Inorg. Chem. **2004**, 43, 785–789

Inorganic Chemistry

Article

Characterization and Structure Determination of Ammonium Bismuth Oxalate Hydrate, $Bi(NH_4)(C_2O_4)_2 \cdot xH_2O$

G. Vanhoyland,*,[†] A. Le Bail,[‡] J. Mullens,[†] and L. C. Van Poucke[†]

Laboratory of Inorganic and Physical Chemistry, IMO, Limburgs Universitair Centrum,
Wetenschapspark 1, 3590 Diepenbeek, Belgium, and Laboratoire des Fluorures,
Université du Maine, 72085 Le Mans, France

Received May 13, 2003

From on-line coupled TGA-MS and TGA-FTIR measurements, in combination with a quantitative chemical analysis, it was deduced that the chemical formula for an unknown bismuth oxalate compound had to be $Bi(NH_4)(C_2O_4)_2 \cdot 3.71(6)H_2O$. Solution of the crystallographic structure on the basis of X-ray powder data proved this formula to be correct. The diffraction pattern was indexed by a tetragonal unit cell [a and c respectively 11.6896(2) and 9.2357(3) Å; $M_{20} = 195$ and $F_{30} = 302$; $Z_{calc} = 4$], from which the space group $I4_1/amd$ (No. 141) was derived. Direct methods were applied to solve the structure. The initial structural model was subsequently refined by means of the Rietveld method ($R_B = 8.0\%$, $R_{wP} = 14.0\%$). Bi is 8-fold coordinated by oxygen from the oxalate anions. Since these BiO_8 polyhedrons do not share any edges or vertexes, an open framework is formed with water and ammonium molecules between. As a result, water can easily be removed, which is clearly indicated by the instant weight loss in the TGA upon heating. Moreover, as shown by HT-XRD, this process of water exchange is reversible as long as the heating temperature does not exceed 100 °C.

Introduction

It is well-known from the literature that ammonium metal oxalates, when thermally decomposed, yield crystalline porous materials with a high surface area.[1,2] This feature makes them attractive as precursors for catalysts and other nanocrystalline oxides. But the oxalates themselves also have, because of their topology, interesting properties such as their capability for ion-exchange. Several of these oxalate-based compounds form porous open-framework structures.[3−7] In the cavities zeolitic water, ammonium ions, and even small organic molecules can be trapped.

In this study the synthesis, characterization, and crystal structure description of ammonium bismuth oxalate hydrate is discussed. This compound was synthesized for reference during a systematic study to characterize multimetal combinations in the Bi−Sr−Ca−Cu system. While at high bismuth concentrations mixtures of $Bi_2(C_2O_4)_3 \cdot 7H_2O$ and $Bi_2(C_2O_4)_3$ were obtained, the diffraction pattern of the material synthesized at low bismuth concentration did not correspond to any of the known bismuth oxalate salts. For this compound, it was not possible to calculate the chemical formula from conventional TGA measurements due to the uncertainty about the nature of the released gases, the small difference in mass between H_2O and NH_3/NH_4^+, and the instant decrease in weight upon heating. Therefore, on-line coupled TGA-MS and TGA-FTIR measurements were carried out, together with a quantitative chemical analysis to determine the correct stoichiometry before solving the crystal structure.

Experimental Section

A stock solution of Bi^{3+} was prepared by dissolving 122 g of $Bi(NO_3)_3 \cdot 5H_2O$ (Merck pa) in 230 mL of HNO_3 (14.44 N) and adding deionized water up to 500 mL. The exact normality was

---

* To whom correspondence should be addressed. E-mail: geert.vanhoyland@luc.ac.be. Tel: ++32/(0)11/26.88.17. Fax: ++32/(0)11/26.88.99.

[†] Limburgs Universitair Centrum.

[‡] Université du Maine.

