DALTON
FULL PAPER

Synthesis and characterization of basic bismuth(III) nitrates

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Received 1st October 1999, Accepted 18th November 1999

The syntheses of the basic bismuth(III) nitrates $[Bi_6O_5(OH)_3](NO_3)_5{\cdot}3H_2O$, **A**, $[Bi_6O_6(OH)_3](NO_3)_3{\cdot}1.5H_2O$, **B**, and $[Bi_6O_5(OH)_3](NO_3)_5{\cdot}2H_2O$, **X**, were investigated. **A** is readily obtained in hydrolysis of bismuth(III) nitrate solutions with sodium hydroxide solutions and in homogeneous hydrolysis with dilute solutions of urea. $[Bi_6O_6(OH)_3](NO_3)_3{\cdot}1.5H_2O$ is obtained in hydrothermal synthesis at 190 °C from $Bi(NO_3)_3{\cdot}5H_2O$ or from $[Bi_6O_5(OH)_3](NO_3)_5{\cdot}3H_2O$. $[Bi_6O_5(OH)_3](NO_3)_5{\cdot}2H_2O$ was obtained at 100 °C from an aqueous solution which was 0.74 M with respect to bismuth(III) nitrate and 1.50 M with respect to urea. The compositions of **B** and **X** were derived from thermogravimetric analysis. Indexed powder patterns are reported for **B**: $a = 3.8175(5)$, $c = 17.149(4)$ Å for a tetragonal cell, and for **X**: $a = 15.185(1)$, $c = 15.834(2)$ Å for a rhombohedral cell using hexagonal setting.

Bismuth(III) nitrate pentahydrate, $Bi(NO_3)_3{\cdot}5H_2O$, is in the inorganic literature described as a compound which is hydrolysed with water to the basic salts $BiO(NO_3)$,[1] $Bi(OH)_2NO_3$,[2] and $Bi_2O_2(OH)NO_3$.[1] Such basic nitrates with the trade names "Magisterium bismuti" or "Bismutum subnitricum" have medical applications[1] as a mild antiseptic.[2] The hydrolysis products of $Bi(NO_3)_3{\cdot}5H_2O$ have more complicated compositions than the formulae given above for the bismuth subnitrates. Table 1 lists X-ray crystallographic data for bismuth(III) nitrate pentahydrate and related basic bismuth(III) nitrates. The single crystal X-ray diffraction investigation of the basic bismuth(III) nitrate by Sundvall[4] and by Lazarini[5–7] gave structures containing the complex ion $[Bi_6O_{4+x}(OH)_{4-x}]^{(6-x)+}$ with $x = 0$ and $x = 1$ for structures in refs. 4–6, and in ref. 7, respectively. Basic bismuth(III) nitrates with three different compositions have thus been established in crystallographic single crystal structure analysis.

The hydrolysis of a bismuth(III) nitrate solution was investigated by Gattow and Schott.[8] Above pH = 1.6 of the solution they isolated a compound which was reported to have the composition $[Bi_6O_4(OH)_4](OH)(NO_3)_5{\cdot}0.5H_2O$.[8] The hydrolysis of $Bi(NO_3)_3$ solution with a sodium hydroxide solution was also investigated by Brcic *et al.*[9] They found three crystalline reaction products: (i) in the pH range 1.8–2.1 a precipitate with a Bi : NO_3 ratio of 1.2 : 1 was formed which was called $[Bi_6O_6(OH)](NO_3)_5{\cdot}(2.5 \text{ to } 3.0)H_2O$. The compound has later been shown to be $[Bi_6O_5(OH)_3](NO_3)_5{\cdot}3H_2O$[7] (called **A** in this work). (ii) In the pH range 2.6–3.5 a compound with the Bi : NO_3 ratio 1.5 : 1 was formed, and the compound was called $[Bi_6O_6(OH)_2](NO_3)_4{\cdot}2H_2O$. The powder pattern of the compound was reported,[9] but a structure analysis has not been published. (iii) At pH values over 3.5 a compound with a Bi : NO_3 ratio of 2 : 1 was obtained.[9] This compound $[Bi_6O_6(OH)_3](NO_3)_3{\cdot}1.5H_2O$ (called **B** in this work) was also obtained when the first precipitated compound $[Bi_6O_6(OH)](NO_3)_5{\cdot}(2.5 \text{ to } 3.0)H_2O$[9] was kept in contact with weak aqueous solutions of HNO_3 or KNO_3. The powder pattern of the compound was reported, but a structure analysis has not been made. The composition of this basic bismuth(III) nitrate has previously been given as $BiONO_3{\cdot}BiOOH$.[8,10,11] The hydrolysis of a bismuth(III) nitrate solution with an alkaline solution thus gives at least three crystalline reaction products of which only the first phase precipitated[9] has been characterized by a single crystal X-ray analysis.[7]

Hydrolysis of urea in aqueous solutions at temperatures up to 100 °C has been used to slowly produce low concentrations of ammonia in a homogeneous precipitation of hydroxides of metal ions.[12] In a test experiment a crystalline bismuth compound was obtained at 100 °C in the reaction of a bismuth(III) nitrate solution with urea. This compound could be a bismuth–urea complex, but could also be a basic bismuth(III) nitrate. To clarify this problem the present investigation was made and describes a series of syntheses and characterizations of basic bismuth(III) nitrates.

