

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.

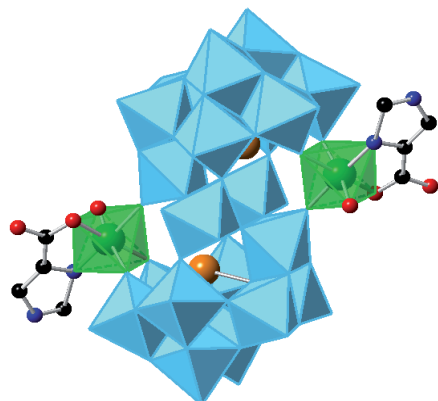


Figure 1. Hybrid POM  $[\{\text{Ni}(\text{C}_4\text{H}_4\text{N}_2\text{O}_2)(\text{H}_2\text{O})\}_2(\text{WO}_2)_2(\beta\text{-SbW}_9\text{O}_{33})_2]^+$ .

[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.

## MS81.P59

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### Inorganic-metalorganic hybrid compounds based on POMs and $\text{Cu-N}_2\text{Py}_2$ 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

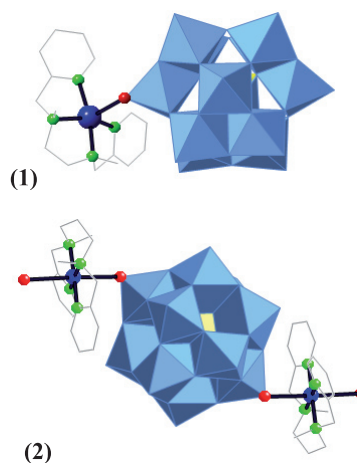
obtained [2]. An intelligent choice of POMs and TMCs may yield materials with fascinating structures and desirable properties.

Currently, we are interested in exploring the applicability of Keggin-POMs and  $\text{TM-N}_2\text{Py}_2$  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:  $\text{N,N}'$ -Dimethyl- $\text{N,N}'$ -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:  $\text{N,N}'$ -Dimethyl- $\text{N,N}'$ -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  $\text{N}_2\text{Py}_2$  ligands

## MS81.P60

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### Solid state arrangement of diruthenium tetracarboxylates and tetraamidates

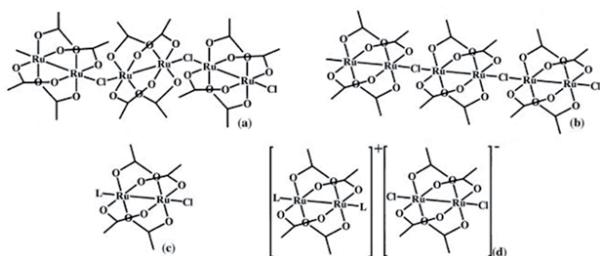
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Diruthenium complexes of the type  $[\text{Ru}_2\text{Cl}(\mu\text{-O}_2\text{CR})_4]$  (R = alkyl, aryl) have been intensively studied due to their interesting electronic and magnetic properties [1]. In these complexes, the ruthenium atoms are strongly 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

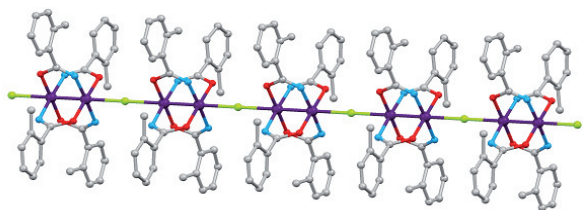
position of an adjacent diruthenium unit leading to zigzag or linear chains. However, a neutral ligand can also coordinate to the free axial position giving rise to discrete dinuclear molecules (Scheme 1).

In the case of the analogous tetraamidate complexes  $[\text{Ru}_2\text{Cl}(\mu\text{-HNOCR})_4]$ , only two crystal structures are known, probably due to the difficulties found in the synthesis processes [2], [4]. These previously reported diruthenium tetraamidate structures are both comprised of zigzag polymeric chains [2], [3].

In this communication, we describe the structural characterisation of several tetra(arylamidate) diruthenium compounds. Two arrangements have been observed in these complexes: zigzag and linear chains. Among the new structural types, we present the first example of a linear diruthenium tetraamidate polymeric chain (Figure 1), and we also study the influence of the aryl ring substituents in the linearity of the chain.



**Scheme 1.** Arrangements observed in diruthenium tetracarboxylate complexes: (a) zigzag chains, (b) linear chains, (c) discrete molecules, and (d) cation/anion species.



