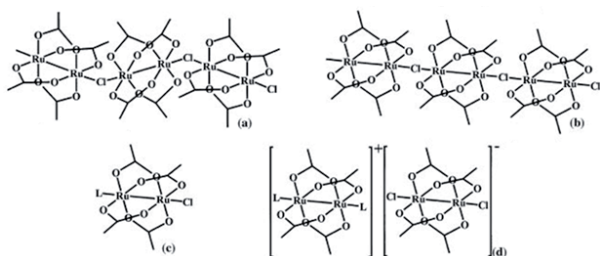


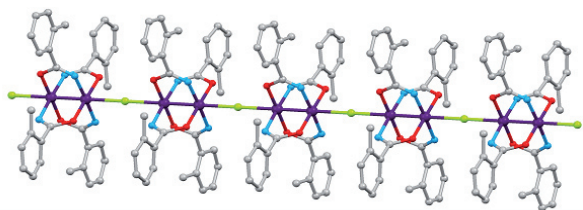
position of an adjacent diruthenium unit leading to zigzag or linear chains. However, a neutral ligand can also coordinate to the free axial position giving rise to discrete dinuclear molecules (Scheme 1).

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

## MS81.P61

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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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[1] G. Férey, *Chemical Society Reviews* **2008**, *37*, 191-214. [2] a) L. Cunha-Silva, L. Mafra, D. Ananias, L.D. Carlos, J. Rocha, F.A.A. Paz, *Chemistry of Materials* **2007**, *19*, 3527-3538. b) L. Cunha-Silva, S. Lima, D. Ananias, P. Silva, L. Mafra, L.D. Carlos, M. Pillinger, A.A. Valente, F.A.A. Paz, J. Rocha, *Journal of Materials Chemistry* **2009**, *19*, 2618-2632. c) L. Cunha-Silva, D. Ananias, L. D. Carlos, F. A. A. Paz, J. Rocha, *Zeitschrift für kristallographie* **2009**, *224*, 261-271. [3] F.-N. Shi, T. Trindade, J. Rocha, F.A.A. Paz, *Crystal Growth and Design* **2008**, *8*, 3917-3920.

**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  $\text{HPO}_2(\text{OH})^-$ .

Phosphate(III)-tetrahedra,  $\text{NaO}_6^-$  and  $\text{ScO}_6^-$  octahedra together form a (3, 6)-connected net. Thermochemical property studies show that during heating hydrogen and water are released while part of the phosphate(III) groups are oxidized to phosphate(V).  $\text{Sc}[\text{PO}_3]_3$  is formed as the main crystalline decomposition product.  $\text{NaSc}_3[\text{HPO}_3]_2[\text{HPO}_2(\text{OH})]_6$  represents the first example containing scandium within the family of  $M^mM^m$  metal phosphates(III). The replacement of phosphate(V) tetrahedra by phosphate(III) groups leads to a reduction of M–O–P connections, resulting in more open frameworks.[2]

[1] S. Chen, Yu. Prots, R. Kniep, S. Hoffmann, *ZAAC* **2011**, accepted. [2] S. Natarajan, S. Mandal, *Angew. Chem. Int. Ed.* **2008**, *47*, 4798-4828.

**Keywords:** scandium, phosphate(III), thermal analysis

## MS81.P63

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### Effect of magnesium on the thermal stability of the hydroxyfluorapatite

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The biological apatite contains minor substituents such as  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SiO}_4^{4-}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Sr}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Mg}^{2+}$ . Therefore, the incorporation of such ions into the synthetic hydroxyapatite would enhance its biocompatibility and bioactivity. Magnesium and fluoride co-substituted hydroxyapatites with the general formula  $\text{Ca}_9\text{Mg}(\text{PO}_4)_6(\text{OH})_{2-2y}\text{F}_y$  ( $y = 0, 0.5, 1, 1.5$  and  $2$ ) have been synthesized through a hydrothermal method. The obtained powders have been characterized using different analyses. The results showed that the substitution of  $\text{F}^-$  for  $\text{OH}^-$  was continuous between the limiting compositions  $\text{Ca}_9\text{Mg}(\text{PO}_4)_6(\text{OH})_2$  and  $\text{Ca}_9\text{Mg}(\text{PO}_4)_6\text{F}_2$ . Indeed, no secondary phases were formed. Furthermore, the incorporation of Mg into the hydroxyfluorapatite lattice influenced considerably its thermal behavior by lowering its decomposition temperature with respect to the nonsubstituted HFA. Also, the nature of the decomposition products tightly depended on the fluorine content. The Fullprof program was used to determine the phase distribution for the powders calcined at different temperatures. The obtained results showed that the amounts of the decomposition products increased with the increase of the calcination temperature. According to the nature of the decomposition products, it seems that the  $\text{MHF}_y\text{A}$  samples exhibit a thermal behavior similar to that of  $\text{MHA}$  rather than that of  $\text{MFA}$ .