Table 1 Composition and crystallographic data for bismuth compounds

	Unit cell parameters and cell volume									
Compound	*a*/Å	*b*/Å	*c*/Å	*α*/°	*β*/°	*γ*/°	*V*/Å^3	Space group	Ref.	ICDD card
$Bi(NO_3)_3{\cdot}5H_2O$	6.520(8)	8.642(8)	10.683(9)	100.82(6)	80.78(6)	104.77(7)	567.7	$P\bar{1}$	3	77-1905
$[Bi_6O_4(OH)_4](NO_3)_6{\cdot}H_2O$	9.289(2)	13.462(4)	19.527(5)		114.13(2)		2228.5	$P2_1/c$	4	71-1360
$[Bi_6O_4(OH)_4](NO_3)_6{\cdot}H_2O$	9.313(2)	13.514(7)	19.575(5)		114.12(1)		2248.5	$P2_1/c$	5	70-2235
$[Bi_6O_4(OH)_4](NO_3)_6{\cdot}4H_2O$	9.059(4)	17.050(2)	18.269(2)		120.00(1)		2444	$P2_1/c$	6	84-2189
$[Bi_6O_5(OH)_3](NO_3)_5{\cdot}3H_2O$	17.152(1)	9.181(1)	17.752(1)		127.83(1)		2208.2	$P2_1/c$	7	70-1226
$[Bi_6O_4(OH)_4](OH)(NO_3)_5{\cdot}0.5H_2O$[a]	17.58(4)	9.15(3)	27.20(5)		83.2(3)		4344.5	$P2_1/c$	8	16-504
$[Bi_6O_6(OH)](NO_3)_5{\cdot}2.5H_2O$[a]									9	[b]
$[Bi_6O_6(OH)_2](NO_3)_4{\cdot}2H_2O$[a]									9	28-654
$[Bi_6O_6(OH)_3](NO_3)_3{\cdot}1.5H_2O$[a]									9	[b]

[a] The composition of these four compounds has not been confirmed in a single crystal structure analysis. [b] The powder patterns are listed in Table 1, ref. 9.

Table 2 Experimental conditions for the hydrolysis of $Bi(NO_3)_3{\cdot}5H_2O$ and $[Bi_6O_5(OH)_3](NO_3)_5{\cdot}3H_2O$ (**A**)

Experiment No.	Composition of reaction mixture				Temp./°C	Time/h	pH of filtrate	Product
	$Bi(NO_3)_3{\cdot}5H_2O$/g	**A**/g	Urea/g	H_2O/ml				
1	1			100	100	0.1	1.41	**A**
2	1			60	190	24		**B**
3		1		60	190	28		**B**
4		1		60	190	27		**B**
5	36.0		9.0	100	100	0.3		**X**
6	36.0		9.0	100	100	0.3	0.42	**X**
7	1		1.2	100	60	22	1.40	**A**
8	0.5		0.6	50	76	23	1.32	**A**
9	0.5		0.9	50	76	23	1.45	**A**
10	0.5		1.2	50	76	23	1.62	**A**
11	1		1.2	100	90	23	1.12	**A**
12	1		3.0	100	90	23	8.06	$Bi_2O_2CO_3$
13	1		5.0	100	90	23	8.17	Amorphous
14	1		0.25	60	108	94		$Bi_2O_2CO_3$
15	1		0.25	60	190	23		$Bi_2O_2CO_3$

Experimental

Chemistry

The bismuth compounds used were $Bi(NO_3)_3{\cdot}5H_2O$ (BDH) and a basic bismuth(III) nitrate from Merck. The X-ray powder pattern of this compound showed that it was $[Bi_6O_5(OH)_3](NO_3)_5{\cdot}3H_2O$. The urea was from Ferak.

The basic bismuth(III) nitrates $[Bi_6O_4(OH)_4](NO_3)_6{\cdot}4H_2O$ and $[Bi_6O_4(OH)_4](NO_3)_6{\cdot}H_2O$ were made by the hydrolysis of nitric acid solutions of $Bi(NO_3)_3{\cdot}5H_2O$ in the following way: 25 g $Bi(NO_3)_3{\cdot}5H_2O$ was dissolved at room temperature in 25 ml 0.86 M HNO_3. The solution was diluted with 500 ml water (to 0.041 M HNO_3), kept at room temperature for 24 h and then further diluted with 125 ml water (to 0.033 M HNO_3). The white precipitate formed was isolated by filtration, washed with 0.63 M HNO_3 and dried in air at room temperature. The X-ray powder pattern of the compound was in agreement with that of $[Bi_6O_4(OH)_4](NO_3)_6{\cdot}4H_2O$,[6] ICDD card No. 84-2189. The compound was further dried at 80 °C, and the X-ray powder pattern of the product was now in agreement with that of $[Bi_6O_4(OH)_4](NO_3)_6{\cdot}H_2O$,[4,5] ICDD card No. 71-1360.

