Thus, a simple hydrolysis process via $[Bi_6O_{4+x}(OH)_{4-x}]^{(6-x)+}$ as the nucleation site can be ruled out. As reported recently, the bismuth−oxygen pattern might be regarded as a cut out of β- or δ-Bi_2O_3 since the bismuth atoms form an almost fcc packing in which all tetrahedral voids are filled by oxygen atoms. Thus, the final product of hydrolysis should be either β- or δ-Bi_2O_3. Even in the case of thermal decomposition it might be assumed that β- or δ-Bi_2O_3 are formed. However, thermal analyses showed that α-Bi_2O_3 is formed starting from **1** and **2**, respectively, and $Bi_{14}O_{20}SO_4$ starting from **3** and **5**. Noteworthy, in the case of compound **5** some β-Bi_2O_3 was detected.

In conclusion, formation of $[Bi_{38}O_{45}]^{24+}$ clusters by partial hydrolysis seems to be independent of the nuclearity of the starting material. While hydrolysis of bismuth nitrate in water mainly tends to afford hexanuclear basic bismuth nitrates, partial hydrolysis of bismuth nitrate as well as of the basic bismuth nitrate **1a** in DMSO gave $[Bi_{38}O_{45}]^{24+}$ cluster species exclusively. DMSO strongly coordinates to the cluster species and thus seems to favor formation of larger clusters.

■ EXPERIMENTAL SECTION

The starting material $Bi(NO_3)_3\cdot 5H_2O$ from Riedel-de Haën was used as received. ATR-FTIR spectra were recorded with a BioRad FTS-165 spectrometer using a golden gate sample adapter. Decomposition residues of the compounds were analyzed by X-ray powder diffraction at 25 °C with a STOE-StadiP diffractometer using monochromated Cu Kα radiation. Single-crystal X-ray diffraction analyses were performed using an Oxford Gemini S diffractometer with graphite-monochromated Mo Kα radiation at 110 K. Structures were solved by direct methods with SHELXS-97 and refined with SHELXL-97. CCDC-876652, CCDC-876654, CCDC-876651, and CCDC-876653 contain supplementary crystallographic data for $[Bi_6O_4(OH)_4(NO_3)_5(H_2O)](NO_3)$ (**1**), $[Bi_6O_4(OH)_4(NO_3)_6(H_2O)_2]\cdot H_2O$ (**2**), $[\{Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{26}\}\cdot 4DMSO]$-$[\{Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{24}\}\cdot 4DMSO]$ (**3**), and $[\{Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{26}\}\cdot 2DMSO][\{Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{24}\}\cdot 0.5DMSO]$ (**5**), respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in geometrically calculated positions except for hydrogen atoms of hydroxide groups in **1** and water molecules. Figures were created by DIAMOND (release 3.0, 2005).

Synthesis of $[Bi_6O_4(OH)_4(NO_3)_5(H_2O)](NO_3)$ (1). Synthesis was carried out according to ref 14. For this purpose 25 g (51.5 mmol) of $Bi(NO_3)_3\cdot 5H_2O$ was suspended in nitric acid (0.9 M, 25 mL). The reaction mixture was diluted with 500 mL of water and then kept at room temperature for 24 h. A precipitate was isolated by filtration and dried in air at room temperature to give $[Bi_6O_4(OH)_4(NO_3)_6(H_2O)_2]\cdot 2H_2O$ (13.1 g, 84%). If the latter was dried at 80 °C (3×10^{-3} mbar) for 12 h $[Bi_6O_4(OH)_4(NO_3)_6]\cdot H_2O$ (**1a**) is formed as shown by the XRPD pattern (ICDD 01-070-2235). The novel polymorph **1** was obtained from a small fraction of the wet precipitate, which was stored for approximately 2 months without removal of the residual water. Slow recrystallization gave colorless crystals of **1** (50.0 mg) suitable for single-crystal X-ray diffraction analysis; mp > 150 °C (decomp). IR (cm^{-1}): 3519 w, 3216 m, 1752 w, 1623 w, 1503 w, 1349 s, 1296 s, 1040 m, 951 w, 878 w, 808 m, 722 m, 552 s. Anal. Calcd for $Bi_6H_6N_6O_{27}$ (1775.94): H, 0.3; N, 4.7. Found: H, 0.2; N, 4.3. The identity of the isolated material **1** was confirmed by XRPD.

Crystal Data for 1. $Bi_6N_6O_{27}$, $M = 1775.99$, crystal size $0.24 \times 0.1 \times 0.06$ mm^3, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 9.2516(6)$ Å, $b = 13.4298(9)$ Å, $c = 17.8471(14)$ Å, $\beta = 94.531(6)°$, $V = 2210.5(3)$ $Å^3$, $D_c = 5.336$ g cm^{-3}, $F(000) = 3048$, μ(Mo Kα) = 47.735 mm^{-1}, $T = 110$ K, $2.98° \leq 2\theta \leq 26.00°$. Completeness to 2θ: 99.4%, max/min. Residual electron density: 4.253/−3.523 e $Å^{-3}$. Of a total of 10 583 reflections collected, 4304 reflections were independent ($R_{int} = 0.0435$). Final $R1 = 0.0365$ (for 4304 reflections $I > 2\sigma(I)$) and $wR2 = 0.0897$ (all data).

Synthesis of $[Bi_6O_4(OH)_4(NO_3)_6(H_2O)_2]\cdot H_2O$ (2). To a solution of $Bi(NO_3)_3\cdot 5H_2O$ in 1 M nitric acid (4 mL, 0.1 M) sodium hydroxide solution (4 mL, 0.5 M) was added. The mixture was stirred for 0.5 h under ambient conditions. Slow diffusion of acetone into the reaction mixture gave colorless crystals of **2** (79.0 mg, 64%); mp > 100 °C (decomp). IR (cm^{-1}): 3179 m, 1753 w, 1620 w, 1369 m, 1291 s, 1040 m, 812 m, 723 w, 706 w, 545 s, 406 s. Anal. Calcd for $Bi_6H_8N_6O_{29}$ (1811.97): H, 0.6; N, 4.6. Found: H, 0.2; N, 4.6.