(1) Hussein, G. A. M.; Ismail, H. M.; Attyia, K. M. E. *J. Anal. Appl. Pyrolysis* **1995**, *31*, 157.
(2) Hussein, G. A. M.; Ismail, H. M. *Colloids Surf.* **1995**, *95*, 53.
(3) Bataille, T.; Louër, M.; Auffrédic, J.-P.; Louër, D. *J. Solid State Chem.* **2000**, *150*, 81.
(4) Trombe, J.-C.; Thomas, P.; Brouca-Cabarrecq, C. *Solid State Sci.* **2001**, *3*, 309.
(5) Audebrand, N.; Vaillant, M. L.; Auffrédic, J. P.; Louër, D. *Solid State Sci.* **2001**, *3*, 483.
(6) Fourcade-Cavillou, F.; Trombe, J.-C. *Solid State Sci.* **2002**, *4*, 1199.
(7) Bataille, T.; Auffrédic, J. P.; Louër, D. *Chem. Mater.* **1999**, *11*, 1559.

10.1021/ic034509h CCC: $27.50

determined by means of a titration with EDTA.[8] For the synthesis, a 0.02 M Bi^{3+} and a 0.3 M $(NH_4)_2C_2O_4{\cdot}H_2O$ solution were mixed dropwise (0.2 mL each time) together under continuous stirring. The fully automated synthesis setup was placed in a thermostatic controlled box, kept at 25 °C. The synthesis yielded a white precipitate, which was subsequently filtered with a Millipore filter (0.2 μm). The as-obtained powder was dried in the thermostatic controlled box and finally lightly ground in a mortar.

The thermal decomposition of the product was studied by means of TGA (TA Instruments, Hi-Res TGA 2950), TGA-MS (TA Instruments, model 951-2000 on-line coupled with a quadrupole mass spectrometer of VG Fisons Instruments), and TGA-FTIR (TA Instruments, model 951-2000 on-line coupled with a Bruker IFS 48). The mass scans in the TGA-MS experiments were done at an ionization energy of 20 eV to distinguish between H_2O (mass 18) and NH_3 (mass 17, a fragment of NH_4^+). A resolution of 8 cm^{-1} was selected for the MCT detector in the TGA-FTIR experiments. Both coupled techniques were used in a complementary way, since TGA-MS is more sensitive for H_2O determination, while TGA-FTIR is more suited to detect NH_3 during decomposition. The coupled experiments were done in an argon atmosphere, while the conventional TGA experiments were done in oxygen, dry air, or argon. To check the proper functioning of the equipment under inert conditions, a test described in ref 9 was used. For all thermal analysis experiments, the heating rate was 10 °C/min.

The ammonium content of the compound was determined in a quantitative way by means of an indirect method described in ref 8. A weighted quantity of the salt is added to an excess NaOH of known normality. NH_3 is released when boiling this solution. Subsequently, the amount of consumed NaOH is determined by means of a titration with HCl of known normality. Instead of using methyl red as an indicator for the titration (as described in ref 8), a mixing indicator of methyl red and bromocresol green in 95% ethanol was used for its sharper color transition. This experiment was repeated 4 times independently of each other.

To correctly calculate the amount of NH_4^+ for this particular compound, not only the release of NH_3 through boiling but also the formation of solid $Bi(OH)_3$ has to be taken into account. According to ref 10, this rather insoluble product dissolves in hot water. But since the equilibrium constant of $[Bi(OH)_3]/\{[Bi_2O_3]_{1/2}$ (s, α)} is log $K = -5.4$,[11] eventually Bi_2O_3 is formed in hot water.