The experimental conditions for the hydrolysis of $Bi(NO_3)_3{\cdot}5H_2O$ and $[Bi_6O_5(OH)_3](NO_3)_5{\cdot}3H_2O$ (**A**) in the temperature range 60-190 °C are listed in Table 2 where the following short notation is used for the reaction products: **X**: Bi compound with unknown composition. **A**: $[Bi_6O_5(OH)_3](NO_3)_5{\cdot}3H_2O$[7] and **B**: $[Bi_6O_6(OH)_3](NO_3)_3{\cdot}1.5H_2O$.[9] At temperatures up to 100 °C the reaction mixtures were kept in pyrex glass flasks. At hydrothermal conditions, over 100 °C, teflon lined pressure vessels were used. The reaction products were isolated by filtration and dried in air at room temperature and the pH of the liquids was measured at 25 °C.

X-Ray powder diffraction

X-Ray powder patterns were recorded at 25 °C on a Stoe-Stadi powder diffractometer with a position sensitive detector. The diffractometer was calibrated with a silicon standard ($a = 5.43050$ Å) and $CuK_{\alpha 1}$ radiation was used ($\lambda = 1.5406$ Å). The compounds were identified from the powder patterns by the use of published patterns[9] and the ICDD base, or from calculated patterns using the program LAZY PULVERIX[13] and the crystallographic data from Ref. 4, 6 and 7.

The X-ray powder diffraction pattern of the reaction product **X** was measured on the diffractometer at the Swiss-Norwegian beam line BM1 at ESRF, Grenoble, using a wavelength of $\lambda = 1.0982(1)$ Å. The pattern was measured in the 2θ range 8–58° with steps of $\Delta(2\theta) = 0.01°$ and is listed in Table 3. The sample was kept in a 0.3 mm diameter silica glass capillary rotated at approximately 60 rpm to randomize the crystallite orientation. The pattern was recorded at 25 °C over 10 h. The X-ray powder diffraction pattern of phase **B**, $[Bi_6O_6(OH)_3](NO_3)_3{\cdot}1.5H_2O$[9] and of a thermal decomposition product of phase **X**, see below, was measured on the X7A diffractometer at NSLS, Brookhaven National Laboratory, Upton, NY, using a wavelength of $\lambda = 0.6996(5)$ Å. A position sensitive detector was used in a step scan mode with steps of 0.25°. Data collection parameters and unit cell parameters are listed in Table 4. The samples were kept in 0.2 mm diameter silica glass capillaries, which were rotated at approximately 60 rpm to randomize the crystallite orientation. The patterns were recorded at 25 °C.

Thermogravimetric analysis

Thermogravimetric analyses were made on the reaction products **A**, **B** and **X** (Table 2) using a Stanton Redcroft TGA–DTA simultaneous thermal analyser STA 1000/1500. A heating rate of 10 °C min^{-1} and a 150 ml min^{-1} flow of Ar gas was applied. The thermogravimetric analysis curves of the compounds **A**, **B** and **X** are displayed in Fig. 1. The loss of weight was also investigated by thermogravimetric analysis where the compounds were heated in Pt crucibles at temperatures up to 600 °C, where Bi_2O_3 was formed. The decomposition of **X** to Bi_2O_3 proceeds in three steps and the decomposition product formed prior to the formation of Bi_2O_3 is referred to above.

Infrared spectra

The infrared spectra of the compounds **A**, $[Bi_6O_5(OH)_3](NO_3)_5{\cdot}3H_2O$, and **X** were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. The two spectra are displayed in Fig. 2.

NMR measurements

The ^1H magic-angle spinning (MAS) NMR spectra of compounds **A**, **B**, and **X** were recorded at room temperature at 399.84 MHz on a Varian INOVA-400 (9.4 T) spectrometer using a home-built CP/MAS probe for 4 mm o.d. rotors. The experiments employed spinning speeds of $\nu_r = 15.0$ kHz (**B** and **X**) and $\nu_r = 15.7$ kHz (**A**), single-pulse excitation with an rf field of $\gamma B_1/2\pi = 70$ kHz, 48–256 scans, and relaxation delays (5–60 s) corresponding to full ^1H spin–lattice relaxation. Isotropic chemical shifts are relative to tetramethylsilane (TMS). Fig. 3 displays the ^1H MAS NMR spectra obtained under these conditions.

X-Ray fluorescence analysis

X-Ray fluorescence analyses were made on the compounds **A** and **X** on a Cam Scan Maxim 2040 Envac electron microscope. The Bi : N ratios found were **A**: 1.37(3), **X**: 1.34(3).