Crystal Data for 2. $Bi_6H_{10}N_6O_{29}$, $M = 1812.02$, crystal size $0.36 \times 0.06 \times 0.06$ mm^3, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 9.0149(3)$ Å, $b = 16.9298(4)$ Å, $c = 15.6864(4)$ Å, $\beta = 90.129(3)°$, $V = 2394.06(12)$ $Å^3$, $D_c = 5.027$ g cm^{-3}, $F(000) = 3128$, μ(Mo Kα) = 44.087 mm^{-1}, $T = 110$ K, $2.87° \leq 2\theta \leq 26.11°$. Completeness to 2θ: 98.7%, max/min. Residual electron density: 3.836/−4.342 e $Å^{-3}$. Of a total of 15 398 reflections collected, 4711 reflections were independent ($R_{int} = 0.0505$). Final $R1 = 0.0379$ (for 4711 reflections $I > 2\sigma(I)$) and $wR2 = 0.0969$ (all data).

Synthesis of $[\{Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{26}\}\cdot 4DMSO]$-$[\{Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{24}\}\cdot 4DMSO]$ (3). To a solution of **1** (0.5 g, 0.3 mmol) in DMSO (15 mL) nitric acid (65%, 0.12 mL, 1.71 mmol) was added. The solution was stirred for 4 h at 80 °C. Slow diffusion of THF into the reaction mixture gave a mixture of crystals containing **3** and **4**. Colorless crystals of **3** (0.2 g, 34%) were separated manually under the microscope; mp > 150 °C (decomp). IR (cm^{-1}): 2998 w, 2917 w, 1736 w, 1638 w, 1430 m, 1378 s, 1266 s, 999 s, 922 s, 816 w, 708 w, 490 s, 421 s. Anal. Calcd for $C_{54}Bi_{38}H_{162}N_{24}O_{144}S_{27}$ (12258.88): C, 5.3; H, 1.3; N, 2.7. Found: C, 5.7; H, 1.4; N, 2.7.

Crystal Data for **3**. $C_{53.5}Bi_{38}H_{160.5}N_{24}O_{144}S_{27}$, $M = 12251.42$, crystal size $0.3 \times 0.2 \times 0.2$ mm^3, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 20.3804(10)$ Å, $b = 20.3871(9)$ Å, $c = 34.9715(15)$ Å, $\alpha = 76.657(4)°$, $\beta = 73.479(4)°$, $\gamma = 60.228(5)°$, $V = 12021.7(9)$ $Å^3$, $D_c = 3.385$ g cm^{-3}, $F(000) = 10775$, μ(Mo Kα) = 28.027 mm^{-1}, $T = 110$ K, $3.03° \leq 2\theta \leq 26.00°$. Completeness to 2θ: 97.7%, max/min. Residual electron density: 5.872/−5.886 e $Å^{-3}$. Of a total of 95 002 reflections collected, 46 210 reflections were independent ($R_{int} = 0.0661$). Final $R1 = 0.0690$ (for 46 210 reflections $I > 2\sigma(I)$) and $wR2 = 0.1883$ (all data).

Synthesis of $[\{Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{26}\}\cdot 2DMSO]$-$[\{Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{24}\}\cdot 0.5DMSO]$ (5). A suspension of $Bi(NO_3)_3\cdot 5H_2O$ (0.9 g, 1.81 mmol) in 15 mL of DMSO was stirred at 80 °C to give a solution. Sodium methacrylate (0.3 g, 2.87 mmol) was added, and the reaction mixture was stirred at 80 °C overnight. After filtration the reaction mixture was kept under ambient conditions to give colorless crystals of **5** (0.3 g, 49%) by slow evaporation of the solvent; mp >150 °C (decomp). IR (cm^{-1}): 3399 w, 3006 w, 2919 w, 1740 w, 1644 w, 1437 s, 1379 s, 1266 s, 1001 s, 928 s, 818 m, 708 w, 481 s. Anal. Calcd for $C_{67}Bi_{38}H_{201}N_{24}O_{150.5}S_{33.5}$ (12766.75): C, 6.3; H, 1.6; N, 2.6. Found: C, 6.3; H, 1.7; N, 2.6.

Crystal Data for 5. $C_{53}Bi_{38}H_{160.5}N_{24}O_{143.5}S_{26.5}$, $M = 12221.38$, crystal size $0.3 \times 0.1 \times 0.1$ mm^3, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 20.0329(4)$ Å, $b = 20.0601(4)$ Å, $c = 34.3532(6)$ Å, $\alpha = 90.196(1)°$, $\beta = 91.344(2)°$, $\gamma = 119.370(2)°$, $V = 12025.8(4)$ $Å^3$, $D_c = 3.375$ g cm^{-3}, $F(000) = 10745$, μ(Mo Kα) = 28.012 mm^{-1}, $T = 115$ K, $2.98° \leq 2\theta \leq 25.00°$. Completeness to 2θ: 99.2%, max/min. Residual electron density: 4.658/ −5.375 e $Å^{-3}$. Of a total of 79 204 reflections collected, 42 013 reflections were independent ($R_{int} = 0.0568$). Final $R1 = 0.0631$ (for 42 013 reflections $I > 2\sigma(I)$) and $wR2 = 0.1610$ (all data).

■ ASSOCIATED CONTENT

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Notes

The authors declare no competing financial interest.

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