

**MS16 P03**

**Expansion of the NASICON-type framework: from metal-sulfates to cluster-zinc cyanides** Pierre Graveriau, ICMCB-CNRS, University of Bordeaux, Pessac, France. E-mail: [graver@icmcb-bordeaux.cnrs.fr](mailto:graver@icmcb-bordeaux.cnrs.fr)

**Keywords:** NASICON-type framework, cell volume expansion, functional solid materials

Physical properties of compounds are strongly related to crystal structures and for a 3D host-framework they can vary widely with lattice expansion. For the NASICON (Na Super Ionic CONductor\*) -type skeleton a strong evolution of the cell volume from  $\sim 1200 \text{ \AA}^3$  (metal sulphate\*) to  $\sim 12550 \text{ \AA}^3$  ((Re<sub>6</sub>Se<sub>8</sub>)cluster-zinc cyanides\*) can be observed.

NASICON-3D framework consists of (AX<sub>6</sub>) octahedra and (BX<sub>4</sub>) tetrahedra sharing corners, leading to general formula A<sub>2</sub>B<sub>3</sub>X<sub>12</sub>. It can be also described with structural units of 2 octahedra linked by 3 tetrahedra. In NASICON-type all these structural units have similar direction. The highest symmetry found is with space group R $\bar{3}c$  and structural units direction is **c** axis.

If **X = O**, the general formula of the framework becomes A<sub>2</sub>(BO<sub>4</sub>)<sub>3</sub>: A is metal or rare-earth and B can be S, P, (Si,P), Si, As, Ge, Mo. If necessary, additional cations could be inserted so to ensure the global electrical neutrality. The usual interstitial sites are labelled M(1) or M(2). Depending on these additional cations and on the relative A-O and X-O lengths, NASICON-structure can be also obtained in subgroups of R $\bar{3}c$ : R3c, R32, R $\bar{3}$ , P $\bar{3}$ , C2/c. For these compounds, expansion of the cell volume goes from  $\sim 1193 \text{ \AA}^3$  (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>; R $\bar{3}$ ) to  $\sim 1894 \text{ \AA}^3$  (K<sub>0.52</sub>(Mn<sub>0.47</sub>Zr<sub>0.45</sub>)(MoO<sub>4</sub>)<sub>3</sub>; R $\bar{3}c$ ).

If **X = C-N group**, the general formula of framework becomes (AC<sub>6</sub>)<sub>2</sub>(BN<sub>4</sub>)<sub>3</sub> or B<sub>3</sub>[A(CN)<sub>6</sub>]<sub>2</sub>. In known examples A can be Fe or (Re<sub>6</sub>Se<sub>8</sub>)-cluster and B is Zn. Here also electrical neutrality can be assumed by additional cations and the expansion is so important that these compounds present zeolitic properties with inserted neutral molecules as H<sub>2</sub>O or other gases. In these cases, expansion of the cell volume goes from  $\sim 4433 \text{ \AA}^3$  (Na<sub>2</sub>Zn<sub>3</sub>[Fe(CN)<sub>6</sub>]<sub>2</sub>·9H<sub>2</sub>O; R $\bar{3}c$ ) to  $\sim 12552 \text{ \AA}^3$  (Na<sub>2</sub>Zn<sub>3</sub>[(Re<sub>6</sub>Se<sub>8</sub>)(CN)<sub>6</sub>]<sub>2</sub>·24H<sub>2</sub>O; R $\bar{3}c$ ).

The poster presents a bibliographic review\* and an illustration of this NASICON-type framework expansion. Beside the cristallochemistry point of view, another interest consists in the prospect for tailoring functional solid materials.