X-ray diffraction experiments were carried out on a Siemens D5000 diffractometer equipped with a Göbel mirror. The powder was first sieved through a 325-mesh sieve. For indexing purposes a diffraction pattern obtained from a parallel beam setup (10−55° 2θ, 0.025°, 5 s/step) was used to correct an extended high-quality dataset for sample displacement errors. In the parallel beam setup, a 0.15° thin film attachment was used on the diffracted beam side. This type of geometry is less sensitive for sample displacement errors compared to the focusing Bragg−Brentano geometry. A high-quality diffraction pattern (10−130°, 0.025° step size, 45 s/step) was obtained using slits on the diffracted beam side. To improve particle statistics, the sample was rotated during the measurement. Moreover, in an effort to decrease possible surface effects (due to the rather high linear absorption coefficient of the compound) and improve randomness in particle orientation, the sample was diluted with glass particles (size < 325 mesh). These glass particles are responsible for the large bump seen in the low-angle region. To describe this behavior adequately, an interpolated background was used instead of a polynomial during Rietveld refinement. HT-XRD experiments were done using a HTK10 heating chamber (Anton Paar) together with a PSD (mBraun) as detector. The latter was replaced by the thin film attachment for indexing the observed phases at some selected temperatures.

Results and Discussion

Identification. As can be seen in Figure 1a,b, the oxalate decomposition occurs in two steps. Due to the uncertainty about the released gases, the TGA curve does not allow calculation of the initial chemical formula on the basis of the finally observed mass. Moreover, the small difference in mass between H_2O and NH_3/NH_4^+ and the immediate weight decrease upon heating make this calculation even more difficult. For this reason, on-line coupled measurements were carried out to characterize the released gases. The TGA-MS result was confirmed by means of an independent TGA-FTIR analysis, for which the intensity of the infrared peak at 968 cm^{-1} (symmetric deformation of NH_3) is plotted as a function of the temperature (Figure 1b). From both experiments, it was established that, in the first decomposition step up to 200 °C, only H_2O is gradually released. During the second, strongly exothermic decomposition step, both NH_3 (from NH_4^+) and CO_2 (from $C_2O_4^{2-}$) are set free.

The final weight percentage is clearly a function of the atmosphere (Table 1). The resulting decomposition products were characterized by means of XRD. In an oxidizing atmosphere, Bi_2O_3 is formed (PDF-2 41-1449), while under inert circumstances metallic Bi is formed (PDF-2 44-1246).

Combining all this information, one can calculate the formula weight of the initial product to be 456(1) g/mol (in Ar atmosphere) and 470(1) g/mol (in O_2 atmosphere), respectively. The slightly lower calculated mass for the experiment under inert conditions is probably due to the fact that the final decomposition product is not pure metallic Bi. There might still be traces of C or O present, which could not be detected with XRD since only a few hard grains were available, because of the low melting point of Bi. If we keep in mind the neutrality principle and ignore the presence of any impurity phase (see structure determination and refinement), the calculated formula weight in oxygen suggests $Bi(NH_4)(C_2O_4)_2{\cdot}3.71(6)H_2O$ as the correct chemical formula. Taking into account the presence of impurity phases would yield a lower water content, but since they are not well characterized and their most intense diffraction peak (if observed) is only 0.5% of the main bismuth oxalate peak, an accurate calculation is not possible. Nevertheless, to get an estimate for possible effects on the water content, the chemical formula has been recalculated on the assumption that 0.5% and 1% (weight basis) of impurity phases (consisting of only C, N, O, and H) would be present. This yields respectively $Bi(NH_4)(C_2O_4)_2{\cdot}3.55(5)H_2O$ and $Bi(NH_4)(C_2O_4)_2{\cdot}3.42(5)H_2O$.

To check the proposed stoichiometry, the ammonium content was quantified by means of a chemical method. First

---

(8) Jeffery, G. H.; et al. *Vogel's textbook of quantitative chemical analysis*, 5th ed.; Longman Scientific & Technical: Harlow, U.K., 1989.

(9) Mullens, J.; Vos, A.; Carleer, R.; Yperman, J.; Van Poucke, L. C. *Thermochim. Acta* **1992**, *207*, 337.

