



PS-08.01.13 THE CRYSTAL STRUCTURE OF THE NEW SYNTHETIC COMPOUND  $\text{Na}_2\text{Cu}_3\text{Bi}_2\text{O}_4(\text{AsO}_4)_2 \cdot \text{H}_2\text{O}$ .

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Hydrothermal syntheses in the system  $\text{Na}_2\text{O}-\text{CuO}-\text{Bi}_2\text{O}_3-\text{As}_2\text{O}_5-\text{H}_2\text{O}$  at 503 K in teflon lined stainless steel autoclaves produced dark green crystals of the compound  $\text{Na}_2\text{Cu}_3\text{Bi}_2\text{O}_4(\text{AsO}_4)_2 \cdot \text{H}_2\text{O}$ . They proved to be monoclinic, the space group is C2:  $a = 9.716(1) \text{ \AA}$ ,  $b = 5.203(1) \text{ \AA}$ ,  $c = 13.362(2) \text{ \AA}$ ,  $\beta = 115.03(1)^\circ$ . The lamellar crystals are elongated parallel to [010] and flattened parallel (100). The crystal structure was investigated from single crystal X-ray data: STOE four-circle diffractometer, graphite monochromatized  $\text{MoK}\alpha$  radiation,  $2\theta \leq 60^\circ$ , peak scan width  $0.78^\circ$  in  $2\theta/\omega$  mode, scan speed  $0.015$  to  $0.030^\circ$  per second. 3585 reflections ( $\pm h \pm k \pm l$ ) have been measured, after averaging ( $R_i = 0.031$ ) a unique data set of 1787 reflections was obtained, 1683 with  $F_o \geq 3\sigma_F$  (Friedel pairs were kept separated due to perceptible anomalous dispersion effects). The structure was solved from a Patterson map and from subsequent Fourier summations. The refinement yielded  $R = 0.037$  and  $wR = 0.038$ ,  $w = 0.720/\sigma_F^2$  (program SHELX-76).

The sodium atom has six ligands with  $2.28(1) \text{ \AA} \leq \text{Na}-\text{O} \leq 2.96(1) \text{ \AA}$  in a distorted octahedral coordination. The two Cu atoms (site symmetries 2 and 1) are [4+2] and [4+1] coordinated forming a tetragonal dipyramid and a tetragonal pyramid, respectively [short Cu-O from  $1.92(1) \text{ \AA}$  to  $1.98(2) \text{ \AA}$ , additional bonds  $2.49(1) \text{ \AA}$  and  $2.51(1) \text{ \AA}$ ]. The Bi atom has three short Bi-O bonds to oxo-oxygen atoms [ $2.18(1) \text{ \AA}$  to  $2.21(1) \text{ \AA}$ ] forming a trigonal pyramid; four

additional Bi-O bonds complete the coordination [one oxo-oxygen atom with  $\text{Bi}-\text{O} = 2.48(2) \text{ \AA}$  and three oxygen atoms belonging to the arsenate tetrahedra with  $\text{Bi}-\text{O}$  from  $2.70(1) \text{ \AA}$  to  $2.94(2) \text{ \AA}$ . The arsenate tetrahedra are as usual (average  $\langle \text{As}-\text{O} \rangle = 1.70 \text{ \AA}$ ). 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  $2.87(2) \text{ \AA}$ , the angle  $\text{O} \cdots \text{O}_w \cdots \text{O}$  is  $70.5(7)^\circ$ ; in addition the  $\text{O}_w$  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,  $\text{BiO}_3$  units are connected *via* oxo-oxygen atom corners to infinite chains and the  $\text{CuO}_4$  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  $\text{Cu}^{I+II}$  and  $\text{Cu}^{I+2I}$  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;  $\text{NaO}_6$  polyhedra share common edges with neighbored  $\text{NaO}_6$  polyhedra and  $\text{CuO}_4$  squares.

Structural work on the isotopic compound  $\text{K}_2\text{Cu}_3\text{Bi}_2\text{O}_4(\text{AsO}_4)_2 \cdot \text{H}_2\text{O}$  is in progress. This compound was obtained as one of the byproducts from systematic experiments to synthesize the mineral mixite,  $\text{BiCu}_6(\text{OH})_6(\text{AsO}_4)_3 \cdot 3\text{H}_2\text{O}$ , under hydrothermal conditions (R. Miletich and J. Zemann, *Aufschluß* 44, 1993, 17-21).

PS-08.01.14 A CRYSTAL STRUCTURE OF Di- $\mu_4$ -(carbonato-O,O,O',O')-tetraakis[diammineplatinum(II)] Nitrate Trihydrate. By Shih-Chi Chang<sup>a</sup>, J. R. Ruble<sup>c</sup>, H. K. Mahtani<sup>b</sup>, P. B. Stein<sup>b</sup>, <sup>a</sup>Department of Physics, <sup>b</sup>Department of Chemistry, Duquesne University, Pittsburgh, PA 15282; <sup>c</sup>Department of Crystallography, University of Pittsburgh, Pittsburgh, PA 15260.

We report on a minority product identified during an investigation of "platinum 2'-deoxyuridine blue". Cis-diamminediacquaplatinum(II) was allowed to react with 2'-deoxyuridine for several hours at  $-40^\circ\text{C}$  under aerobic conditions, addition of  $\text{NaNO}_3$  and incubation at  $-0^\circ\text{C}$ .

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  $0.2 \times 0.15 \times 0.04 \text{ mm}$  were observed and selected for study. The crystallographic data is summarized as:  $a=11.324$   $b=12.151$   $c=10.926$   $\alpha=103.792$   $\beta=111.266$   $\gamma=75.845$  space group=PI  $Z=2$   $R=0.039$   $R_w=0.041$ . The ORTEP drawing shows the  $[\text{Pt}_4(\text{NH}_3)_8(\mu_4\text{-CO}_3)_2]^{4+}$  cation with nearly  $D_{2d}$  point symmetry and a square arrangement of the four Pt atoms. The absence of 2'-deoxyuridine and the occurrence of carbonate coordination is noted.

Carbonate ions, which are picked up from the air as  $\text{CO}_2$ , are known to be present in similar reactions (Lippert B., *J. Clin. Hemat. Oncol.* 7, 26-50). This is the first reported crystal structure of  $\mu_4\text{-CO}_3$  coordination with Pt(II) metal species. It is also the first example of a L2,M4 carbonato complex.

