

**1** has high sensitivity to the toxic metal ions of Hg<sup>2+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup> as well as Ag<sup>+</sup> ion. After the addition of Hg<sup>2+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup>, or Ag<sup>+</sup> alone at 0.01 M or the mixture of Hg<sup>2+</sup>, Pb<sup>2+</sup>, and Cd<sup>2+</sup> with the total concentration of 0.01 M to the DMF emulsion of **1**, the luminescence of **1** quenched completely (Fig 2).

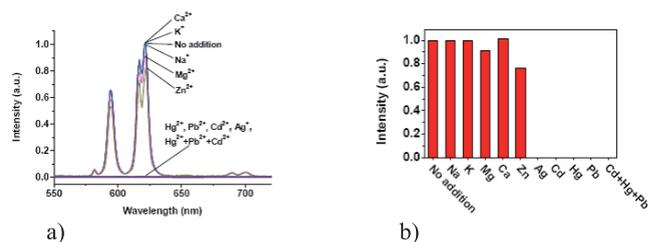


Figure 2 a) Emission spectra of **1** in DMF emulsion in the presence of various metal ions in 0.01 M M(NO<sub>3</sub>)<sub>x</sub>; b). Normalized luminescence intensities of the <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>5</sub> transition of **1** in DMF emulsions at 621 nm upon the addition of various metal ions in 0.01 M M(NO<sub>3</sub>)<sub>x</sub>.

[1] K.L. Wong, Y.Y. Yang, W.T. Wong *et al. Adv. Mater.* **2006**, *18*, 1051. [2] B. L. Chen, G.D. Qian *et al. Angew. Chem. Int. Ed.* **2009**, *48*(3), 500. [3] J.R. Long, O.M. Yaghi, *Chem. Soc. Rev.* **2009**, *38*, 1213; [4] M.D. Allendorf, C.A. Bauer, R.K. Bhakta, *et al. Chem. Soc. Rev.* **2009**, *38*(5), 1330; [5] K. Binnemans, *Chem. Rev.* **2009**, *109*(9), 4283.

**Keywords:** europium, carboxylate, complexe

## MS81.P20

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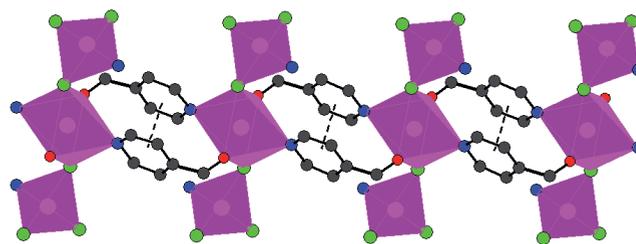
### Coordination driven and/or H-bonded M(II)-N,N-dialkylisonicotinamide networks

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The search for strategies enabling assembling of transition metal complexes into multidimensional frameworks is one of the main challenges in crystal engineering. The metal embedded supramolecular networks, having specific dimensions and topologies are associated with many magnetic, electronic, zeolitic, catalytic and optical properties thus leading to the creation of “functional materials” [1], [2], [3]. Coordination polymerization or hydrogen bonding are the two strategies employed in assembling metal complexes into multidimensional networks. Recently, a combination of the two has also been used effectively to increase the dimensionality. The strength of coordinate bond along with the flexibility imparted by hydrogen bonding provide ideal environment for multi-dimensional framework expansion. Among various ligands used for construction of supramolecular networks, the pyridine based ligands such as nicotinic acid, isonicotinic acid and their amide derivatives are ideal as they have the structural adaptability for both: metal-ligand coordination [4], [5] as well as the intermolecular hydrogen bonding [6].

Our work involving the Metal(II)-N,N-dialkylisonicotinamide complexes [7] has shown that these fully substituted amide derivatives of isonicotinic acid provide the necessary rigidity and binding sites that enhance the chances of formation of coordination networks instead of isolated entities and therefore provide a fertile route to metal organic frameworks (MOF's). Furthermore, intermolecular interactions among 1D coordinated and/or H-bonded chains make feasible the formation of more complex networks (2D and 3D). Each of these levels contains remarkable features making the complexes

unique from a structural point of view. This work also reinforces the role played by counter ions present in the lattice such as perchlorates and nitrate to enable assembling of metal complexes into networks. To explore the magnetism among such systems, in depth magnetic measurements (variable temperature magnetic susceptibility, epr etc.) have also been made [7].



