Thermochimica Acta, 46 (1981) 53--55
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

Note

THERMAL DEHYDRATION OF SOME BASIC BISMUTH NITRATES

F. LAZARINI

Department of Chemistry, Faculty of Natural Sciences and Technology, University Edvard Kardelj of Ljubljana, Murnikova 6, 61000 Ljubljana (Yugoslavia)

(Received 31 October 1980)

The crystal structures of several solid products of the hydrolysis of bismuth(III) nitrate were determined by X-ray structural analysis [1—3] in order to elucidate the mechanism of the hydrolysis. It has been noticed that water molecules are very loosely bound in these structures. This may be one of the reasons for some confusion arising from the older literature about the water content of these compounds [4]. The thermal dehydration of three basic bismuth nitrates has been studied in order to obtain additional information about the properties of these compounds.

The first solid product of the hydrolysis of bismuth(III) nitrate at pH below 1.0 is $[Bi_6O_4(OH)_4](NO_3)_6 \cdot 4\,H_2O$ (quoted in the older literature as $Bi_2O_3 \cdot N_2O_5 \cdot 2\,H_2O$ or $BiONO_3 \cdot H_2O$). Its crystal structure [1] consists of nitrate anions, water molecules and cage-like $[Bi_6O_4(OH)_4]^{6+}$ polycations, with the Bi atoms arranged octahedrally and the O atoms above the octahedral faces, each interconnecting three Bi atoms. At pH between 1.2 and 1.8 further hydrolysis occurs and another solid product crystallizes, $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 3\,H_2O$ (quoted in the older literature as $6\,Bi_2O_3 \cdot 5\,N_2O_5 \cdot 9\,H_2O$). Its crystal structure [2] contains nitrate anions, water molecules and polycations in which pairs of $[Bi_6O_5(OH)_3]^{5+}$ groups, similar to the $[Bi_6O_4(OH)_4]^{6+}$ cations, are joined through two bridging O atoms. By heating the suspension of the first product of the hydrolysis at 50°C a further basic bismuth nitrate can be obtained, $[Bi_6(H_2O)(NO_3)O_4(OH)_4](NO_3)_5$ (quoted in the older literature as $Bi_2O_3 \cdot N_2O_5 \cdot H_2O$ or $2\,BiONO_3 \cdot H_2O$). In the crystal structure [3] the water molecule and a NO_3^- anion are bound to two neighbouring Bi atoms of the $[Bi_6O_4(OH)_4]^{6+}$ group.

EXPERIMENTAL

The compounds were prepared as described by Rutten [4] and identified by X-ray powder diffraction. The thermal dehydration was studied with a Mettler TA 1 thermoanalyser. Experimental conditions were: TG—Ma sample holder, platinum flat crucible 12 mm in diameter, 100 mg sample masses, atmosphere of dry air with $5\,l\,h^{-1}$ flow rate, heating rate $2°C\,min^{-1}$.

RESULTS AND DISCUSSION

The TG curves are shown in Fig. 1. The results of the thermal dehydration are in close agreement with those obtained by X-ray structural analysis. The dehydration of $[Bi_6O_4(OH)_4](NO_3)_6 \cdot 4\,H_2O$ and $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 3\,H_2O$ starts at relatively low temperatures (at about 40° C). This observation is compatible with the weakness of the hydrogen bonds present in the crystal structures [1,2] (only few hydrogen bonds in the range 2.60—2.80 Å were found). Unfortunately, the positions of the light O atoms in the crystal structures cannot be determined with a good precision in the presence of heavy Bi atoms, because of relatively small contribution of the O atoms to the total scattering power. Therefore a further correlation of the structural data with the observed stepwise dehydration does not seem reasonable. In contrast to the low thermal stability of these compounds, $[Bi_6(H_2O)(NO_3)O_4(OH)_4](NO_3)_5$ is stable up to 115° C, because the water molecules are bound to the Bi atoms, as concluded from the determined interatomic distances [3]. Sundvall [5] determined independently the crystal structure of the same compound. The results are comparable, considering the accuracy of the determined interatomic distances, but from the slightly different interatomic distances the author concluded that the water molecule and the NO_3^- anion are not bound to the $[Bi_6O_4(OH)_4]^{6+}$ group. The thermogravimetric results as well as the inequality of the NO_3^- anions suggested by vibrational spectroscopy [6] do not support Sundvall's conclusion.

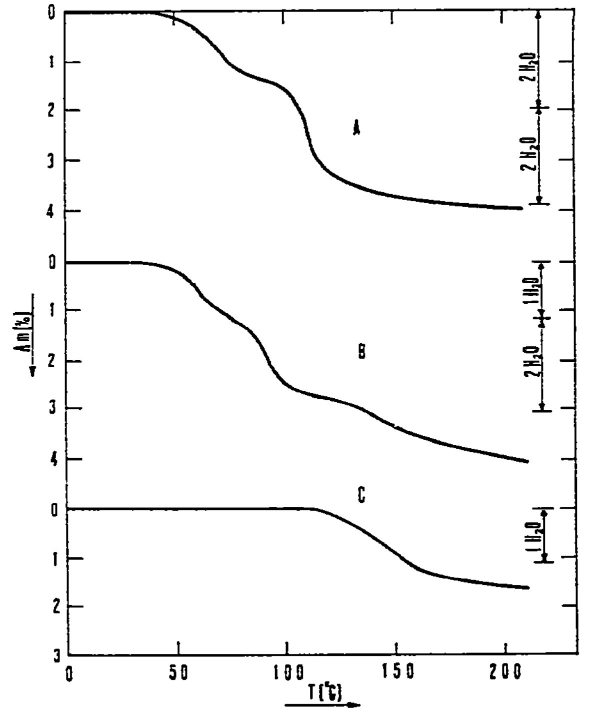

Fig. 1. TG curves: A, $[Bi_6O_4(OH)_4](NO_3)_6 \cdot 4\,H_2O$; B, $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 3\,H_2O$; C, $[Bi_6(H_2O)(NO_3)O_4(OH)_4](NO_3)_5$.

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