**Figure 1.** Linear polymeric chain of  $\text{Ru}_2\text{Cl}(\mu\text{-HNOCR})_4$ .

[1] F.A. Cotton, C.A. Murillo, R.A. Walton, *Multiple Bonds between Metal Atoms*, **2005**. [2] A.R. Chakravarty, F.A. Cotton, D.A. Tocher, *Polyhedron* **1985**, *4*, 1097. [3] A.R. Chakravarty, F.A. Cotton, *Polyhedron* **1985**, *4*, 1957. [4] M.C. Barral, I. de la Fuente, R. Jiménez-Aparicio, J.L. Priego, M.R. Torres, F.A. Urbanos, *Polyhedron* **2001**, *20*, 2537.

**Keywords:** ruthenium, carboxylate, amidate

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### Synthesis and structural study of photoluminescent lanthanide-organic frameworks

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During the last few decades, worldwide researchers have been devoting significant efforts towards the design, synthesis and characterization of new multi-dimensional Coordination Polymers, also

known as Metal-Organic Frameworks (MOFs). These compounds have been extensively studied for gas storage and separation, ion exchange, in optical sensors, catalysis, among several others [1].

Our research group has been interested in the construction of Lanthanide-Organic Frameworks (LnOFs) using phosphonate ligands and various lanthanide centers [2]. In this communication we report the synthesis and structural characterization of micro- and nano-sized LnOFs obtained using distinct synthetic approaches (hydrothermal, ultrasonic- and microwave-assisted synthesis). Crystalline and phase-pure  $[\text{Ln}(\text{Hpmd})(\text{H}_2\text{O})]$  materials [where  $\text{Ln}^{3+} = \text{Eu}^{3+}$  (**1**),  $\text{Tb}^{3+}$  (**2**),  $(\text{Tb}_{0.95}\text{Eu}_{0.05})^{3+}$  (**3**);  $\text{H}_4\text{pmd} = 1,4\text{-phenylenebis(methylene)diphosphonic acid}$ ] were fully studied and characterized by standard solid-state techniques and their structures unveiled by powder X-ray diffraction.

All prepared LnOFs exhibit similar structural features to the previously reported  $[\text{Ce}(\text{Hpmd})(\text{H}_2\text{O})]$  and  $[\text{Pr}(\text{Hpmd})(\text{H}_2\text{O})]$  compounds [3]. Compound **1** has a single  $\text{Eu}^{3+}$  site coordinated to one water molecule and to five phosphonate groups, overall describing a  $\{\text{EuO}_7\}$  seven-coordination environment resembling a significantly distorted monocapped trigonal prism. The two independent phosphonate moieties promote the formation of lanthanide dimers with  $\text{Eu}\cdots\text{Eu}$  intermetallic distances of 4.05 Å. This terminal group also connects adjacent dimers along the [010] direction of the unit cell, leading to the formation of a 1D zigzag array. Bridges between this array are ensured by strong  $\text{O}\cdots\text{H}\cdots\text{O}$  hydrogen bonds involving the hydrogenophosphate and the coordinated water molecule. This arrangement of supramolecular interactions promotes structural cohesion within the inorganic lanthanide (hydrogeno)phosphonate layer. Connections between adjacent layers are ensured by the  $\text{Hpmd}^{3-}$  organic linkers leading to an alternation along the *c*-axis of organic and inorganic fragments. All compounds exhibit intense photoluminescence under UV excitation.

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**Keywords:** lanthanide-organic frameworks, phosphonates, photoluminescence

## MS81.P62

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### Synthesis, crystal structure and thermal decomposition of $\text{NaSc}_3[\text{HPO}_3]_2[\text{HPO}_2(\text{OH})]_6$

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$\text{NaSc}_3[\text{HPO}_3]_2[\text{HPO}_2(\text{OH})]_6$  was prepared by use of a phosphorous acid flux route ( $\text{H}_3\text{PO}_3$ , mp: 73.6 °C).[1] The crystal structure was determined from single-crystal X-ray diffraction data: triclinic, space group  $\bar{P}1$  (No. 2),  $a = 7.4507(11)$  Å,  $b = 9.6253(17)$  Å,  $c = 9.6141(16)$  Å,  $\alpha = 115.798(4)^\circ$ ,  $\beta = 101.395(4)^\circ$ ,  $\gamma = 101.136(3)^\circ$ ,  $V = 577.29(16)$  Å<sup>3</sup> and  $Z = 1$ . The crystal structure of  $\text{NaSc}_3[\text{HPO}_3]_2[\text{HPO}_2(\text{OH})]_6$  contains two kinds of phosphate(III) groups:  $\text{HPO}_3^{2-}$  and  $\text{HPO}_2(\text{OH})^-$ .