PS-08.01.13 THE CRYSTAL STRUCTURE OF THE NEW SYNTHETIC COMPOUND Na₂Cu₆Bi₂O₁₂(AsO₄)₄·H₂O.

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Hydrothermal synthesis in the system Na₂O-CuO-Bi₂O₃-As₂O₅-H₂O at 503 K in tetlon lined stainless steel autoclaves produced dark green crystals of the compound Na₂Cu₆Bi₂O₁₂(AsO₄)₄·H₂O. They proved to be monoclinic, the space group is C2: a = 9.716(1) Å, b = 5.203(1) Å, c = 13.362(2) Å, β = 115.03(1)°. The lamellar crystals are elongated parallel to [010] and flattened parallel to (100).

The crystal structure was investigated from single crystal X-ray data: STOE four-circle diffractometer, graphite monochromatized MoKα radiation, 2θ ≤ 60°, peak scan width 0.78° in 2θω mode, scan speed 0.015° to 0.030° per second. 3585 reflections (hlkl≠0) have been measured, after averaging (R = 0.031) a unique data set of 1781 reflections was obtained, 1683 with F > 3σ(F). Friedel pairs were kept separated due to perceptible anomalous dispersion effects.

The structure was solved from a Flack map and from subsequent Fourier summations. The refinement yielded R = 0.037 and wR = 0.038, w = 1/σ² (program SHELX-76).

The sodium atom has six ligands with 2.28(1) Å ≤ Na-O ≤ 2.96(1) Å in an distorted octahedral coordination. The two Cu atoms (site symmetries 2 and 1) are [4+2] and [4+1] coordinated forming a tetragonal elipsoid and a tetragonal pyramid, respectively [short Cu-O from 1.92(1) Å to 1.98(2) Å, additional bonds 2.49(1) Å and 2.51(1) Å]. The Bi atom has three short Bi-O bonds to oxygen atoms [2.18(1) Å to 2.21(1) Å] forming a trigonal pyramid; four additional Bi-O bonds complete the coordination (one o xo-oxygen atom with Bi = 2.48(2) Å and three oxygen atoms belonging to the arsenate tetrahedra with Bi-O from 2.70(1) Å to 2.94(2) Å. The arsinite tetrahedra are as usual (average As-O = 1.70 Å). The two oxo-oxygen atoms are coordinated to two Bi and to two Cu atoms (short Cu-O bonds). The hydrogen bond lengths of the water molecule (site symmetry 2) are 2.87(2) Å, the angle O-Cu-O is 70.5(7)°; in addition the O₃ atom is coordinated to two Na atoms resulting in a tetrahedral environment.

The compound shows a pronounced layer structure parallel (001) with predominant interconnections parallel [010]. Considering only the nearest neighbour environments, Bi₂O₂ units are connected via oxo-oxygen atom corners to infinite chains and the CuO₄ squares to ribbons parallel [010]. These chains and ribbons share common O-O edges to form layers parallel (001). Including the additional Bi-O bonds into the connection scheme, Bi chains are maintained; in contrast, considering Cu⁴⁺ and Cu²⁺ coordination results in layers solely formed by the copper coordination polyhedra. The arsenate tetrahedra are branched to these complex layers. The layers are interconnected by the sodium atoms and by the water molecule; NaO₄ polyhedra share common edges with neighbored NaO₄ polyhedra and CuO₄ squares.

Structural work on the isotypic compound K₂Cu₆Bi₂O₁₂(AsO₄)₄·H₂O is in progress. This compound was obtained as one of the byproducts from systematic experiments to synthesize the mineralinate, BiC₁₈H₁₆(OH)₂(AsO₄)₄·3H₂O, under hydrothermal conditions (R. Mileitich and J. Zechner, Aufschluss 44, 493, 19–21).

PS-08.01.14 A CRYSTAL STRUCTURE OF Bi₆Na₂(Carbonato- Na₂O)-O(OH₂)₄(O₂C₂O₄)₄·H₂O (Kanwiri) Diaminoplatinum (III) Nitrate Trihydrate. By Shih-Chi Young², J. H. Buks², H. K. Mahran³, P. B. Stein⁴, Department of Physics, Department of Chemistry, Duquesne University, Pittsburgh, PA 15282 /Department of Crystallography, University of Pittsburgh, Pittsburgh, PA 15260.

We report on a minority product identified during an investigation of "platinum 2-deoxyoxazidine blue". Di-aminocobaltic platinum(III) was allowed to react with 2-deoxyoxazidines for several hours at 40°C under aerobic conditions, addition of Na₂O₅ and incubation at 0°C. Most crystals from the above reaction are blue and appear as dendritic aggregates of thin flakes. The crystallinity is of poor quality and unsuitable for X-ray diffraction work. However, a few thin colorless transparent plates with dimensions about 0.2×0.15×0.04 cm were observed and selected for study. The crystallographic data is summarized as: a = 11.324 b = 12.151 c = 30.926 w = 103.792.

The ORTEP drawing shows the [Bi₆Na₂(CO₃)₂(AsO₄)₂]₄⁺ cation with nearly η⁴ point symmetry and a square arrangement of the four Bi atoms. The absence of 2-deoxyoxazidime and the occurrence of carbonate coordination is noted. Carbone ions, which are picked up from the air as CO₂, are known to be present in similar reactions (Lippert R., J. Clin. Hemat. 13/7, 26–50). This is the first reported crystal structure of η⁴,CO₃ coordination with Bi₆L₄(III) metal species. It is also the first example of a 12K4 carbonate complex.