[\*] list of principal references will be provided during poster session

**MS16 P04**

**The dihydrogen-malonato- $\mu$ -3-calcium (II): A supramolecular framework constructed from binuclear entities** <sup>(1)</sup>Guehria-Laidoudi A., <sup>(1)</sup>Aliouane K., <sup>(1)</sup>Rahahlia N., <sup>(2)</sup>Dahaoui S. and <sup>(2)</sup>Lecomte C. <sup>a</sup>Laboratoire de cristallographie appliquée, Institut de Chimie, U.S.T.H.B., B.P. 32, El-Alia 16111, Bab-Ezzouar, Alger, ALGERIE. <sup>b</sup>LCM<sup>3</sup>B-CNRS UMR 7036, Faculté des Sciences Université Henri Poincaré BP 239, 54506 Vandoeuvre-lès-Nancy, France

**Keywords:** polymeric structure, earth-alkaline, dicarboxylate

New generation of metal-organic coordination polymers have emerged in last years, enhancing the field of supramolecular chemistry. The anions stemming from malonic acid are the most flexible ligands for building supramolecular framework. Moreover, if the connector is the calcium cation, the resulting model complex is designed to permit the significance of interactions tacking place in biological systems [1, 2]. The title compound is one of the few hydrogen malonate complexes involving alkaline-earth metals [3]. It has been prepared under hydrothermal conditions, in single crystal form. Four  $\mu$ -1,1 oxo-bridges link two crystallographically equivalent Ca cations and construct a basic binuclear building block. The distance within this cage assembly is very short (3.626(9)) $\text{\AA}$ . The unique independent ligand is tridentate, involves all its deprotonated oxygen atoms in the coordination to the metal and displays an  $\eta^5$  chelation, and both  $\mu$ -1,1 and  $\mu$ -1,3 bridges.

The overall network is somewhat similar to that of the barium-glutarate recently reported [4]. However, the lack of symmetry centre in the space group here, affects some features, like the basic unit which is formed of two bicapped dodecahedra sharing one face, and the orientation of the binding sites giving a complex 3D packing and replacing the two carboxylic ends in anti-parallel orientation, by end-to-end hydrogen bonding. But the substructure containing alkaline-earth atoms and forming a pseudo-eight-sided grid network is kept. This study shows that no M-O-M infinite linkage is present, confirming that this later is prevented by cage assembly around the metal.

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**MS16 P05**

**Substituted Salicylaldiminato and Related Cobalt Complexes at 173 K** Jarno Kansikas, Ahlam Shibaud, Timo Repo, Ilpo Mutikainen and Markku Leskelä, Department of Chemistry, Laboratory of Inorganic Chemistry, University of Helsinki, Finland. E-mail: [jarno.kansikas@helsinki.fi](mailto:jarno.kansikas@helsinki.fi)

**Keywords:** cobalt compounds, catalyst structure, salicylaldiminato

Here will be presented two cobalt(II) and two cobalt(III) catalyst compounds formed by variously substituted salicylaldiminato ligands in three structures and an imine derivative in one structure. The studied compounds are bis[isopropyl-*N*-(3,5-di-*tert*-butylsalicylaldiminato)]cobalt(II) (**I**), bis{[(2-ethylphenylimino)ethyl]phenoxy}cobalt(II) (**II**), bis[2-phenylethyl-*N*-(3,5-di-*tert*-butylsalicylaldiminato)]bis(phenylethylamino)cobalt(III) iodide (**III**) and tris[4-fluorobenzyl-*N*-(salicylaldiminato)]cobalt(III) (**IV**). Compound (**I**) crystallizes in *P*<sub>4</sub>(3) (78) with *Z*=8, (**II**) in *P*<sub>2</sub>/*c* (14) with *Z*=4, (**III**) in *C*<sub>2</sub>/*c* (15) with *Z*=4 and (**IV**) in *P*<sub>2</sub>/*n* (14) with *Z*=8.

Cell parameters using Nonius Kappa CCD at 173 K (Å and °) are: (I) 14.071(2), 14.071(2), 39.993(4), 90.0, 90.0 and 90.0; (II) 21.114(4), 4.972(1), 25.710(4), 90.0, 94.27(3) and 90.0; (III) 10.708(3), 19.143(3), 29.027(4), 90.0, 94.70(3) and 90.0; (IV) 10.937(2), 27.320(5), 15.120(3), 90.0, 105.23(3) and 90.0.

