80-Inorganic and Mineralogical Crystallography

A large number of inorganic crystal structures with at least one short translation period are built up of two alternating atomic layers where the atoms of each layer are located above and below the centres of the polygons formed by the atoms in the neighbouring layers. Such structures can be decomposed into interpenetrating, centred straight prisms with equal planar faces. For different combinations of elements, different prisms are expected. For a given combination of elements, it is then possible to derive the most probable structure from knowledge of the coordination numbers and individual contributions of the atoms. (Gladyszewski, R.E., Czuczolai, K. & Pardy, E. (1992). J. Solid State Chem. 100, 9-15.) Combining interpenetrating prisms, hypothetical atom arrangements may be designed for particular structure families. For example, the hypothetical structure shown below is built up of the same kind of prism as the known structure of YNaAl₃ (Gladyszewski, R.E. & Pardy, E. (1992). Acta Cryst. C48, 229-232).

For ternary rare earth transition metal - (B, Al, Ga, In) compounds some 60 two-layer structure types are known. It can be seen from the diagram below that in the crystals the transition metal atoms preferentially occupy trigonal prisms of composition BP₃Al₂ or Al₃, and the rare earth metal atoms pentagonal or hexagonal prisms. The structure of compounds where each components centres a particular kind of prism are to be found on straight lines in the ternary diagram (for aluminiumides K₁₂[Al₃]Al₄, and K₁₂[Al₃]Al₄P₃).

In the corresponding ternary borides larger (heptagonal or octagonal) prisms must also be taken into consideration for the rare-earth metal atoms, whereas the smaller prisms are preferred by the small boric atoms. In gallides and indides the polyhedra around the constructing atoms are similar to those observed for aluminides, but in the case of gallides both gallium and transition metal atoms can be found inside trigonal and larger prisms.

A detailed report of this work will be submitted to the Acta Cryst. B.
PS-08.01.13 THE CRYSTAL STRUCTURE OF THE NEW SYNTHETIC COMPOUND Na₃Cu₂Bi₂O₆(AsO₄)₃·H₂O

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Hydrothermal synthesis of the system Na₂O-CuO-Bi₂O₃-As₂O₅·H₂O at 503 K in tetlon lined stainless steel autoclaves produced dark green crystals of the compound Na₃Cu₂Bi₂O₆(AsO₄)₃·H₂O. They proved to be monoclinic, the space group is C2: a = 9.7167(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 2θ mode, scan speed 0.015° to 0.030° per second. 3585 reflections (±3σ) have been measured, after averaging (R = 0.031) a unique data set of 1787 reflections was obtained. 1683 with F ≥ 3σ(F) (Prodet 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 = 0.720σ² (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 dipyramid 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 two different oxygen atoms [2.18(1) Å to 2.21(1) Å] forming a trigonal pyramid; four additional Bi–O bonds complete the coordination (one tri-oxygen atom with Bi–O = 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 arsenate tetrahedra are as usual (average <As–O> = 1.70 Å). The two tri-oxygen atoms are coordinated to two Bi and to two Cu (short Cu–O bonds). The hydrogen bond lengths of the water molecule (site symmetry 2) are 2.87(2) Å, the angle O–H···O is 70.5(7)°; in addition the O₂⁻ 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, Bi₂O₅ units are connected via oxygen atoms to infinite chains and the CuO₄ squares to ribbon 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 Cu²⁺ and Cu⁺⁺ 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 neighboured NaO₄ polyhedra and CuO₄ squares.

Structural work on the isotypic compound K₂Cu₂Bi₂O₆(AsO₄)₃·H₂O is in progress. This compound was obtained as one of the byproducts from systematic experiments to synthesize the mineral minite. BiCu₃(OH)₆(AsO₄)₃·3H₂O, under hydrothermal conditions (R. Milewich and J. Zevenaar, Aufschrift 44, 993, 19-21).

PS-08.01.14 A CRYSTAL STRUCTURE OF Bi₂(H₂O₄)₄(C₂O₄)₄[Cr(CN)₆]·H₂O, NITRITE TRIHYDRATE

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We report on a minority product identified during an investigation of "platinum 2'-deoxoyuridine blue". Nitrogen-triimido-triscyanometalatriplatinum(II) was allowed to react with 2'-deoxoyuridine for several hours at 40°C under aerobic conditions. Addition of NaNO₂ 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 x 0.1 x 0.04 mm were observed and selected for study. The crystallographic data is summarized as: a = 11.324 b = 12.151 c = 10.926 α = 103.792 β = 112.266 γ = 95.845 space group-P2₁/a with space group-P2₁/z (R = 0.039, R = 0.041).

The ORTEP drawing shows the [PdCl₃(NH₃)₃NO₃]⁺ cation with nearly Na⁺ point symmetry and a square arrangement of the four Pd atoms. The cation of 2'-deoxoyuridine and the occurrence of carbonate coordination is noted.

Carbonate ions, which are picked up from the air as CO₂, are known to be present in similar reactions (Lippert B., J. Clin. Hematol. 2010, 7, 26-52). This is the first reported crystal structure of PdCO₃ coordination with Pd(II) metal species. It is also the first example of a 2.9.4 carb trade complex.

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