(10) *CRC Handbook of Chemistry and Physics*, 1983−1984 ed.; CRC: Boca Raton, FL, 1983.

(11) Martell, A. A.; Smith R. M. *Critical Stability Constants*; Plenum Press: New York, 1977.

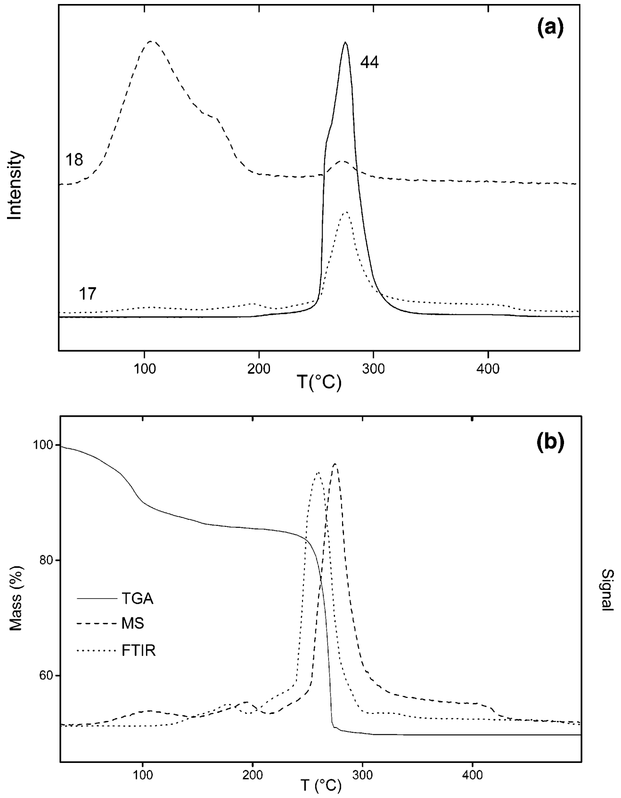

Figure 1. (a) MS data for respectively H_2O (18), NH_3 (17), and CO_2 (44). (b) TGA curve, MS (mass 17), and FTIR (968 cm^{-1}) signal.

Table 1. Thermal Decomposition under Inert and Oxidizing Conditions

atmosphere	wt at 1st plateau (%)	final wt (%)	visual	phase (PDF-2)
argon	86.06	45.81	metallic grayish melt	Bi (44-1246)
oxygen	86.21	49.63	light yellow powder	Bi_2O_3 (41-1449)

Table 2. Experimental Information

λ	Cu Kα_{1+2}
chem formula	$Bi(NH_4)(C_2O_4)_2 \cdot 3.71(6)H_2O$
fw	470(1)
color	white
space group	$I4_1/amd$ (No. 141:2)
a	11.6896(2) Å
c	9.2357(3) Å
V	1262.03(5) Å^3
M_{20}	195
F_{30}	302 (0.0032; 31)
D_{calc}	2.47 g/cm^3
Z	4
R_{wP}[a]	14.0%
R_B	8.0%

[a] Background corrected.

