

Poster Sessions

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Organic-inorganic hybrids constitute an important class of compounds in the exploratory research area of advanced materials design. In this connection, metal phosphonates represent a particularly versatile field for investigation because of the great latitude open to the investigator. During the past two decades a lot of research attention has been devoted to the chemistry of metal phosphonates for their potential applications in ion exchange, catalysis, and in sensor devices [1-5]. The wide choice of metals and the variety of organic ligands, and since that almost any desired organic compound may be converted into a phosphonic acid by known reactions, it is thus possible to introduce phosphonate ligands with different functional groups into the hybrid structures, which suggests the possibility of rational design of structures for highly specific function, and even with unusual properties. Recently, investigations of di-, tri-, and tetra-valent metal phosphonates have yielded exciting structural diversity with interesting chemistries and applications, including porous pillared layered structures [6, 7]. However, reports on the structure and photoluminescence properties of lanthanide (Ln) arylphosphonates or aryldiphosphonates are scarce [8, 9].

Herien, we present a series of novel organic-inorganic hybrids based on trivalent lanthanide (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho) and 1,4-phenylbis(phosphonate) formulated as $\text{Ln}[\text{O}_3\text{P}(\text{C}_6\text{H}_4)\text{PO}_3\text{H}]$ and obtained as single phases under hydrothermal conditions either by oven or microwave heat. In the praseodymium compound (Za1) single crystals have been obtained and the crystal structure determined. Za1 crystallize in monoclinic space group, C2/c, with $a = 5.6060(4) \text{ \AA}$, $b = 20.251(7) \text{ \AA}$, $c = 8.2740(6) \text{ \AA}$, $\beta = 108.52(1)^\circ$. All other compounds are isostructural to Za1 as confirmed by Rietveld refinement by using X-ray powder diffraction data. Compounds are characterized by thermal analyses (TG-MS and SDTA), elemental analysis, IR spectra, and X-ray thermodiffraction analysis. These series of compounds exhibit an unusual very high thermal stability. Eu- and Tb-based compounds exhibit, respectively, strong red and green emissions.

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Keywords: lanthanide, phosphonate, MOFs, luminescence.

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Novel 3D Fluorinated-MOFs: Structure, topology and magnetic properties

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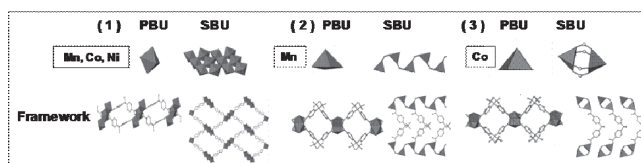
The metal-organic frameworks (MOFs) are a class of materials that are constantly attracting significant attention not only for their potential applications as functional crystalline materials, but also for their fascinating topologies and structural diversity [1]. The use of flexible and extended ligands contributes to the development of porous frameworks with diverse structural topologies, which, in turn, can lead to obtain varied properties even for the same constitutive units. On the other hand, the magnetic behavior of MOFs, which extended inorganic networks or local paramagnetic centers are linked by diamagnetic linkers that can efficiently mediate magnetic exchange, have evoked considerable interest [2]. However, in MOFs, the magnetism may be introduced through the incorporation of magnetic moment carriers such as paramagnetic metals, or open-shell organic ligands, or both [3].

In this way, we decided to proceed our studies obtaining Fluorinated Metal Organic Frameworks (F-MOFs) constructed of the flexible 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) (H_2hfipbb) as ligand and transition metal ions {Mn(II), Co(II) and Ni(II)}, in order to induce interesting magnetic properties. Besides, we have explored several synthesis conditions to expand the possibilities to get diverse crystal topologies expecting different magnetic properties.

Three novel compounds (1a-c) with formula $[\text{M}_3(\text{hfipbb})_2(\text{OH})_2(\text{H}_2\text{O})]$, M = Mn, Co, Ni has been hydrothermally synthesized and completely characterized. The compound 1a's structure corresponding to the P2₁/c space group, has been determined by single crystal synchrotron XRD at the ESRF- BM16 beam line, while for compounds 1b and 1c powder diffraction methods were applied in order to obtain both cell parameters and the space groups. Such study indicated the isostructural character of compounds 1a-c. Besides, another two compounds with formula $[\text{M}_2(\text{hfipbb})_2(\text{H}_2\text{hfipbb})]$, M = Mn (2) and Co (3), were hydrothermally obtained at different synthesis conditions and their structures, corresponding to the C2/c and P2₁/n space groups, respectively, were determined by conventional single crystal XRD data.

Magnetic behavior of compounds 1a-c and 3 has been studied and such results indicate that compounds 1a and 3 have antiferromagnetic interactions while 1b and 1c are ferromagnetics.

The topological study of 2 and 3, having the same composition but different crystal structure has also been performed.



