

P.09.03.12*Acta Cryst.* (2005). A61, C358**Characterization of a Novel Quaternary Dielectric Crystallographic Family**Ricardo Rodríguez-Mijangos, *Centro de Investigación en Física, Universidad de Sonora. A. P. 5-88., Hermosillo, Sonora, México.* E-mail: mijangos@cajeme.cifus.uson.mx.

In this work is reported the growth and characterization of a novel family of alkali halide crystals, produced for the mixing of four ionic salts. These quaternary crystals imply the existence of four ternary crystals [1] and six known binary crystals. The characterization is applied to two crystals with different component concentration, one of these with a Europium impurity. It was obtained the lattice constant by X ray diffractometry. The optical absorption spectra of irradiated crystals shown a single F band. The Generalized Vegard's law, applied to the novel ternary system recently studied [2], was extended to the quaternary crystal. Good agreement with the experimental results was obtained.

[1] Mijangos R. R., Cordero-Borboa A., Camarillo E., Riveros H., Castaño V., *Physics Letters A*, 1998, **245**, 123. [2] Mijangos R. R., Cordero-Borboa A., Alvarez E., Cervantes M., *Physics Letters A*, 2001, **282**, 512.

Keywords: solid solutions, accurate lattice parameters measurements, absorption spectroscopy experimental

P.09.03.13*Acta Cryst.* (2005). A61, C358**Co(II) *n*-alkyl Phosphonates: Examples of Hybrid Organic-inorganic Compounds**

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Organic-inorganic hybrids like metal alkyl phosphonates are very flexible systems because of the possibility of designing the organic moiety [1]. In this work we present our studies on the synthesis and single crystal structure determination of two new Co(II) *n*-alkyl phosphonates, i.e. Co(II) *methyl*-phosphonate, Co[(CH₃PO₃)(H₂O)], and Co(II) *ethyl*-phosphonate, Co[(C₂H₅PO₃)(H₂O)]. Cobalt(II) *methyl*-phosphonate, crystallizes in the orthorhombic space group *Pna*2₁ with *a*=17.408(6)Å, *b*=4.790(3)Å, *c*=5.652(1)Å. Cobalt(II) *ethyl*-phosphonate crystallizes in the monoclinic space group *Pn*, with the following unit-cell parameters: *a*=4.806(2)Å, *b*=10.243(3)Å, *c*=5.674(1)Å and β=90.56(3)°. An hybrid layered structure made of alternation of inorganic and organic layers was found for both Co alkyl phosphonates. In both cases the inorganic layer is based on distorted [CoO₆] chromophores with five oxygens from the [PO₃]²⁻ group and one from the water molecule. The organic layer is composed by the alkyl groups of the adjacent ligands with van der Waals contacts between them.

[1] See for example "Functional Hybrid Materials" P. Gomez-Romero & C. Sanchez Eds., Wiley&VCH, 2004.

Keywords: crystal engineering, organic hybrid materials, metal phosphonates

P.09.04.1*Acta Cryst.* (2005). A61, C358**Crystal Packing in Co(II) Pyromellitate Complexes tuning the Water Aggregation**

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Three different polymeric complexes were designed and synthesized from Co(II) and 1,2,4,5-benzenetetracarboxylic acid (H4-

bt). These complexes exhibit a zeolite-like structure; which cavities are suitable to host water molecules. The dimensionality and crystal packing depend on the syntheses methods. Closer packed structures are obtained from gels to hydrothermal method synthesis.

The clusters of water play an important role in the stabilization of supramolecular systems [1], their structural study is important for understanding the behavior of biological systems. A great number of metal-organic frameworks (MOF) have been reported to accommodate clusters and chains of water [2]. We present herein three cobalt(II) MOF's where the crystal packing controls and templates the formation of different kinds of water aggregation (discrete clusters or nanowires).

Stabilization of guest molecules is due to weak directional intermolecular forces such as hydrogen bonds. Special attention has been paid to these interactions for understanding the anchoring between host-guest molecules.

[1] Ludwig R., *Angew. Chem. Int.*, 2001, **40**, 1808-1827. [2] Yaghi O. M., O'keeffe M., Ockwig N.W., Chae H. D., Eddaoudi M., Kim J., *Nature*, 2003, **432**, 705-714.

Keywords: hydrothermal method, gels, water structure

P.09.04.2*Acta Cryst.* (2005). A61, C358**Alkali-Templated Malonate Copper(II) Complexes**

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In the context of our copper(II) malonate complexes studies [1,2], we have synthesized and characterized the compounds of formula {[A(H₂O)_n]₂[Cu(mal)₂(H₂O)_m]} (A = Li, Na, K, Rb, Cs).

