

MS81.P56

Acta Cryst. (2011) A67, C724**Pseudosymmetry and unusual Cu²⁺O₅ coordination figures in Na₁₈Cu₃(PO₄)₈·2H₂O**Herta Effenberger, *Institut für Mineralogie und Kristallographie, Universität Wien (Austria)*. E-mail: herta.silvia.effenberger@univie.ac.at

Single crystals of Na₁₈Cu₃(PO₄)₈·2H₂O were synthesized under hydrothermal conditions from a mixture of Na₂HPO₄ + NaNO₃ + CuO / Cu(OH)₂ + H₂O (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, $\beta = 92.50(3)^\circ$, $V = 6252.7$ Å³, 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 Cu₂(PO₄)₆ groups; the latter are linked by phosphate tetrahedra to columns. These groups and columns are linked by the Na⁺ 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 CuO₄ squares (Cu—O = 1.88 - 1.97 Å) parallel (010) corner-linked by two P8O₄ tetrahedra; each two P1O₄ and P5O₄ tetrahedra are branched. These Cu₂(PO₄)₆ groups are intercalated by P7O₄ tetrahedra which are solely linked to Na atoms.

The atoms Cu2 to Cu5 are located on $[0y\frac{1}{4}]$. The Cu₂O₄ and Cu₄O₄ squares (Cu—O = 1.88 - 1.97 Å) are arranged parallel to each other and corner-linked by two P6O₄ tetrahedra to dimers. With four additional phosphate tetrahedra (P2O₄ and P4O₄), Cu₂(PO₄)₆ groups are formed again.

Similarly, the atoms Cu3 and Cu5 are linked by two P3O₄ tetrahedra. These [Cu₃Cu₅(P3O₄)₂] groups are corner linked to the P2O₄ and P4O₄ tetrahedra forming continuous —Cu—(PO₄)₂—Cu—(PO₄)₂— rows with formula [Cu(PO₄)₂(H₂O)]. 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 Cu₃—Op = 1.93 and 2.10 Å, each 2H, Cu—Ow = 2.04 Å; Cu₅—Op = 1.91 and 2.13 Å, each 2H, Cu—Ow = 2.06 Å. Moreover, the two longer Cu₃—O and Cu₅—O bonds are in a *cis*-arrangement. Such five-fold coordination figures are not compatible with the expectations for the surrounding of Cu²⁺ 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

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Acta Cryst. (2011) A67, C724**Copper-carboxylate complexes supported on kegglin polyoxometalates**Aroa Pache, Amaia Iturrospe, Pablo Vitoria, Santiago Reinoso, Luis

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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 α -Keggin polyanions are set by the metalorganic blocks, which contain a copper centre coordinated to two picolinate ligands, [Cu(2-pic)₂], 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.

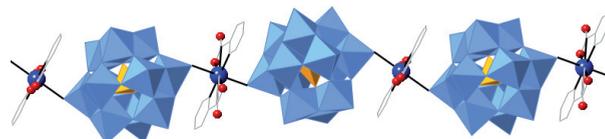


Figure 1: Hybrid chain trough [101] direction.

[1] H.Y. An, E.B. Wang, L. Xu, *Angew. Chem.* **2006**, *118*, 918; L. Lisnard, A. Dolbecq, P. Mialane, *Dalton Trans.* **2005**, 3913. [2] Y. Ishii, Y. Takenaka, K. Konishi, *Angew. Chem., Int. Ed. Eng.* **2004**, *43*, 2702; J.M. Knaust, C. Inman, S.W. Keller, *Chem. Commun.* **2004**, 492. [3] E. Burkholder, V. Golub, C.J. O'Connor, J. Zubietta, *Chem. Commun.* **2003**, 2128. A. Muller, S.Q.N. Shah, H. Bogge, M. Schmidtman, *Nature* **1999**, *48*, 397. A. Dolbecq, E. Dumas, C.R. Mayer, Pierre Mialane, *Chem. Rev.* **2010**, *110*, 6009–6048.