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Keywords: F-MOFs, magnetic properties, crystal engineering

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Lanthanide-organic frameworks of Bis-Gd complexes: composed by carbonate ions spacers

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A new lanthanide-organic framework (LOF) based on a long (21.2Å) and rigid bid-Gd complex synthon (complex 1) and carbonate anion spacers was discovered. Complex 1 is comprised of two Gd³⁺ ions complexed with a pyridine tetracarboxylate ligand and a bridging linear 1,4-diethynylbenzene unit. Two water molecules are coordinated to each Gd ion in order to satisfy its high coordination number. Carbonate anions are coordinated to the Gd³⁺ ions linking between two synthons, resulting in the construction of two network types (type A and B). All three oxygen atoms of the carbonate anion are utilized in its function as a spacer between two synthons (complex 1) in the networks. In addition, the carbonate anions also serve as acceptors for hydrogen bonding (O-H...O), with water molecules coordinated to Gd³⁺ ions in both the networks. While all the synthons adopt a planar conformation in network A, they are backed alternately in plane and vertical conformation in network B. Auxiliary Na⁺ ions and water molecules are positioned around the carbonate ions and connect between the networks. Overall, in this new LOF the synthons are packed in criss-cross fashion and tethered by carbonate spacers, creating a crystal lattice perforated by 10.6 × 15.6Å and 18.6 × 15.6Å wide-open channels.

Keywords: supramolecular assembly, gadolinium complexes, crystal design.

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Synthesis and Crystal Structure of a Two-Dimensional Di-Aqua Pyromellitate Strontium(II) Complex: [Sr₂{(OOC)₂-C₆H₂(COOH)₂}(H₂O)₂]_n

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In recent years, metal-organic coordination polymers have attracted considerable attention and been rapidly developed due to their fascinating molecular topologies and crystal-packing motifs along with potential applications as smart optoelectronic, magnetic, and porous materials[1–2]. These specific features are due to the carboxylate group which acts as a linker between inorganic moieties and to the flexible or relatively rigid carbon backbone, which gives a modular nature to the resulting MOFs[3-5]. Most of the bridging ligands used in construction of the porous MOFs are rigid such as benzene-polycarboxylate. Benzene-1,2,4,5-tetracarboxylic acid (H₄BTC) is an important carboxylate ligand as it has multiple coordinating modes. Moreover, the various coordination geometry of metal ions and the four carboxylic groups of (H₄BTC) completely or partially deprotonated, have led to the generation of products containing 1D chains, 2D layers and three-dimensional packings[7].

We report here the synthesis and structure of a novel alkaline-earth metal benzene-tetracarboxylate complex [Sr₂{(OOC)₂-C₆H₂(COOH)₂}(H₂O)₂]_n. The asymmetric unit consists of two Sr(II) cations, two pyromellitate dianions (H₂BTC)²⁻ and two aqua ligands. The two independent [H₂BTC]²⁻ ligands adopt different coordination mode. They are heptadentate and octadentate and coordinate to five and six metals centers respectively. The coordination polyhedra around

the two Sr atoms can be described as a distorted monocapped square antiprism and a distorted dodecahedron respectively. Among all the nine coordinated oxygen atoms, one come from one coordinated water molecule and the remaining from six [H₂BTC]²⁻ dianions ligands while the eight oxygen atoms around the second metal center belong to one coordinated water molecule and five [H₂BTC]²⁻ dianions ligands.

Each strontium atom is linked to two Sr metals through μ_{oxo} bridges leading to the formation of an infinite zigzag chains of one-edge sharing SrO₉/SrO₈ polyhedra. The chain running parallel to the a axis are further connected through pyromellitate ligands resulting in a two-dimensional network. The crystal structure is further stabilized by hydrogen bonds between chains, involving the four acid groups and the two coordination water molecules as donors.

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Synthesis and structural study at 100K of a new double metal oxalate Cs₂Cr(C₂O₄)₂(H₂O)₄

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In the course of our studies dealing with oxalate-based bimetallic compounds potentially leading to Metal-organic-frameworks (MOFs) and Coordination polymers (CPs), we have obtained single crystals of [M_xCr(C₂O₄)₂(H₂O)_y]_n. When M=Rb⁺, a new supramolecular isomer RbCr(C₂O₄)₂(H₂O)₂]_n has revealed a 3D extended framework built up from layers containing bi-polyedra surrounding Rb and Cr respectively [1].

This structure is completely different from the previously known^[2]. When M=Cs⁺, and replacing RbCl by a caesium salt in the same synthesis conditions and mixture, including a Cr³⁺ starting salt, few pink prismatic crystals studied by XRD at 100K, brought out a polymeric structure corresponding to a tetraaqua complex, with x=2, owing to the fact that the transition metal has been reduced during synthesis process leading to the unexpected dication Cr²⁺.

This poly[tetraaquad-μ₆-oxalato]chromium(II)dicaesium(I)] is isotypic with Cs₂M(C₂O₄)₂.4H₂O (M=Mg(II); Co(II)) [3], [4]. It belongs to C2/c space group, with a=16.1880(4)Å; b=7.3212(2)Å; c=13.5268(3)Å; β=128.3640(10)°.

The asymmetric unit contains one unique Cs atom, one Cr atom, one oxalate dianion and two water molecules. Only the Cr(II) atom is located on a special position (O y ¼). The nine-coordinated caesium atom is surrounded by six oxalate ligands involving all their donor atoms. One O atom of each functional group chelates to the central alkali in a typical five-membered ring. The coordination sphere is completed by the two independent water molecules. The nearly regular CrO₄(H₂O)₂ octahedron consists of four O atoms from two dianions in a η⁴-chelation and two O atoms from two equivalent water molecules in *cis* position. Consequently, the oxalato ligand is bis-bidentate,