Table 3 Synchrotron X-ray powder diffraction pattern of **X**, sample No. 5, Table 2. Indexed with the hexagonal unit cell $a = 15.185(1)$, $c = 15.834(2)$ Å. Figure of merit $M(50) = 14.1$

$2\theta_{obs}/°$	$2\theta_{calc}/°$	d_{obs} Å	d_{calc} Å	I_{obs}	h	k	l
8.29	8.29	7.597	7.593	100	1	1	0
9.28	9.29	6.791	6.783	27	0	1	2
10.37	10.38	6.076	6.073	1	0	2	1
12.46	12.46	5.060	5.058	1	2	0	2
14.39	14.39	4.383	4.384	12	3	0	0
14.98	14.99	4.212	4.210	1	1	2	2
16.64	16.63	3.795	3.796	50	2	2	0
18.63	18.64	3.392	3.391	4	0	2	4
18.73	18.74	3.374	3.372	1	3	0	3
19.08	19.08	3.313	3.313	9	3	1	2
19.65	19.64	3.218	3.219	1	4	0	1
20.53	20.53	3.081	3.082	1	2	2	3
21.35	21.35	2.964	2.964	1	3	2	1
22.06	22.06	2.870	2.870	6	4	1	0
22.46	22.46	2.820	2.819	1	2	3	2
23.62	23.63	2.683	2.682	5	1	3	4
24.01	24.02	2.640	2.639	11	0	0	6
25.07	25.06	2.530	2.531	10	3	3	0
25.15	25.16	2.522	2.521	1	1	4	3
25.44	25.45	2.494	2.493	3	1	1	6
26.46	26.46	2.400	2.400	2	3	2	4
26.55	26.55	2.391	2.391	1	3	1	5
26.78	26.78	2.371	2.371	1	4	2	2
28.09	28.08	2.263	2.263	1	1	5	2
29.02	29.02	2.192	2.192	39	6	0	0
29.35	29.36	2.167	2.167	4	2	2	6
30.24	30.24	2.105	2.105	2	4	2	4
30.53	30.53	2.086	2.086	1	3	4	2
31.42	31.41	2.028	2.028	1	5	1	4
31.48	31.48	2.024	2.024	1	6	0	3
32.82	32.81	1.944	1.944	1	6	1	2
33.64	33.63	1.898	1.898	2	4	4	0
34.97	34.96	1.828	1.828	1	5	3	2
35.75	35.75	1.789	1.789	3	1	6	4
36.75	36.75	1.742	1.742	14	7	1	0
37.76	37.75	1.697	1.697	3	3	5	4
38.01	38.01	1.686	1.686	3	6	0	6
38.72	38.72	1.656	1.656	1	6	2	4
38.95	38.95	1.647	1.647	2	4	5	2
39.90	39.89	1.609	1.610	1	8	0	2
40.84	40.82	1.574	1.575	1	7	2	2
40.90	40.89	1.572	1.572	2	1	0	10
41.52	41.51	1.549	1.549	1	5	4	4
41.75	41.75	1.541	1.541	1	4	4	6
42.40	42.41	1.518	1.518	13	0	8	4
43.29	43.29	1.489	1.489	1	2	7	4
44.14	44.15	1.461	1.461	5	9	0	0
44.39	44.38	1.454	1.454	13	7	1	6
45.01	45.00	1.435	1.435	3	8	2	0
46.10	46.07	1.402	1.403	1	6	3	6

Table 4 Experimental data and unit cell parameters for bismuth subnitrates

Sample, powder	Phase **X**	Phase **B**	Decomposition product
Diffractometer	BM1 ESRF	X7A NSLS	X7A NSLS
$2\theta_{min}/°$	8	2	2
$2\theta_{max}/°$	58	53	71
$\Delta 2\theta/°$	0.01	0.01	0.01
λ/Å	1.0982(1)	0.6996(5)	0.6996(5)
Max $\sin\theta/\lambda$(Å^{-1})	0.44	0.64	0.83
Capillary Diameter/mm	0.3	0.2	0.2
Rotation/rpm	60	60	60
Temperature/°C	25	25	25
a/Å	15.185(1)	3.8175(5)	8.146(5)
b/Å	15.185(1)	3.8175(5)	11.659(9)
c/Å	15.834(2)	17.149(4)	3.463(4)
β/°			92.3(2)
γ/°	120.0		

Results and discussion

The results of the hydrolysis of aqueous solutions of bismuth(III) nitrate are displayed in Fig. 4. The hydrolysis of nitric acid solutions of bismuth(III) nitrate yields $[Bi_6O_4(OH)_4](NO_3)_6\cdot 4H_2O$ which on drying at 80 °C is converted to $[Bi_6O_4(OH)_4](NO_3)_6\cdot H_2O$.

An aqueous solution of $Bi(NO_3)_3\cdot 5H_2O$ is readily hydrolysed (Table 2) with water at 100 °C to $[Bi_6O_5(OH)_3](NO_3)_5\cdot 3H_2O$ and at 190 °C to $[Bi_6O_6(OH)_3](NO_3)_3\cdot 1.5H_2O$. In agreement with this, $[Bi_6O_5(OH)_3](NO_3)_5\cdot 3H_2O$ is hydrolysed with water at 190 °C to $[Bi_6O_6(OH)_3](NO_3)_3\cdot 1.5H_2O$. The simultaneous hydrolysis of solutions of $Bi(NO_3)_3\cdot 5H_2O$ and urea in relatively low concentrations at temperatures up to 90 °C gives the basic bismuth(III) nitrate $[Bi_6O_5(OH)_3](NO_3)_5\cdot 3H_2O$. With higher concentrations of urea or at hydrothermal conditions the reaction product is $Bi_2O_2CO_3$.