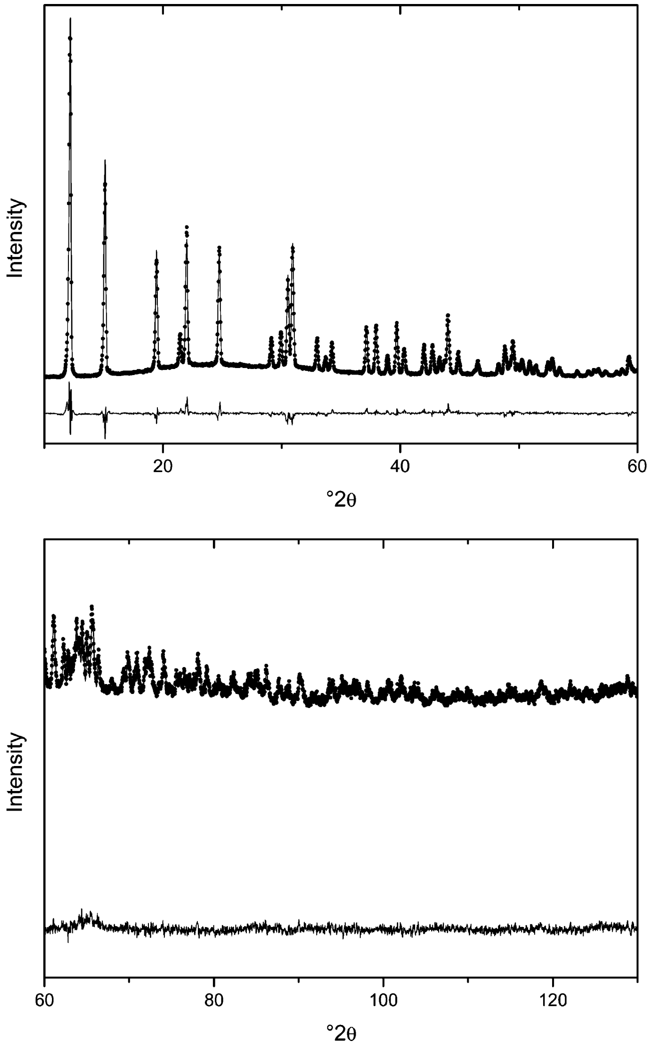

Figure 2. Final Rietveld plot (two parts, high-and low-angle regions).

it was confirmed by means of XRD that the resulting powder after boiling and consequent NH_3 release is indeed pure Bi_2O_3 (PDF-2 41-1449). Taking $Bi(OH)_3$ formation into account means that only a quarter of the total amount of consumed NaOH is due to the NH_3 release. As a result, 3.8(1) % of the total molecular weight can be attributed to NH_4^+, which is in accordance with the calculated amount of 3.8%, on the assumption that $Bi(NH_4)(C_2O_4)_2 \cdot 3.71(6)H_2O$ is the correct stoichiometry for the unknown salt.

Structure Determination and Refinement (Table 2). After correction for peak shifts, both Treor97[12] and Dicvol91[13] were used for indexing. Some very low intensity lines (at 14.67 and 17.01°), which were only found in some sample batches and showed markedly broader peaks than the main phase, could not be indexed and were consequently not included. They can probably be assigned to $NH_4HC_2O_4 \cdot 1/2H_2O$ (PDF-2 70-1286) and/or $(NH_4)_2C_2O_4 \cdot H_2O$ (oxammite, PDF-2 87-0648), which are frequently reported as minor impurities in these types of compounds.[5] Both indexing programs suggested the same tetragonal unit cell, of which the dimensions were subsequently least-squares refined in Pirum[14] using 92 diffraction peaks. On the basis of the systematic absences, the space group $I4_1/amd$ (No. 141) was chosen. The choice of this space group was additionally confirmed by means of the program Chekcell.[15] Nevertheless, attempts were made to solve the structure in other potential space groups of lower symmetry such as $I4_1/a$ and $I4_1md$, but no improvement was obtained. Taking space group restrictions for $I4_1/amd$ into account resulted in excellent figures of merit: $M_{20} = 195$ and $F_{30} = 302$ (0.0032, 31).

---

(12) Werner, P. E.; Eriksson, L.; Westdahl, M. *J. Appl. Crystallogr.* **1985**, *18*, 367.

(13) Boultif, A.; Louër, D. *J. Appl. Crystallogr.* **1991**, *24*, 987.

(14) Werner, P. E. *Ark. Kemi* **1969**, *31*, 513.