Keywords: polyoxometalate, metalorganic, copper-picolinate

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Acta Cryst. (2011) A67, C724-C725**The novel Krebs-type polyoxometalate $\{[Ni(C_4H_4N_2O_2)(H_2O)]_2(WO_2)_2(\beta-SbW_9O_{33})_2\}^{4-}$**

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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^{III}-

containing polyoxotungstates precludes the closing of the Keggin unit and allows for the formation of many sandwich type structures. Among the well-known class of TM substituted sandwich POMs, Krebs-type polyanions $[M_4(H_2O)_{10}(\beta\text{-SbW}_9\text{O}_{33})_2]^{10-}$ [1] are good candidates for preparing hybrid compounds. Only a few hybrid structures derived from TM bi-substituted Krebs type POMs with a general formula $[(\text{TM-L})_2(\text{WO}_2)_2(\beta\text{-SbW}_9\text{O}_{33})_2]$ [2] (L=organic ligand) have been reported to our knowledge.

Here we report the synthesis, chemical and spectroscopic characterization and X-ray crystal structure of $\text{Na}_4\{[\text{Ni}(\text{L})(\text{H}_2\text{O})]_2(\text{WO}_2)_2(\beta\text{-SbW}_9\text{O}_{33})_2\}^+$ (Figure 1) comprises two $[\text{B-}\beta\text{-SbW}_9\text{O}_{33}]^{9-}$ components joined together *via* two $\{\text{WO}_2\}$ units and two octahedral coordinated Ni(II) ions forming a Krebs-type sandwich. Each Ni(II) ion is bonded to one O atom of one $[\text{B-}\beta\text{-SbW}_9\text{O}_{33}]^{9-}$ moiety and two O atoms of the other one. The coordination sphere is completed by the N, O-donor 4-imidazole carboxylic acid ligand and a water molecule. The crystal packing is built up by discrete molecular hybrid-POMs linked through the coordination sphere of Na cations showing corrugated layers parallel to the (101) plane. This arrangement creates channels along the [001] direction where almost all water molecules are located.

The structure of the polyoxoanion $\{[\text{Ni}(\text{L})(\text{H}_2\text{O})]_2(\text{WO}_2)_2(\beta\text{-SbW}_9\text{O}_{33})_2\}^+$ (Figure 1) comprises two $[\text{B-}\beta\text{-SbW}_9\text{O}_{33}]^{9-}$ components joined together *via* two $\{\text{WO}_2\}$ units and two octahedral coordinated Ni(II) ions forming a Krebs-type sandwich. Each Ni(II) ion is bonded to one O atom of one $[\text{B-}\beta\text{-SbW}_9\text{O}_{33}]^{9-}$ moiety and two O atoms of the other one. The coordination sphere is completed by the N, O-donor 4-imidazole carboxylic acid ligand and a water molecule. The crystal packing is built up by discrete molecular hybrid-POMs linked through the coordination sphere of Na cations showing corrugated layers parallel to the (101) plane. This arrangement creates channels along the [001] direction where almost all water molecules are located.

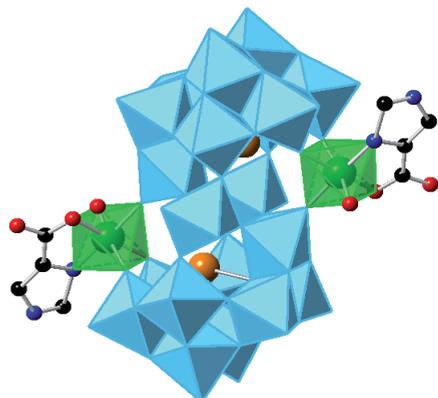


Figure 1. Hybrid POM $[\{\text{Ni}(\text{C}_4\text{H}_4\text{N}_2\text{O}_2)(\text{H}_2\text{O})\}_2(\text{WO}_2)_2(\beta\text{-SbW}_9\text{O}_{33})_2]^+$.