Experiment nos. 5 and 6 (Table 2) resulting in the bismuth compound **X** of unknown composition and structure will be described in more detail below. The two experiments show that it is possible to reproduce the synthesis of the compound **X**. 9.0 g

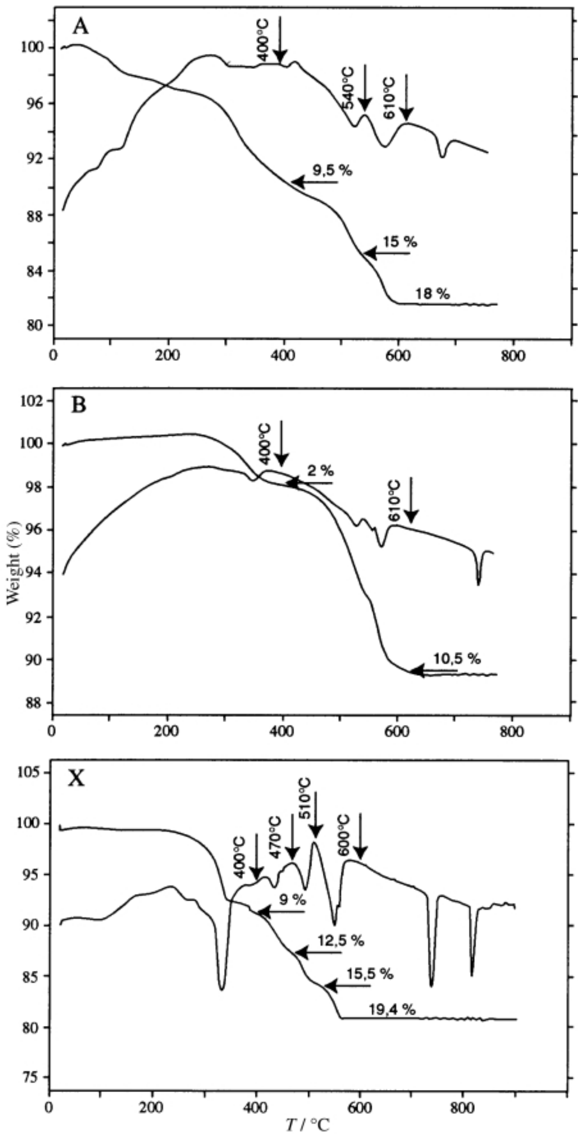

Fig. 1 TGA–DTA diagrams for the compounds **A**, **B** and **X**.

urea was dissolved in 100 ml water and 36.0 g $Bi(NO_3)_3 \cdot 5H_2O$ was added. The solution was thus 1.50 M with respect to urea and 0.74 M with respect to Bi^{3+}. The solution was heated to 100 °C and boiled for 2 min. At this stage the milk-white solution/suspension precipitated the white compound **X**, which was isolated by filtration, washed with water and dried in air at room temperature. 16.6 g of the compound was obtained. The mother liquid from above was titrated with a 1 M NaOH solution from pH = 0.42 to pH = 2.10. During the titration a white crystalline precipitate was formed which was filtered, washed with water and dried in air at room temperature. 3.80 g of the compound was obtained. An X-ray powder pattern of the compound showed that it was $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 3H_2O$, **A**.

The infrared spectra of **A** and **X**, Fig. 2, are rather similar to each other which indicates that the **X** contains water molecules, hydroxyl groups, and nitrate ions which is also the case for the **A**.

The ^1H MAS NMR spectra reveal the presence of two resonances for **B** and **X**, while the spectrum for **A** shows a dominating resonance at 6.1 ppm with a shoulder at 12 ppm. The broadened resonances at 6.1 ppm (**A**), 3.2 ppm (**B**), and 5.9 ppm (**X**) are assigned to ^1H in water molecules while the shoulder/resonance at 12 ppm (**A** and **X**) and the resonance at 4.6 ppm (**B**) are ascribed to ^1H in hydroxyl groups. This assignment utilizes the fact that the ^1H isotropic chemical shift is very sensitive to variations in hydrogen bondings for water molecules and hydroxyl groups. Thus, the ^1H MAS NMR spectra indicate that