[1] C. Janiak, *Dalton Trans.* **2003**, 2781-2804. [2] S.L. James, *Chem. Soc. Rev.* **2003**, *32*, 276-288. [3] B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629-1658. [4] J. Moncol, M. Mudra, P. Lönnecke, M. Hewitt, M. Valko, H. Morris, J. Svorec, M. Melnik, M. Mazur, M. Koman, *Inorg. Chim. Acta.* **2007**, *307*, 3213-3225. [5] B.R. Bhogala, P.K. Thallapally, A. Nangia, *Cryst. Growth Des.* **2004**, *4*, 215-218. [6] C.B. Aakeröy, A.M. Beatty, D.S. Leinen, *Angew. Chem., Int. Ed.* **1999**, *38*, 1815-1819. [7] P. Kapoor, A.P.S. Pannu, G. Hundal, R. Kapoor, M. Corbella, N. Aliaga-Alcalde, M.S. Hundal, *Dalton Trans.* **2010**, *39*, 7951-7959.

**Keywords:** 1D, 2D, 3D

## MS81.P21

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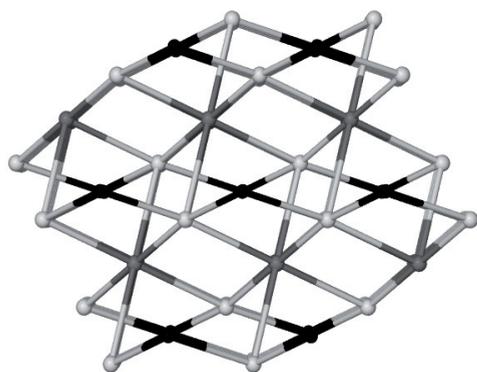
### Five new metal-organic frameworks: novel topologies and characteristics.

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Metal-organic frameworks (MOFs) are a subgroup of coordination polymers and coordination networks. We are engaged in the preparation of MOFs using a range of common metal salts and organic ligands, including multitopic aromatic carboxylates. Topological analysis is a useful tool for analysing coordination networks. It allows one to see the arrangement of molecules in a structure in a simple manner and therefore helps in the determination of why that structure was formed. This enables a more systematic design of coordination polymers<sup>1</sup>.

Three MOFs were prepared from gadolinium(III) nitrate and 5-nitroisophthalic acid (NIA) using the same method with only the concentration of starting materials in the solvent system varying. [Gd<sub>2</sub>(NIA)<sub>9</sub>(DMF)<sub>4</sub>]·1.5H<sub>2</sub>O (**1**), [Gd(NIA)<sub>5</sub>(DMF)<sub>2</sub>]·3H<sub>2</sub>O (**2**) and [Gd<sub>4</sub>(NIA)<sub>14</sub>(DMF)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]·4DMF·xH<sub>2</sub>O (**3**) have a distinctive paddle-wheel motif with four NIA molecules coordinated to a pair of gadolinium metal centres.

Network analysis revealed the six connected (4<sup>12</sup>.8<sup>3</sup>)-**pcu** net for **1**. **1** and **2** are related by rotation around one C-C bond which reduces the symmetry of the network. This is easy to see through the topology as the six-connected node reduces to a four-connected node. **2** is found to have the square and tetrahedron four-connected (4<sup>2</sup>.8<sup>4</sup>)(4<sup>2</sup>.8<sup>4</sup>)-**pts** net. **3** has the unprecedented four-, five- and six-connected (4<sup>4</sup>.6<sup>2</sup>)(4<sup>6</sup>.6<sup>4</sup>)(4<sup>8</sup>.6<sup>6</sup>.8) network (Figure 1). The four-connected node of **3** is the same as that square four- node of the **pts** net while the six-connected node is the same as that of the **pcu** net.



**Figure 1:** The four- (black), five- (white) and six- (grey) connected  $(4^4.6^2)(4^6.6^4)(4^8.6^6.8)$  network of **3**

Two MOFs were prepared from zinc(II) sulphate and 1,3,5-benzenetricarboxylic acid ( $H_3BTRI$ ) using the same method although the concentration of starting materials in the solvent system was varied.  $[Zn_6(\mu_3-(OH)_2(BTRI)_4(DMF)_2)_5(H_2O)_2] \cdot [Zn(H_2O)_3(DMF)_3] \cdot 3 \cdot 1H_2O$  [**1**] and  $[Zn_2(HBTRI)(BTRI)(H_2O)_3] \cdot DMA \cdot 3H_2O$  [**2**] are both anionic networks. The counter ions are located in channels in the structure. Scanning electron microscopy (SEM) reveals that **2** “self-heals” upon dehydration and rehydration. **1** demonstrates the six- and three-connected  $(4.6^2)(4^2.6^{10}.8^3)$ -**sab** net while **2** demonstrates the five- and three-connected  $(6^3)(6^{10})$ -**kdd** net<sup>2</sup>.

Topological analysis allows for a simple comparison between different MOFs.

[1] L. Öhrström, K. Larsson, *Molecule-Based Materials: The Structural Network Approach*, Amsterdam, The Netherlands: Elsevier, **2005**. [2] K. Davies, S.A. Bourne, C.L. Oliver, L. Öhrström, *Dalton Trans.*, **2010**, 39, 2869.