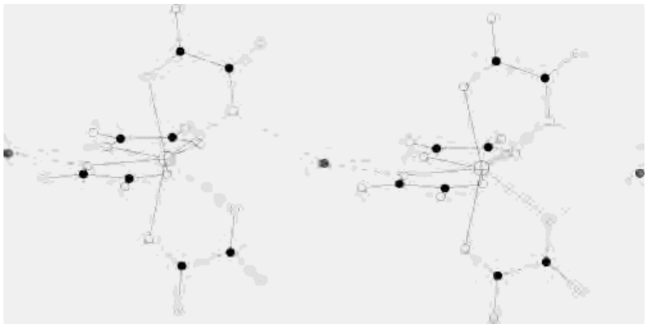

Figure 3. Coordination of Bi^{3+} and NH_4^+ ions. Hydrogen bonds are displayed by means of dotted lines. Key: Bi (cross); C (black); O (white); N (gray).

With calculation of the density for different Z values, $\rho_{calc} = 2.47$ g/cm^3 for $Z = 4$ is the most likely combination, compared to literature values for other oxalates. In the space group $I4_1/amd$ this indicates that Bi and N occupy the positions 4a and 4b. Moreover, this implies that certain oxygen positions (from the water molecules) are only partially occupied. Peak intensities were extracted by means of a Le Bail fit with the direct methods program EXPO.[16] When direct methods were applied, one phase set showed a much higher figure-of-merit (CFOM = 0.999) compared to all the other propositions (CFOM < 0.388). From this phase set, a nearly correct model was obtained. After a default Rietveld refinement of this model in EXPO, a Fourier difference map was made, which revealed another position of positive electron density at position 8d. On the basis of the interatomic distances, an oxygen atom was included in the model at this position.

For the final Rietveld refinement in FULLPROF,[17] the atomic displacement parameter was initially constrained to be the same for all atoms and the total occupancy of the O_{water} positions to 62%. The latter corresponds to 3.7 water molecules to fit the TGA results. Moreover, it was assumed that both O_{water} positions were equally occupied. At the end of the refinement, the isotropic atomic displacement parameters for (chemically) similar types of atoms were refined separately although this yields rather high B_{iso}'s for the lighter elements, which is probably due to the weight of the high scattering power of Bi. The occupancies of the O_{water} positions were not refined since they are highly correlated to the scale factor and B_{iso}'s of the water molecules. During refinement it was observed that the two first diffraction peaks were always calculated too low. Initially, it was thought that the X-ray beam was too large at low angles. However, it was confirmed that this was not the case. From the literature[18,19] it is known that surface roughness and microabsorption particularly affect the low angle diffraction peaks, which are consequently underestimated. Since the linear absorption coefficient for this compound is rather high ($\mu \sim 275$ cm^{-1}) and both low-angle diffraction peaks are most intense, it is believed that these effects are at the origin of the observed aberrations in the diffraction pattern. Since no a priori way is known to correct the raw data for this effect, a factor ("sent0" in Fullprof, which is normally used to compensate for a too large beam at low angles) was manually adjusted to compensate for the lower intensity. Leaving out this correction results in strong distortions of the bond lengths. Finally, after refinement of 24 parameters of which 13 were intensity dependent, a satisfactory result was obtained [$R_B = 8.0\%$ and $R_{wP} = 14.0\%$ (background subtracted)]. Despite the use of an asymmetry correction, the highly asymmetric first diffraction peak is still not adequately fitted (Figure 2). A more accurate fit would definitely improve the R-values.

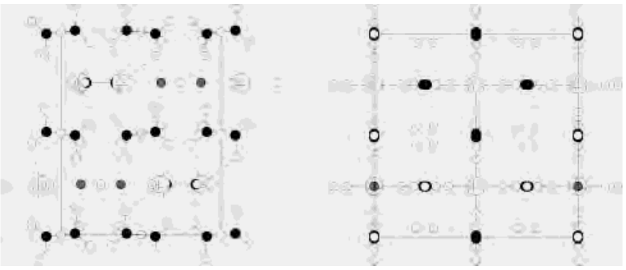

Figure 4. View along the *a* axis (left) and view along the *c* axis (right). Key: Bi (cross); C (black); O (white); N (gray). Bi−O bonds displayed as dotted lines.