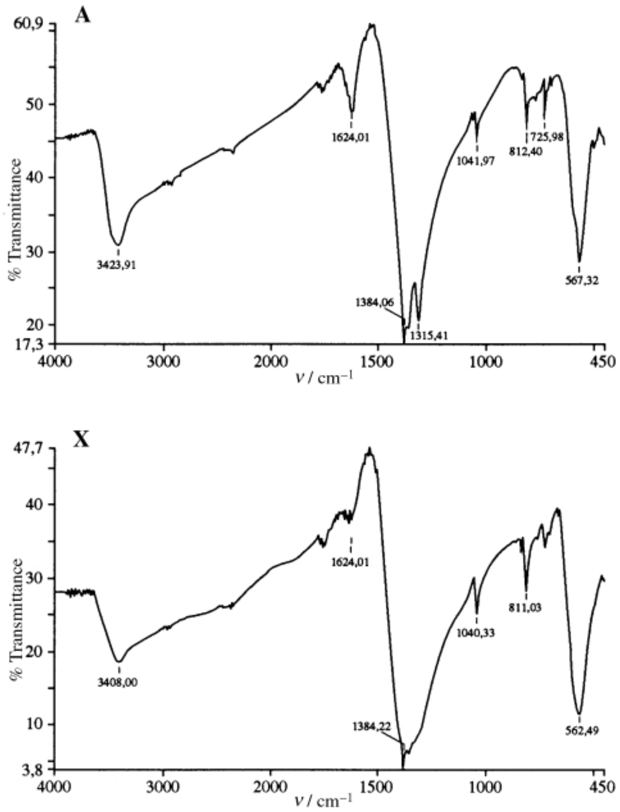

Fig. 2 Infrared spectra of the compounds **A** and **X**.

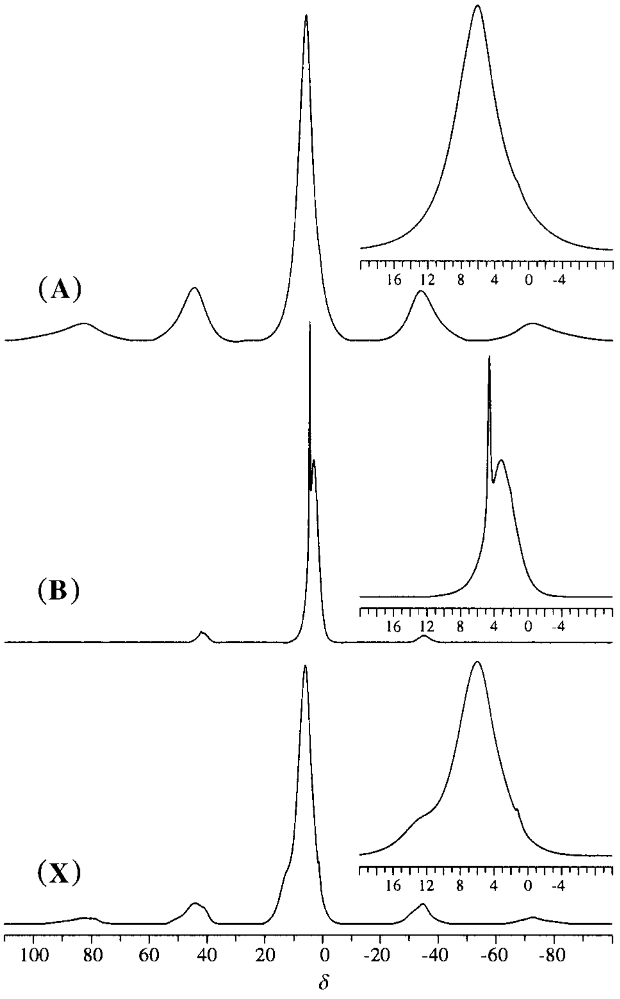

Fig. 3 ^1H MAS NMR spectra of compounds **A**, **B**, and **X** obtained at 399.84 MHz using spinning speeds of 15.7 kHz (**A**) and 15.0 kHz (**B** and **X**).

Table 5 Synchrotron X-ray powder pattern of phase **B**. Indexed with a tetragonal unit cell $a = 3.8175(5)$, $c = 17.149(4)$ Å. Figure of merit $M(30) = 24.4$

$2\theta_{obs}/°$	$2\theta_{calc}/°$	d_{obs} Å	d_{calc} Å	I_{obs}	h	k	l
4.68	4.68	8.568	8.575	100	0	0	2
9.38	9.36	4.281	4.287	5	0	0	4
10.79	10.77	3.722	3.726	3	1	0	1
11.53	11.51	3.484	3.487	23	1	0	2
12.66	12.65	3.173	3.175	3	1	0	3
14.08	14.06	2.855	2.858	63	0	0	6
	14.10		2.851		1	0	4
14.91	14.89	2.697	2.699	10	1	1	0
15.08	15.08	2.667	2.667	3	1	1	1
15.63	15.62	2.573	2.575	3	1	1	2
17.62	17.59	2.285	2.288	4	1	0	6
	17.62		2.284		1	1	4
18.79	18.78	2.143	2.144	9	0	0	8
18.98	18.99	2.122	2.121	1	1	1	5
20.55	20.54	1.962	1.963	6	1	1	6
21.13	21.12	1.908	1.909	11	2	0	0
21.26	21.25	1.897	1.897	8	2	0	1
21.58	21.57	1.869	1.869	3	1	0	8
21.65	21.64	1.863	1.863	4	2	0	2
22.27	22.24	1.811	1.814	3	1	1	7
	22.28		1.810		2	0	3
23.12	23.15	1.746	1.744	1	2	0	1
23.64	23.65	1.708	1.707	1	2	1	0
23.76	23.77	1.700	1.699	2	2	1	1
24.06	24.06	1.678	1.679	2	1	1	8
24.14	24.12	1.673	1.674	5	2	1	2
24.69	24.70	1.637	1.636	4	2	1	3
25.49	25.46	1.586	1.587	8	2	0	6
	25.48		1.586		2	1	4
25.84	25.84	1.564	1.564	7	1	0	10
26.46	26.46	1.529	1.528	2	2	1	5
26.87	26.87	1.506	1.506	1	2	0	7
27.62	27.62	1.466	1.466	1	2	1	6
28.33	28.33	1.430	1.429	7	0	0	12

