

## MS81.P56

*Acta Cryst.* (2011) A67, C724**Pseudosymmetry and unusual Cu<sup>2+</sup>O<sub>5</sub> coordination figures in Na<sub>18</sub>Cu<sub>3</sub>(PO<sub>4</sub>)<sub>8</sub>·2H<sub>2</sub>O**Herta Effenberger, *Institut für Mineralogie und Kristallographie, Universität Wien (Austria)*. E-mail: herta.silvia.effenberger@univie.ac.at

Single crystals of Na<sub>18</sub>Cu<sub>3</sub>(PO<sub>4</sub>)<sub>8</sub>·2H<sub>2</sub>O were synthesized under hydrothermal conditions from a mixture of Na<sub>2</sub>HPO<sub>4</sub> + NaNO<sub>3</sub> + CuO / Cu(OH)<sub>2</sub> + H<sub>2</sub>O (the temperature was kept at 503 K for 3 days). The obtained crystals form dark blue prisms. They are corrugated after extraction from the mother liquid already and stable in air for a few weeks only. The unit cell is unusually large for an inorganic compound, especially for a non-zeolitic one:  $a = 21.620(4)$ ,  $b = 14.157(3)$ ,  $c = 20.448(4)$  Å,  $\beta = 92.50(3)^\circ$ ,  $V = 6252.7$  Å<sup>3</sup>, space group  $C2/c$ . There are 18 Na sites, 5 Cu sites, and 8 phosphate tetrahedra in the asymmetric unit. The crystal structure was determined from single-crystal X-ray diffraction data. As indicated by the cell metrics, the atomic arrangement features a *pseudo*-tetragonal symmetry in the [010] direction. The Cu atoms are located at  $[\frac{1}{4}y0]$  and  $[0y\frac{1}{4}]$ ; the former exhibit Cu<sub>2</sub>(PO<sub>4</sub>)<sub>6</sub> groups; the latter are linked by phosphate tetrahedra to columns. These groups and columns are linked by the Na<sup>+</sup> ions forming a three-dimensional network. The crystal structure exhibits some disorder with respect to one Na-atom position, the water molecules and at least one phosphate group. During crystal-structure refinement different models were considered including spitted atom positions as well as symmetry reductions.

The arrangement in  $[\frac{1}{4}y0]$  consists of two CuO<sub>4</sub> squares (Cu—O = 1.88 - 1.97 Å) parallel (010) corner-linked by two P8O<sub>4</sub> tetrahedra; each two P1O<sub>4</sub> and P5O<sub>4</sub> tetrahedra are branched. These Cu<sub>2</sub>(PO<sub>4</sub>)<sub>6</sub> groups are intercalated by P7O<sub>4</sub> tetrahedra which are solely linked to Na atoms.

The atoms Cu2 to Cu5 are located on  $[0y\frac{1}{4}]$ . The Cu<sub>2</sub>O<sub>4</sub> and Cu<sub>4</sub>O<sub>4</sub> squares (Cu—O = 1.88 - 1.97 Å) are arranged parallel to each other and corner-linked by two P6O<sub>4</sub> tetrahedra to dimers. With four additional phosphate tetrahedra (P2O<sub>4</sub> and P4O<sub>4</sub>), Cu<sub>2</sub>(PO<sub>4</sub>)<sub>6</sub> groups are formed again.

Similarly, the atoms Cu3 and Cu5 are linked by two P3O<sub>4</sub> tetrahedra. These [Cu<sub>3</sub>Cu<sub>5</sub>(P3O<sub>4</sub>)<sub>2</sub>] groups are corner linked to the P2O<sub>4</sub> and P4O<sub>4</sub> tetrahedra forming continuous —Cu—(PO<sub>4</sub>)<sub>2</sub>—Cu—(PO<sub>4</sub>)<sub>2</sub>— rows with formula [Cu(PO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)]. However, the co-ordinations of the Cu3 and Cu5 atoms are worthy to note. Besides four ligands belonging to the phosphate tetrahedra, each of these two Cu atoms has two sites of the half occupied O1 atom belonging to water molecules in their surroundings. Notwithstanding the accurate location of the O1 atom, the five ligands and the vacancy form an only slightly distorted octahedron. The bond length distribution is Cu<sub>3</sub>—Op = 1.93 and 2.10 Å, each 2H, Cu—Ow = 2.04 Å; Cu<sub>5</sub>—Op = 1.91 and 2.13 Å, each 2H, Cu—Ow = 2.06 Å. Moreover, the two longer Cu<sub>3</sub>—O and Cu<sub>5</sub>—O bonds are in a *cis*-arrangement. Such five-fold coordination figures are not compatible with the expectations for the surrounding of Cu<sup>2+</sup> ions because of the distortion in an octahedral field. The existence of a dynamically disordered Jahn-Teller effect is discussed. Extensive dislocations are indicated by the anisotropic displacement parameters.