**Keywords:** apatite, magnesium

## MS81.P64

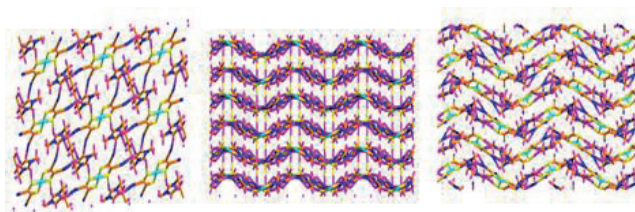
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### Role of supramolecular interactions on electronic absorption spectra of metal dithiolene complexes

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Metal-maleonitriledithiolate (mnt) complexes have received considerable attention in the areas of conducting and magnetic materials, dyes, non-linear optics, and catalysis [1]. Typically, the geometry around the transition metal ions (Cu, Ni) possesses square-planar arrangement, and in case of Mn, Fe, Co-mnt complexes, the geometry is noticeably distorted square-planar [2]. We describe here a series of highly distorted

square-planar ion-pair complexes in which  $[\text{M}(\text{mnt})_2]^{2-}$  ( $\text{M} = \text{Cu}, \text{Ni}$ ) anions are associated with alkyl imidazolium cations of varied alkyl chain lengths. In the present study, a systematic study of variation of square planar geometries (in terms of distortion) around the metal ion in customary square planar metal-dithiolene complexes has been discussed. This distortion in the geometry around the metal ion can be ascribed due to un-balanced supramolecular interactions, that include  $\text{S}\cdots\text{H}$ ,  $\text{N}\cdots\text{H}$  and  $\text{M}\cdots\text{S}$  type of weak contacts. The title complexes show a moderate absorption band in the NIR region at 1210 nm and 800 nm, in their solution states for the copper and nickel dithiolene ion-pair complexes respectively. The absorption maxima in the solid-state diffuse reflectance spectra is mainly depends on the geometry around the copper metal, e.g., the square planar copper-dithiolene complexes exhibit broad band at 1150 nm whereas distorted square planar ( $\lambda = 38.31^\circ$ ) copper-dithiolene complexes show a broad band at 1260 nm, indicating a bathochromic for the more distorted square planar copper complexes. All the compounds are unambiguously characterized by single crystal X-ray crystallography, and further characterized by IR,  $^1\text{H}$  NMR, LCMS, EPR spectral- and electrochemical-studies.



[1] (a) N. Robertson, L. Cronin, *Coord. Chem. Rev.* **2002**, *227*, 93-127. (b) Y. Kobayashi, B. Jacobs, M.D. Allendorf, J.R. Long, *Chem. Mater.* **2010**, *22*, 4120-4122. [2] (a) X.M. Ren, P.H. Wu, W.W. Zhang, Q.J. Meng, X.Y. Chen, *Trans. Met. Chem.* **2002**, *27*, 394-397. (b) G. Christou, J.C. Huffman, *J. Chem. Soc. Chem. Commun.* **1983**, 558-560.

**Keywords:** supramolecular interactions, diffuse reflectance spectra.

## MS81.P65

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### Crystal structure and phase transition of $\text{Rb}_{1-x}(\text{NH}_4)_x\text{IO}_3$ mixed crystal

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Ammonium iodate,  $\text{NH}_4\text{IO}_3$ , is a well known electro-optic material [1] and exhibits a strong piezoelectric effect [2]. Ferroelectricity was reported at 1975 with a transition temperature to paraelectric phase near  $85^\circ\text{C}$  [3]. In Rubidium iodate,  $\text{RbIO}_3$ , there is no report of the existence of ferroelectricity and phase transition. On the other hand, Potassium iodate,  $\text{KIO}_3$ , is known as successive phase transition within ferroelectricity [4]. Therefore, it is strange that  $\text{RbIO}_3$  does not undergo the phase transition, like as  $\text{KIO}_3$  or  $\text{NH}_4\text{IO}_3$ . In order to clarify this question, we carried out the measurement of differential scanning calorimetry and the experiment of powder X-ray diffraction of  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{IO}_3$  with  $x=0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0$ .

According to the results, the following things have become clear now. In all compositions of  $x$ ,  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{IO}_3$  mixed crystals were the single crystalline solid solution. The crystal structure of  $x=0.1, 0.2$  and  $0.3$  was approximately-same crystal structure of  $\text{RbIO}_3$ , and one