**Keywords:** MOF, topology, SEM

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### Structural characterization of $LaTi_2Al_9O_{19}$

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$LaTi_2Al_9O_{19}$  [1] was prepared as single phase ceramics that was structurally characterized by means of laboratory X-ray powder diffraction. The compound was found to be isostructural with  $SrTi_3Al_8O_{19}$  [2] and it crystallizes in monoclinic  $C2/c$  space group with the following unit cell parameters:  $a=22.59355(18)$  Å,  $b=10.99919(9)$  Å,  $c=9.72968(7)$  Å,  $\beta=98.5634(5)^\circ$ ,  $V=2390.97(3)$  Å<sup>3</sup>,  $Z=8$ .

The fundamental building units are  $AlO_6$ - and  $TiO_6$ -octahedra which are interconnected by  $AlO_4$ -tetrahedra and  $La^{3+}$  ions into a complex network. Most simply, the structure can be represented as a system of close-packed octahedral layers of three types, i. e. layers A, B and C. In each unit cell, ten of these layers stack along  $a$  edge in a sequence ABCBABCBA. Typical fragments for layer A are pairs of edge-sharing  $AlO_6$ -octahedra which are further connected *via* vertices to  $La^{3+}$  ions and  $AlO_4$ -tetrahedra, respectively. Typical fragments of layers B and C are  $(TiAl_5Ti)O_{28}$  hook-like groups of edge-sharing octahedra; the main difference between B and C layers is that B layers additionally include  $La^{3+}$  ions while C layers consist of  $AlO_4$ -tetrahedra. Layers of octahedra are linked *via* edge- and vertex- sharing between A-B and

C-C layers whereas the connections between B and C layers run only through the sharing of vertices. Neither within the layers nor between them there are any face-sharing octahedra and  $AlO_4$ -tetrahedra connect with the other fragments only through vertices. With the described packing of the layers and their connections, the 12-fold coordination of lanthanum ions is achieved. The plausibility of the obtained structure was confirmed by bond valence sums and global instability index calculations.

The initial pattern matching shows resemblance between  $LaTi_2Al_9O_{19}$  and one of the largest structures determined *ab initio* from powder data,  $La_3Ti_5Al_{15}O_{37}$  [3]. In our opinion, the latter is not completely physically and chemically reasonable as it contains compositional as well as structural inconsistencies (e. g. some metal-metal distances are too short) that result in significant discrepancies of bond valence sums from the nominal atomic valences and high value of global instability index of 0.65 valence units.

[1] P.E.D. Morgan, *Mat. Res. Bull.* **1984**, 19, 369-376. [2] M. Strunk, H. Mueller-Buschbaum, *J. Alloys Compd.* **1993**, 198, 101-104. [3] R.E. Morris, J.J. Owen, J.K. Stalick, A.K. Cheetham, *J. Solid State Chem.* **1994**, 111, 52-57.

**Keywords:** rietveld refinement, XRPD,  $LaTi_2Al_9O_{19}$

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### Composition-dependent negative thermal expansion in tetracyanidoborate materials

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Coordination framework materials are extended crystalline networks composed of repeating units of metal ions and bridging ligands. As virtually limitless combinations of metal ions, ligands and structures are possible, these materials can display a wide variety of different properties, including porosity, catalysis, gas storage, magnetic behaviour, and negative thermal expansion [1]. This research expands the current literature on the properties of cyanide ( $C\equiv N$ ) bridged framework materials by presenting the first negative thermal expansion results for a series of isostructural materials containing the tetracyanidoborate anion,  $[B(CN)_4]^-$ , with a range of  $s$ - and  $d$ -block metal ions ( $Li^+$ ,  $Na^+$ ,  $Cu^+$  and  $Ag^+$ ).

Negative thermal expansion (NTE) describes the tendency of a material to shrink reversibly upon heating and has been demonstrated in a number of cyanide-bridged framework materials to date, including the compounds  $Zn(CN)_2$  and  $Cd(CN)_2$ , [2] which are each isostructural with the materials in this study. Cooperative transverse vibrations (phonon modes) are responsible for the overall contraction of materials in this class,[3] and this work contributes to a greater understanding of the influence of framework flexibility on observed NTE by studying the effects of systematically changing the metal ion in otherwise identical structures. Results to date from synchrotron powder X-ray diffraction, neutron powder diffraction and single crystal X-ray diffraction indicate that two of these compounds,  $Na[B(CN)_4]$  and  $Ag[B(CN)_4]$ , undergo amongst the largest isotropic NTE currently known ( $\alpha = -31 \times 10^{-6} K^{-1}$  and  $-25 \times 10^{-6} K^{-1}$  at 100 K, respectively;  $\alpha = \delta l / l \cdot \delta T$ , where  $l$  is the cubic unit cell dimension) [4]. The magnitude of transverse vibrations and thus NTE in these compounds appears strongly correlated with the strength and flexibility of the metal-ligand interactions and the degree of proximity of the two interpenetrated nets that comprise the structures.