Table 3. Selected Bond Lengths (Å) and Angles (deg)

Bi−O1	2.465(8)		
Bi−O2	2.434(8)	O1−C−O2	123(1)
C−C	1.49(1)	O1−C−C	113.2(9)
C−O1	1.26(1)		
C−O2	1.22(1)		

The crystallographic structure exhibits a high symmetry with Bi fully coordinated by 4 oxalate molecules (Figure 3, Table 3). As is frequently observed in ammonium oxalate salts,[4] all oxalates are bichelating ligands. In such a way, every bismuth center is connected to its four neighboring bismuth centers. The resulting BiO_8 polyhedra can be described as bisdisphenoids. The Bi−O distances are respectively 2.465(8) and 2.434(8) Å, which is comparable to what can be found in the literature for $K[Bi(C_2O_4)_2]\cdot 5H_2O$.[20] The same holds for the oxalate ion, with 1.22(1) and 1.26(1)Å respectively for both C−O bonds, although the C−C bond of 1.49(1) Å is somewhat shorter than generally found in oxalate compounds. Since each oxalate is fully coordinated by two Bi atoms, the BiO_8 polyhedra share neither edges nor vertexes. Due to the symmetry imposed, these oxalate molecules are planar and parallel along the *ac*- and the *bc*-plane, respectively. The basic building block is a ring formed by 6 Bi and 6 oxalate molecules. Such six-membered rings are also found in $YK(C_2O_4)_2\cdot 4H_2O$ (Figure 3 in ref 7). In this way, an open bismuth−oxalate network is formed, displaying large channels along the [111]

---

(15) Chekcell is a modified version of Celref: Laugier, J.; Bouchu, B. http://www.ccp14.ac.uk/tutorial/lmgp.

(16) Altomare, A.; Burla, M. C.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G. *J. Appl. Crystallogr.* **1995**, *28*, 842.

(17) Rodriguez-Carvajal, J. *Abstracts of the Satellite Meeting on Powder Diffraction of the XVth Congress of the International Union of Crystallography*; 1990; p 127.

(18) Suortti, P. *J. Appl. Crystallogr.* **1972**, *5*, 325.

(19) David, W. I. F.; Shankland, K.; McCusker, L. B.; Baerlocher, Ch. *Structure Determination from Powder Diffraction Data*; Oxford University Press: Oxford, U.K., 2002; p 65.