Slightly distorted coordination spheres are tetrahedral in four-coordinated compounds (I) and (II) and octahedral in six-coordinated compounds (III) and (IV). Bond distances (Å) within the coordination spheres for Co-O vary from 1.927(3) to 1.947(3) in (I), from 1.889(3) to 1.906(3) in (II), 1.897(2) in (III) and from 1.878(2) to 1.901(2) in (IV) and for Co-N from 1.940(4) to 2.019(4) in (I), from 1.982(4) to 1.984(4) in (II), from 1.962(2) to 1.994(2) in (III) and from 1.947(2) to 1.963(2) in (IV). The values are comparable to those found in some similar compounds [1-3].

Salicylaldehydes can be prepared from salicylaldehyde and respective aliphatic or aromatic amines heating overnight.

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#### MS16 P06

##### Organic-Donor Inorganic-Acceptor Salts:

$[(TTF)_6(XMO_{12}O_{40})(Et_4N)]$ , X=Si and P.

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**Key words: Donor Acceptor compound, Magnetism, Crystallography**

The preparation, X-ray crystal structure, optical and magnetic properties of two Organic-Donor Inorganic-Acceptor (ODIA) salts:  $[(TTF)_6(XMO_{12}O_{40})(Et_4N)]$ , X= Si (1) and P(2) are presented.

The two materials are isostructural. Their X-ray crystal structures are characterized by 1-D TTF chains lying inside the channels formed by the inorganic anions and isolated TTF molecules. Magnetic experiments for both salts are compared: they are different and suggest, in particular, the presence of one non-interacting electron in 2, in contrast with the diamagnetic behaviour of 1. The optical absorption measurements of the two compounds are essentially identical. They show the presence of both intense charge transfer bands around 4800 cm<sup>-1</sup> and vibronic modes in the middle IR range (1300-1400 cm<sup>-1</sup>), characteristic of mixed valence salts.

#### MS16 P07

##### Crystal structure and magnetic properties of mononuclear Co(II) and Ni(II) complexes

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#### Keywords: Metal complexes-1, Magnetism-2, ZFS - 3

There has recently been great interest in the study of the properties of molecular magnets. In the last two decades many molecular magnetic compounds have been synthesized [1]. Our interest is an investigation of interesting coordinating properties of Co(II) and Ni(II) with N - donor base and carboxylate ligand. The heteroleptic complexes with the  $\{MeN_2O_2O_2\}$  [2, 3],  $\{MeN_4O_2\}$  [4, 5],  $\{MeN_6\}$  [6] chromophore, where M = Ni and Co have been prepared, structurally characterized and subjected to magnetochemical investigation down to 2 K (susceptibility and magnetization measurement). They show magnetic behavior typical for zero-field splitting (ZFS) systems. The axial parameter of the ZFS, *D*, adopts either positive or negative values and correlates with axial distortion of the coordination polyhedra.

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#### MS16 P08

##### Triphenylguanidinium benzoate: Crystal structure and

DFT calculations P. S. Pereira da Silva<sup>a</sup>, M. Ramos Silva<sup>b</sup>, C. Cardoso<sup>c</sup>, S. R. Domingos<sup>b</sup>, J. A. Paixão<sup>b</sup>, A.

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**Keywords; DFT calculations, optical activity, structure determination**

Triphenylguanidine (TPG) is an octupolar molecule. Such molecules are particularly interesting from the point of view of nonlinear optics. Their null dipole moment does not stand as a drawback for its crystallization and still allows the crystal to present large third order susceptibilities if some symmetry requirements are fulfilled. A non-centrosymmetric crystal was obtained mixing an ethanolic solution of benzoic acid with TPG. In the resulting salt, the anions and cations are linked in chains via hydrogen bonds. Although none of the molecules is chiral, the propeller like arrangement of the phenyl rings of TPG<sup>+</sup> promotes such chiral crystallization (space group Cc). In the cation, the dihedral angles between the phenyl rings and the plane defined by the central guanidinium fragment are very similar, in the range 57.73(13)-59.94(14)°. The corresponding angles for other TPG<sup>+</sup> salts reported in the literature are within the range 32.6(3)-70.2(3)° [1-5], a variability that attests the