**Keywords:** copper(II), Jahn-Teller effect, pseudosymmetry

## MS81.P57

*Acta Cryst.* (2011) A67, C724**Copper-carboxylate complexes supported on kegglin polyoxometalates**Aroa Pache, Amaia Iturraspe, Pablo Vitoria, Santiago Reinoso, LuisLezama, Beñat Artetxe and Juan M. Gutiérrez-Zorrilla. *Department of Inorganic Chemistry, Universidad del País Vasco, Facultad de Ciencia y Tecnología, Bilbao (Spain)*. E-mail: aroa\_pache@ehu.es

Much current research activity of polyoxometalate chemistry is driven by potential, perceived, and realized applications in many areas, especially catalysis, imaging, sorption, medicine, functional materials, and molecular electronics in addition to optical, electrical, magnetic fields [1]. Polyoxometalates (POMs), as one kind of significant metal oxide clusters have recently been employed as inorganic building blocks for constructing supramolecular arrays with various organic ligands [2]. Incorporation of POMs into organic-inorganic hybrid materials have resulted in large numbers of one-, two- and three-dimensional organic-inorganic hybrid materials with coexistence of novel structure characteristics and physical properties [3].

In this work we report the synthesis, chemical and spectroscopic characterization, X-ray structure and magnetic properties of a new hybrid inorganic-metalorganic compound based on Keggin polyoxometalate with copper-picolinate:  $K_{4n}[SiW_{12}O_{40}\{Cu(C_6H_4NO_2)_2\}_n] \cdot 6nH_2O$ .

This compound was prepared by both hydrothermal and open air methods.

The compound presents a hybrid chain running along the direction [101]. The joints between the  $\alpha$ -Keggin polyanions are set by the metalorganic blocks, which contain a copper centre coordinated to two picolinate ligands, [Cu(2-pic)<sub>2</sub>], and connects the polyanions through the terminal oxygen O4(POM). (Figure 1).

Furthermore, the ESR spectroscopy for the compound indicates that there is an isolated chromophore copper(II) with a g tensor of axial symmetry.

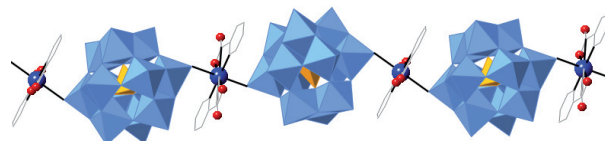


Figure 1: Hybrid chain trough [101] direction.

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**Keywords:** polyoxometalate, metalorganic, copper-picolinate

## MS81.P58

*Acta Cryst.* (2011) A67, C724-C725**The novel Krebs-type polyoxometalate  $\{[Ni(C_4H_4N_2O_2)(H_2O)]_2(WO_2)_2(\beta-SbW_9O_{33})_2\}^{4-}$** Beñat Artetxe, Pablo Vitoria, Santiago Reinoso, Amaia Iturraspe, Aroa Pache, Juan M. Gutiérrez-Zorrilla. *Department of Inorganic Chemistry, Facultad de Ciencia y Tecnología, Universidad del País Vasco (UPV/EHU), Bilbao (Spain)*. E-mail: benat\_artetxe@ehu.es

The functionalization of polyoxometalate (POM) anions is a recent trend in POM chemistry in order to extend their versatility and lead to new and more selective applications. The chemistry of POM-based hybrids has been significantly enriched by the inclusion of transition metal (TM) coordination complexes into the hybrid system, either to provide charge compensation or as a part of the inorganic POM framework itself. The presence of a lone pair of electrons on the Sb<sup>III</sup>-