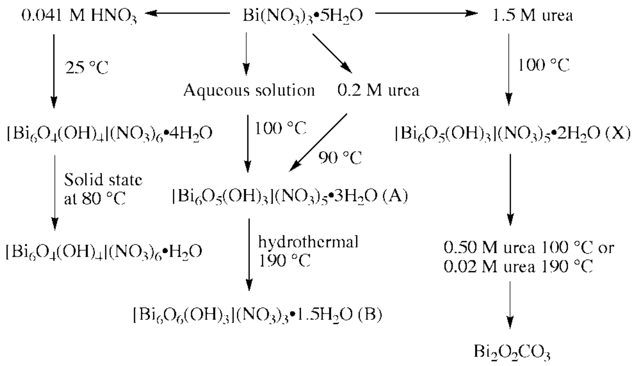

Fig. 4 Summary of the hydrolysis reactions of aqueous bismuth(III) nitrate solutions.

A, **B**, and **X** contain hydroxyl groups and water molecules. Single-pulse ^{13}C MAS NMR spectra of urea and **X**, obtained using ^{1}H high-power decoupling and a 7 mm CP/MAS probe, displayed a ^{13}C resonance at 162.6 ppm for urea and no resonances at all for phase **X**. This rules out the possibility that **X** could contain urea.

The synchrotron X-ray powder pattern of compound **X**, Table 3, was indexed with the program DICVOL91[14] on a hexagonal cell, $a = 15.185(1)$, $c = 15.834(2)$ Å, with a figure of merit $M(50) = 14.1$. The observed intensities, Table 3, were obtained in a profile fit to the pattern using the program ALLHKL.[15] The Miller indices indicate a rhombohedral cell. However, the pattern could also be indexed on an orthorhombic cell, $a = 15.848(4)$, $b = 13.154(2)$, $c = 7.592(1)$ Å, with a figure of merit $M(20) = 25.7$, and on a monoclinic cell, $a = 10.237(2)$, $b = 7.592(2)$, $c = 6.863(2)$ Å, $\beta = 98.65(2)°$, and a figure of merit $M(20) = 60.9$. The three cells are related, having the cell volumes 3162, 1583, and 527 Å^3, respectively. All reflections observed in the 2θ range 8–26° could be indexed with the three unit cells. No attempts were made to solve the structure from the powder diffraction data.

The synchrotron X-ray powder pattern of **B** $[Bi_6O_6(OH)_3](NO_3)_3·1.5H_2O$ was indexed using DICVOL91,[14] on a tetragonal cell, $a = 3.8175(5)$, $c = 17.149(4)$ Å, with a figure of merit $M(30) = 24.4$. The powder pattern is listed in Table 5. The unit cell cannot contain one of the formula units suggested in ref. 9 $[Bi_6O_6(OH)_3](NO_3)_3·1.5H_2O$ but possibly two units of a composition close to $BiONO_3·BiOOH$.

The thermal decomposition of **A** and **X** goes through a number of basic bismuth(III) nitrates. One of these was obtained at 485 °C in ref. 9 and at 390 °C in this work. The compound is yellow in contrast to **A** and **X** which are white. The synchrotron X-ray powder pattern of this thermal decomposition product was indexed using the program DICVOL91[14] on a monoclinic cell, $a = 8.146(5)$, $b = 11.659(9)$, $c = 3.463(4)$ Å, $\beta = 92.3(2)°$, with a figure of merit $M(15) = 17.3$. The powder pattern is listed in Table 6.

The TGA–DTA diagrams (Fig. 1) of $[Bi_6O_5(OH)_3](NO_3)_5·3H_2O$ up to 850 °C show formation of three basic bismuth(III) nitrates before the formation of Bi_2O_3. The loss in weight of $[Bi_6O_5(OH)_3](NO_3)_5·3H_2O$ of 18% is in fair agreement with the calculated value of 20.1%. However, in a thermogravimetric analysis where a sample of $[Bi_6O_5(OH)_3](NO_3)_5·3H_2O$ was heated in a Pt crucible to 600 °C for 1 h, the measured loss in weight was 20.1% in excellent agreement with the calculated value. The TGA–DTA diagrams of $[Bi_6O_6(OH)_3](NO_3)_3·1.5H_2O$ up to 510 °C indicate the formation of one basic bismuth(III) nitrate before Bi_2O_3 is formed and the loss in weight of 11.5% is only in fair agreement with the calculated loss of 13.4%. For the bismuth compound **X** the diagrams indicate the formation of three basic bismuth(III) nitrates. The loss in weight of 19.1% indicates a composition $[Bi_6O_5(OH)_3](NO_3)_5·2H_2O$.