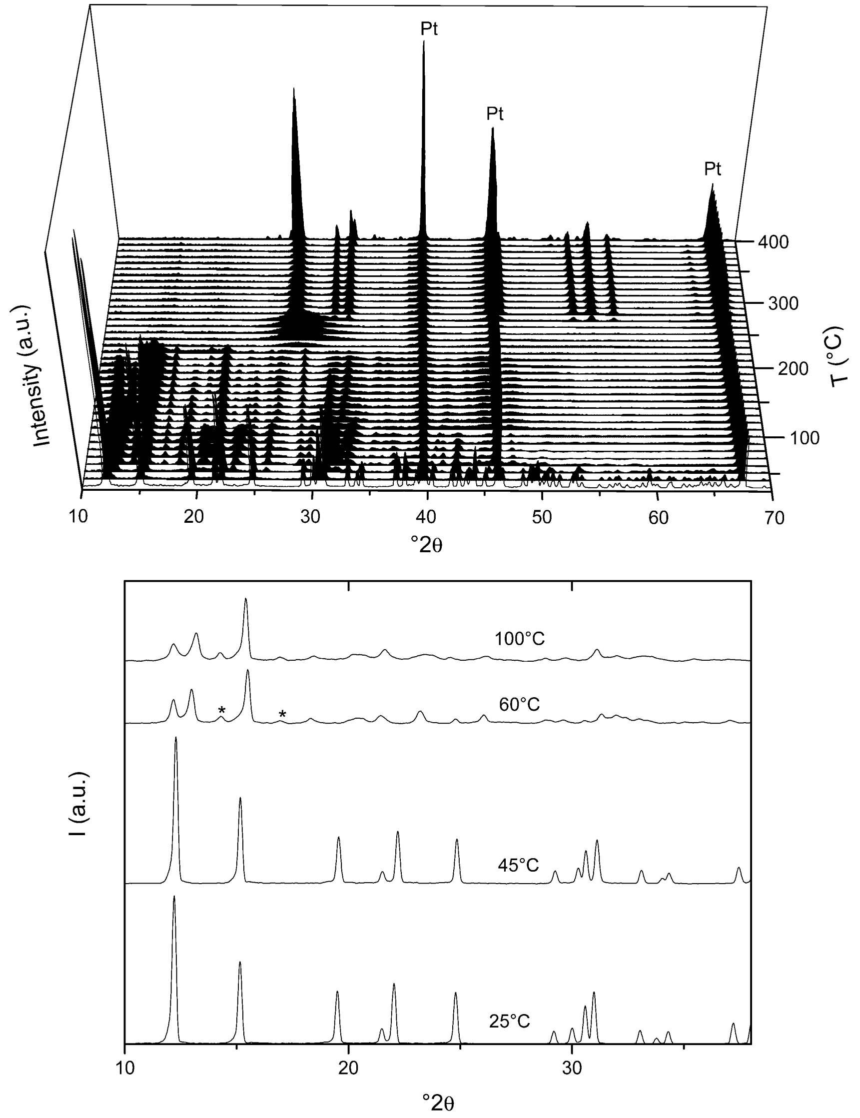

Figure 5. HT-XRD (two parts). Overview and more detailed diffraction patterns for some selected temperatures below 100 °C. Diffraction peaks indicated by asterisks in the diffraction pattern of 60 °C remain upon cooling to room temperature.

direction. In these cavities the ammonium ions are bound by weak hydrogen bonds (Figures 3 and 4). The ammonium ion is 4-fold coordinated by O1 of the oxalate, with N−O 2.996(8) Å. On the other hand, both water molecules have no hydrogen bond contacts within 3.00 Å. As a consequence, they are set free relatively easily. This can also be observed in the TGA experiments from the instant weight decrease upon heating. In this respect, $Bi(NH_4)(C_2O_4)_2 \cdot 3.71(6)H_2O$ differs from other mixed hydrated oxalates described in the literature. In some of the latter, water is coordinated to the counterion (e.g. K^+ in refs 7 and 20) while in others even to the metal ion (e.g. La^{3+} in ref 3).

From HT-XRD measurements (Figure 5), this process of water removal was found to be, at least partially, reversible as long as the temperature did not exceed 100 °C. Up to 45 °C, dehydration results only in a decrease of the cell volume, an effect which is most pronounced along the *c* axis ($a = 11.673(3)$ Å, $c = 9.146(3)$ Å, and $V = 1246.24$ Å^3 at 45 °C). Above 50 °C the structure becomes less crystalline and a mixture of at least two phases is formed. One of these remains stable after cooling (Figure 5, indicated by an asterisk), leading to only a partial recovery of the initial oxalate. Due to poor crystallinity, its diffraction pattern could not be indexed, although diffraction peaks seem to appear at the positions of the impurity phase found in some batches of the oxalate salt.

Acknowledgment. G.V. is a Postdoctoral Fellow of the Fund for Scientific Research − Flanders, Belgium (F.W.O. − Vlaanderen).

Supporting Information Available: Crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC034509H

---

(20) Heinl, U.; Hinse, P.; Mattes, R. *Z. Anorg. Allg. Chem.* **2001**, *627*, 2173.