[1] M. Bosing, I. Loose, H. Pohlmann, B. Krebs, *Chemistry, European Journal*, **1997**, *8*, 1232-1237. [2] See for example, A. Dolbecq, J.-D. Compain, P. Mialane, J. Marrot, E. Rivière, F. Sécheresse, *Inorganic Chemistry* **2008**, *47*, 3371-3378.

Keywords: polyoxotungstate, hybrid, antimony.

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Inorganic-metalorganic hybrid compounds based on POMs and Cu-N₂Py₂ complexes

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It has been widely recognized that the polyoxometalates (POMs) exhibit a variety of structures and properties that make them useful in catalysis, material science and medicine [1]. Recently a new advance in the POM chemistry is that a large -number of hybrid compounds with unprecedented structures constructed from the combination of POMs and transition metal coordination complexes (TMCs) have been

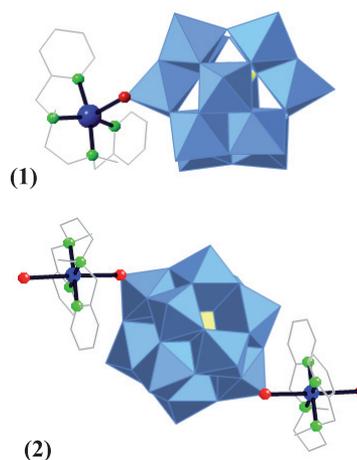
obtained [2]. An intelligent choice of POMs and TMCs may yield materials with fascinating structures and desirable properties.

Currently, we are interested in exploring the applicability of Keggin-POMs and TM-N₂Py₂ complexes in the preparation of new hybrid compounds.

Here we report the synthesis, chemical and spectroscopic characterization, X-ray crystal structure, and magnetic properties of $[\text{Cu}(\text{bpmen})(\text{H}_2\text{O})][\text{SiW}_{12}\text{O}_{40}\{\text{Cu}(\text{bpmen})\}]$ (1) (bpmen: N,N'-Dimethyl-N,N'-bis(2-pyridylmethyl)ethylenediamine) and $[\text{Cu}(\text{bpmpn})(\text{H}_2\text{O})]_2[\text{SiW}_{12}\text{O}_{40}]\cdot\text{H}_2\text{O}$ (2) (bpmpn: N,N'-Dimethyl-N,N'-bis(2-pyridylmethyl)ethylenediamine). The compounds (1) and (2) are prepared by hydrothermal synthesis.

Compound (1) can be viewed as a sequence along the [001] direction of hybrid inorganic-metalorganic corrugated layers built of $[\text{SiW}_{12}\text{O}_{40}\{\text{Cu}(\text{bpmen})\}]$ chains, linked through the apical water molecule of the unsupported $[\text{Cu}(\text{bpmen})]$ and the axial oxygen atoms of supported $[\text{Cu}(\text{bpmen})(\text{H}_2\text{O})]$ complex.

Compound (2) present a 2D arrangement formed by layers parallel to (110) plane built of POMs linked both via copper complexes coordination sphere and water molecules.



[1] D.-L. Long, R. Tsunashima, L. Cronin, *Angew. Chem. Int. Ed.* **2010**, *49*, 2-25. [2] S. Reinoso, P. Vitoria, J.M. Gutiérrez-Zorrilla, L. Lezama, L. San Felices, J.I. Beitia, *Inorg. Chem.* **2005**, *44*, 9731.

Keywords: polyoxometalate, hybrid, tetradentate N₂Py₂ ligands

MS81.P60

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Solid state arrangement of diruthenium tetracarboxylates and tetraamidates

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Diruthenium complexes of the type $[\text{Ru}_2\text{Cl}(\mu\text{-O}_2\text{CR})_4]$ (R = alkyl, aryl) have been intensively studied due to their interesting electronic and magnetic properties [1]. In these complexes, the ruthenium atoms are strongly bonded by four bridging carboxylate ligands, with one axial position occupied by a chloride ion. The chloride ligand of the $[\text{Ru}_2\text{Cl}(\mu\text{-O}_2\text{CR})_4]$ molecule is usually also bonded to the free axial