Table 6 Synchrotron X-ray powder pattern of the thermal decomposition product. Indexed with a monoclinic unit cell $a = 8.146(5)$, $b = 11.659(9)$, $c = 3.463(4)$ Å, $\beta = 92.3(2)°$. Figure of merit $M(15) = 17.3$

$2\theta_{obs}/°$	$2\theta_{calc}/°$	d_{obs} Å	d_{calc} Å	I_{obs}	h	k	l
3.45	3.44	11.638	11.660	15	0	1	0
4.93	4.93	8.129	8.141	11	1	0	0
6.02	6.01	6.668	6.675	5	1	1	0
6.90	6.88	5.817	5.830	2	0	2	0
8.42	8.47	4.765	4.740	3	1	2	0
10.31	10.33	3.895	3.887	6	0	3	0
10.40	10.45	3.840	3.843	2	2	1	0
12.44	12.43	3.229	3.232	100	1	0	−1
12.89	12.90	3.118	3.115	3	1	1	−1
13.80	13.79	2.912	2.915	23	0	4	0
14.55	14.55	2.763	2.763	15	1	2	1
14.66	14.65	2.742	2.744	8	1	4	0
14.82	14.81	2.713	2.714	15	3	0	0
20.10	20.10	2.005	2.005	17	4	1	0
20.29	20.29	1.986	1.986	15	3	4	0

Conclusion

The composition of **A** is $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 3H_2O$ known from a single crystal X-ray diffraction analysis.[7] Thermogravimetric analysis gave a loss in weight of 20.1%, calculated value 20.1% for the formation of α-Bi_2O_3 from the compound. X-Ray fluorescence analysis showed a Bi : N ratio of 1.37(7), calculated value from the formula 1.20. The nitrogen content is thus underestimated by 14%. For **X** the X-ray fluorescence analysis showed a Bi : N ratio of 1.34(3) which is comparable to the value measured for $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 3H_2O$.

The conversion to α-Bi_2O_3 in the thermogravimetric investigation gave a loss in weight of 19.4%. The calculated value for the formula $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 2H_2O$ is 19.2%. As the IR spectra of **A** and **X** are similar to each other, it is suggested that **X** has the formula $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 2H_2O$.

Furthermore, the ^1H MAS NMR spectra show a relatively higher intensity for the ^1H resonance from hydroxyl groups for **X** as compared to **A**, which is in accord with the suggested formula for **X**.

Acknowledgements

The Danish Natural Science Research Council has supported this investigation with grants. Carlsbergfondet is acknowledged for financial support by purchase of furnace equipment and the TGA–DTA thermal analyzer. The possibility of collecting data at the Swiss-Norwegian beam line, BM1, at the European Synchrotron Radiation Facility and at the beam line X7A at the National Synchrotron Light Source is gratefully acknowledged. Dr J. Chevallier, Mrs C. Secher, Mr N. J. Hansen and Mr A. Lindahl are thanked for valuable assistance.

References

1 A. F. Holleman and E. Wiberg, *Lehrbuch der Anorganischen Chemie*, Walter de Gruyter & Co., Berlin, 1971, p. 440.
2 G. Hägg, *General and Inorganic Chemistry*, John Wiley & Sons, Inc., New York, 1969, p. 580.
3 F. Lazarini, *Acta Crystallogr., Sect. C*, 1985, **41**, 1144.
4 B. Sundvall, *Acta Chem. Scand.*, 1979, **A33**, 219.
5 F. Lazarini, *Acta Crystallogr., Sect. B*, 1979, **35**, 448.
6 F. Lazarini, *Cryst. Struct. Commun.*, 1979, **8**, 69.
7 F. Lazarini, *Acta Crystallogr., Sect. B*, 1978, **34**, 3169.
8 G. Gattow and D. Schott, *Z. Anorg. Allg. Chem.*, 1963, **324**, 31.
9 B. S. Brcic, D. Kolar, F. Lazarini and M. Malesic, *Monatsh. Chem.*, 1973, **104**, 365.
10 D. Swinehart and A. B. Garret, *J. Am. Chem. Soc.*, 1951, **73**, 507.
11 P. Pascal, *Nouveau traité de chimie minérale*, Vol. XI, Masson & Cie, Paris, 1958, p. 795.
12 A. N. Christensen, M. S. Lehmann and A. Wright, *Acta Chem. Scand.*, 1982, **A36**, 779.
13 K. Yvon, W. Jeitschko and E. Parthè, *J. Appl. Crystallogr.*, 1977, **10**, 73.
14 A. Boultif and D. Loüer, *J. Appl. Crystallogr.*, 1991, **24**, 987.
15 G. S. Pawley, *J. Appl. Crystallogr.*, 1981, **14**, 357.

Paper a908055d