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 polyoxocations \( [M(H_2O)_3]^{2+}(\beta-SbW_12O_40)] \) are good candidates for preparing hybrid compounds. Only a few hybrid structures derived from TM bi-substituted Krebs type POMs with a general formula \((TM-L_2)\beta-SbW_12O_40\) have been reported to our knowledge.

Here we report the synthesis, chemical and spectroscopic characterization and X-ray crystal structure of \( Na_4\{[Ni(L)(H_2O)]\beta-SbW_12O_40\}\) (Figure 1) comprising two \([\beta-SbW_12O_40]\) components joined together via two \([WO_4]\) 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 \([\beta-SbW_12O_40]\) 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 \( \{[Ni(C_4H_4N_2O_2)(H_2O)]\beta-SbW_12O_40\} \).**


**Keywords: polyoxometalate, hybrid, tetradeutate N2Py2 ligands**

**MS81.P59**


**Inorganic-metalorganic hybrid compounds based on POMs and Cu-N-Py 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-NPy 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 \([Cu(bpmpn)(H_2O)][SiW_12O_40][Cu(bpmpn)]\) \((1)\) (bpmpn: N,N'-Dimethyl-N,N'-bis(2-pyridylimethyl)ethylendiamine and \([Cu(bpmpn)(H_2O)],[SiW_12O_40]H_2O\) \((2)\) (bpmpn: N,N'-Dimethyl-N,N'-bis(2-pyridylimethyl)ethylendiamine). 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 \([SiW_12O_40][Cu(bpmpn)]\) chains, linked through the apical water molecule of the unsupported \([Cu(bpmpn)]\) and the axial oxygen atoms of supported \([Cu(bpmpn)(H_2O)]\) 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.

**Keywords: polyoxotungstate, hybrid, antimony.**

**MS81.P60**


**Solid state arrangement of diruthenium tetracarboxylates and tetraamidates**

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Diruthenium complexes of the type \([Ru_2Cl_2(p-O-CR)](R = alkyl, aryl)\) 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 \([Ru_2Cl_2(p-O-CR)]\) 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 tetramidate complexes [Ru₂Cl₂(μ-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(arylaminate) 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.

Figure 1. Linear polymeric chain of Ru₂Cl₂(μ-HNOCR)₄.

Keywords: ruthenium, carboxylate, amidate

MS81.P61

Synthesis and structural study of photoluminescent lanthanide-organic frameworks.


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 characterisation of micro- and nano-sized LnOFs obtained using distinct synthetic approaches (hydrothermal, ultrasonic- and microwave-assisted synthesis). Crystalline and phase-pure [Ln(Hpmd)(H₂O)] materials [where Ln⁺ = Eu⁺, Tb⁺, Tb⁺(2), (Tb₀,Er⁺)³⁺ (3); H₄pmd = 1,4-phenilenbis(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 [Ce(Hpmd)(H₂O)] and [Pr(Hpmd)(H₂O)] compounds [3]. Compound I has a single Eu⁺ site coordinated to one water molecule and to five phosphate groups, overall describing a {EuO₄} seven-coordination environment resembling a significantly distorted monocapped trigonal prism. The two independent phosphonate moieties promote the formation of lanthanide dimers with Eu–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 bridge. Bridges between this array are ensured by strong O–H–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 Hpmd⁻-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

Synthesis, crystal structure and thermal decomposition of NaSc₃[HPO₄]₀.₃[HPO₄(OH)]₄.

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NaSc₃[HPO₄]₀.₃[HPO₄(OH)]₄ was prepared by use of a phosphorous acid flux route (H₂PO₄, mp: 73.6 °C).[1] The crystal structure was determined from single-crystal X-ray diffraction data: triclinic, space group P1 (No. 2), a = 7.4507(1) Å, b = 9.6253(17) Å, c = 9.6141(16) Å, α = 115.798(4)°, β = 101.395(3)°, γ = 101.136(3)°, V = 577.29(16) Å³ and Z = 1. The crystal structure of NaSc₃[HPO₄]₀.₃[HPO₄(OH)]₄ contains two kinds of phosphate(III) groups: HPO₄²⁻ and HPO₄(OH)⁻.

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