The structure of these compounds consists of [Cu(mal)₂(H₂O)_m]²⁻ anions and [A(H₂O)_n]⁺ cations that are held together by means of carboxylate bridges and water molecules leading to three-dimensional networks.

We want to show how the size of alkali metal ion can control the malonate-bridged copper(II) structure, so we have analyzed the networks that both cationic and anionic units build up.

First, the [A(H₂O)_n]⁺ units are connected through μ-oxo bridges affording thus, different cationic structures: dimmers (Li), single chains (Na, K), double helical chains (Rb) and layers (Cs).

Depending on the alkali metal ion the [Cu(mal)₂(H₂O)_m]²⁻ units are linked to other ones through malonate carboxylate bridges to give anionic networks exhibiting different topologies: monomers (Li, Cs), chains (Rb) and layers (Na, K).

We have also studied the magnetic properties of these compounds. The behaviour being ferromagnetic when the copper(II) units are connected through *anti-anti* carboxylate bridges (Na, K, Rb).

[1] Pasán J., Delgado F.S., Rodríguez-Martín Y., Ruiz-Pérez C., Sanchiz J., Lloret F., Julve M., *Polyhedron*, 2003, **22**, 2143. [2] Delgado F.S., Ruiz-Pérez C., Sanchiz J., Lloret F., Julve M., *Cryst.Eng.Comm.*, 2004, **6**, 443.

Keywords: carboxylic acids, alkali metal anionic salts, crystal engineering

P.09.04.3*Acta Cryst.* (2005). A61, C358-C359**(4,4)-Metal-Organic Framework Templated by 1,2,3,4-Butanetetracarboxylic Acid**

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The design or selection of a suitable ligand containing certain features, such as flexibility, versatile binding modes and ability to form hydrogen bonds are crucial in the building of polymeric complexes. In this line we have chosen a new ligand, known as 1,2,3,4-butanetetracarboxylic acid, which possesses several

interesting characteristics: (a) it has four carboxyl groups that after partial or full deprotonation, can be coordinated to the metal ions in a wide variety of coordination modes leading to high dimensional structures; (b) it can act not only as hydrogen-bond acceptor but also as hydrogen-bond donor, depending upon the number of deprotonated carboxylic groups; (c) its carboxylic groups may not lie in the same plane upon complexation to metal ions owing to geometrical constraints and thus, the ligand may connect metal ions in different directions; (d) finally, its conformation without any phenyl ring gives new possibilities of torsion angles in the structure. All these characteristics make the ligand an excellent candidate to build three-dimensional architectures.

Herein we report the synthesis and X-ray structure of several novel complexes with 1,2,3,4-butanetetracarboxylic acid $[M_2(\text{but})(\text{H}_2\text{O})_5] \cdot x\text{H}_2\text{O}$ with $M =$ Transition metals.

Keywords: synthesis and characterization of coordination compounds, carboxylic acids, crystal engineering

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Supramolecular Isomerism of Three Dimensional 3-connected Coordination Polymers

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Polymorphism and supramolecular isomerism are widely encountered in the crystalline compounds. However, most coordination complexes referred to these concepts contain different guest/solvent molecules. No example has been reported to have supramolecular isomerism in the context of the 3-connected topologies.[1] We have developed a straightforward construction strategy for 3-connected coordination networks.[2] We have also just successfully designed and synthesized four novel supramolecular isomers based on low-dimensional coordination compounds.[3] Here we report three supramolecular isomers based on binary Cu^I 3,5-dimethyl-1,2,4-triazolate (\hat{a} , \hat{a} , \hat{a}) isolated from different solvothermal conditions. The topologies of \hat{a} , \hat{a} , and \hat{a} can be rationalized to be $8^2 10$ - a , $4.8.16$, 6.10^2 , respectively.[2] It should be noted that the 3-connected $4.8.16$ and 6.10^2 nets can also be simplified as 4-connected $4^2 8^4$ and 6-connected \hat{a} -Po nets, respectively. The three isomers also display different photoluminescence properties.

[1] Moulton B., Zaworotko M. J., *Chem. Rev.*, 2001, **101**, 1629. [2] Zhang J.-P., Zheng S.-L., Huang X.-C., Chen X.-M., *Angew. Chem. Int. Ed.*, 2004, **43**, 206. [3] Zhang J.-P., Lin Y.-Y., Huang X.-C., Chen X.-M., *Chem. Commun.*, 2005, doi:10.1039/b416095a.

