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Structure Investigation of a Novel Complex $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 2H_2O$

A.N. Christensen, M.D. Andersen, T.R. Jensen (U. Aarhus) and J.C. Hanson (BNL)

Beamline: X7B

Introduction: A number of basic bismuth(III) nitrates are obtained in hydrolysis of bismuth(III) nitrate solutions, and a review of these hydrolyses was recently reported [1]. One of these basic bismuth(III) nitrates is obtained in a homogeneous hydrolysis with urea. The hydrolysis of urea in aqueous solutions at temperatures up to 100°C slowly produces a low concentration of ammonia.

Results: The basic bismuth(III) nitrate investigated here is obtained at 100°C in the reaction of a bismuth(III) nitrate and 1.5 M urea solution. Chemical analysis and thermo gravimetric analyses suggest the composition $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 2H_2O$. The compound is obtained as a crystalline powder with the typical crystal size 0.01 x 0.01 x 0.05 mm. Synchrotron X-ray powder patterns of the compound can be indexed [2] with different cells:

	a/Å	b/Å	c/Å	α/°	β/°	γ/°	V/Å^3
Monoclinic	10.237(2)	7.592(2)	6.863(2)		98.65(2)		526.9
Monoclinic	11.431(6)	7.594(4)	6.853(3)		117.71(4)		526.9
Orthorhombic	15.837(4)	13.155(3)	7.591(2)				1581.5
Hexagonal	15.185(1)	15.185(1)	15.834(2)			120	3161.9

Assuming a density similar to that of $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 3H_2O$ [3] of 5.26 g cm^{-3}, these unit cells would correspond to 1, 1, 3, and 6 formula units, respectively, in the cells.

A single crystal measurement on the MAR-diffractometer at beam line X7B using a wave length λ= 0.9269 Å gave a set of data with an internal R-value of 1.7% and a monoclinic C-cell of a = 13.74, b = 15.17, c = 10.17 Å, β = 98.98°, V = 2093.8 Å^3, thus corresponding to four formula units in the cell. A structure solution with the direct method program SIR [4] gave positions of Bi-atoms using the space group C2/m. This is twice the number of coordinates expected, and a number of the Bi-Bi distances are too short compared to the expected distances in the Bi_6O_8-coordination polyhedra usually found in basic bismuth(III) nitrates. This suggests twinning of the crystal investigated, and the structure analysis is in progress using this hypothesis.

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