Keywords: coordination polymers, supramolecular isomerism, network topology

P.09.04.5

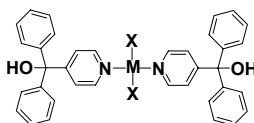
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Novel Organometallic Molecular Building Blocks for Crystal Engineering

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Triphenylmethanol (TPM) and its derivatives, for example 4,4'-bis(biphenylhydroxymethyl)biphenyl (DHMB), form chalcate compounds in the solid state [1]. Their crystal structures are usually assembled through host-host $-\text{OH} \cdots \text{HO}-$ or through host-guest $-\text{OH} \cdots \text{X}$ interactions[2].

Our current work is addressed to the engineering of crystalline systems combining TPMs interlinked by metal centres structured in porous frameworks, potentially able of hosting small guests. Our approach to the rational design of such architectures is based on the molecular tectonics method, in which the crystal structure is deconvoluted into the contributions of the single inorganic and organic building blocks, which are separately analyzed and optimized. The first step in the modeling of such systems consists in the introduction of a transition



metal as bridge between two aromatic rings. The model ligand studied is α -(4-pyridyl)benzhydrol (LOH), which combines both the molecular structure of TPMs and the coordinating pyridine functionality. In this work we describe the solid-state organization of $[\text{M}(\text{LOH})_2\text{X}_2]$ (M : Pd, Pt, Cu, Zn, $X =$ halide, acetate) and we correlate the supramolecular arrangement of the organic-inorganic matrix to the stereochemical attitudes of the inorganic component.

[1] Toda F., *Comprehensive supramolecular chemistry*, 6, cap.15. [2] Weber E., Skobridis K., Goldberg I., *Chem. Comm.*, 1989, 1195.

Keywords: crystal engineering, coordination compounds, wheel-and-axle

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Constitutional Dynamic Self-Amplification in Double-Helix Imine Systems

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Constitutional dynamic chemistry [1,2] expresses adaptative behaviour as its entities are in principle capable of responding to external effectors via reorganization/amplification of their constitution through reversible covalent bonds in order to generate a dynamic functional diversity.

We will present here the ability of a set of imine-metal complexes to undergo such a process in response to the effect of external factors which promote both ligand and imine exchange in order to drive to a constitutional evolution of dynamic mixture toward the selection and amplification of specific components.

From a conceptual point of view these results express a synergistic adaptative strategy for a evolutive generation of crystalline functional devices. Moreover, the self-assembling behaviour of these systems leads to tubular double-helix solid state structures [3]. Different superstructures of this type could be generated by selection and amplification and they will be discussed in detail.

[1] Lehn J.-M., *Proc. Natl. Acad. Sci.*, 2002, **99**, 4763-4768. [2] Barboiu M., Vaughan G., Graff R., Lehn J.-M., *J. Am. Chem. Soc.*, 2003, **125**, 10257-10265. [3] Dumitru F., Legrand Y.-M., Barboiu M., van der Lee A., 2005, *in press*.

Keywords: crystal engineering, crystallography, structure

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Trisiloxane-Diols and Cyclosiloxanes with Bulky Substituents on the Si Atoms

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A series of siloxane compounds have been synthesized as monomers for the preparation of polymers used as polarisable stationary phases for capillary chromatography [1]. Four trisiloxane-1,5 diols (with different organic substituents on the Si atoms, $\text{R}_1 = 2$ -methoxybenzene and $\text{R}_2 = 2,6$ -dimethoxybenzene), have been found to have different configurations of the O-Si-O-Si-O-Si-O skeleton. In the crystal structure they are linked to one another by different types of hydrogen bonding. The terminal Si-O distances are significantly longer than the central Si-O distances as reported previously for similar compounds [2].

In a series of cyclosiloxane molecules, containing 3 to 5 SiO units and different organic substituents on the Si atoms (Me , Ph , R_1 , R_2 and $\text{R}_3 = 2,4,6$ -trimethoxybenzene), it has been shown that the Si-O bond distances and packing of the molecules in the crystal structures are very different, depending on the size of the ring. These features will be discussed in relation to the formation of the polymers.

[1] Monziane M., *PhD thesis*, Université de Neuchâtel, 1995. [2] Graalman O., Klingebiel U., Clegg W. *Chem. Ber.*, 1984, **117**, 2988.

Keywords: crystal structure, hydrogen bonding, polymers