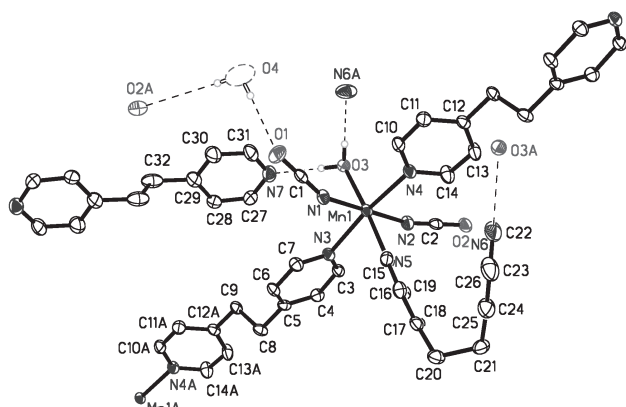


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An hybrid organic-inorganic chain compound of the family Mn(II)-bpa-(NCO) is presented:  $[\text{Mn}_4(\text{NCO})_8(\mu\text{-bpa})_4(\text{bpa})_4(\text{H}_2\text{O})_4]_n \cdot 2n(\text{bpa}) \cdot n\text{H}_2\text{O}$  (**1**). It contains, unusually, five different dispositions for the bpa [1,2-bis(4-pyridyl)ethane] ligand. Water molecules and free bpa ligands occupy the voids of the structure. Single-crystal X-ray diffraction reveals **1** to crystallize in the P21/n monoclinic space group. It consists of infinite chains of Mn(II) cations extending along the [100] direction and bridged by single N,N'-bpa bridges [Mn-N(3): 2.336(2) Å; Mn-N(4): 2.344(2) Å], that are in anti conformation with a torsion angle of 177.03° (Mn...Mn intrachain distance: 13.9 Å, Fig. 1). The distorted octahedral coordination of the cation is completed by a terminal bpa ligand [Mn-N(5): 2.296(2) Å], two N-terminal cyanate ligands [Mn-N(1): 2.189(2) Å; Mn-N(2): 2.163(2) Å], and a water molecule [Mn-O(3): 2.000(2) Å]. These chains are connected through intermolecular hydrogen bonding involving the atoms O(3) (water molecule) and N6 (non coordinating N-atom of the terminal bpa) [O(3)...N(6): 2.789(3) Å] or C(8) (ethane group of the bridging bpa) [O(3)...C(8): 3.414(4) Å]. Besides, the C(11) (bridging bpa) establish intermolecular connection with the O(2) (cyanate oxygen) [C(11)...O(2): 3.324(3) Å]. Interchain Mn...Mn distances are 8.6 Å and 9.0 Å and the packing is on the plane (110). The disposition of these sheets gives raise to hollows that are occupied by free molecules (water and bpa). Thus, a free bpa ligand acts as a solvate molecule occupying the voids in the lattice, in the same way as a water molecule acts.

The compound shows moderate antiferromagnetic type interactions through single bpa bridges, together with other exchange pathways. Electron spin resonance spectrum for **1** has been recorded at room temperature. The signal can be described as isotropic and is centred at 3300 Gauss.



**Keywords:** manganese, magnetochemistry, EPR

## MS25.P10

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### Thermal behaviour (HT and LT) in minerals of the cryptomelane group

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Single-crystal X-ray diffraction measurements were carried out on two minerals belonging to the cryptomelane group (hollandite, ideally  $\text{BaMn}^{4+}_6\text{Mn}^{3+}_2\text{O}_{16}$ ; ankangite, ideally  $\text{BaTi}^{4+}_6\text{V}^{3+}_2\text{O}_{16}$ ) at

several temperatures (from 100 to 900 K), to gather information on the structural behavior of these compounds with temperature, as a part of an ongoing study on the crystal-chemistry of the minerals of the cryptomelane group. The structure of the members of this group is characterized by octahedra arranged in edge-sharing columns, which in turn link together, again by edge-sharing, giving rise to walls, two octahedra wide. Cross-linking of these walls by corner-sharing result in a tunnel structure, with a squared 2x2 outline [1]. The ideal topological symmetry of 2x2 tunnel oxides is tetragonal, *I4/m*; the symmetry may lower to monoclinic due to cation ordering within both the octahedral framework and the tunnels [2]. It has been observed that these structural variations, and also phase transitions, may be induced by variations of temperature [3].

Accurate refinements of the unit cell parameters on selected specimens of hollandite from Vagli (Apuan Alps, Tuscany, Italy) and from the Kajlidongri mine (Jhabua district, Madhya Pradesh, India) were carried out in the T range from *ca.* 100 to *ca.* 900 K. At RT the studied samples are monoclinic, *I2/m*. As expected, the unit cell volume increases quite regularly with T, moreover a progressive transition of the symmetry from monoclinic to tetragonal is observed, with *a* approaching *c* and  $\beta$  approaching 90°. The T of transition is estimated at *ca.* 530 K. After a number of successive heating and cooling experiments carried out with various crystals of hollandite, we note that the monoclinic-tetragonal transition is reversible up to a T of *ca.* 900 K. Above that temperature, the transition becomes irreversible.

Complete crystal structure refinements were carried out on samples of ankangite from the Monte Arsiccio mine (Apuan Alps, Tuscany, Italy) in the T range from 100 to 800 K. Ankangite is tetragonal, *I4/m*, within the whole above T range. At varying T we observe, on one side, a regular increase of the unit cell parameters, and of all the interatomic distances, on the other side a significant variation in the occupancy of the extra-framework site. In ankangite the extra-framework cation is Ba, which is hosted in two distinct and partially occupied sites, Ba1 (at 0, 0, ½) and Ba2 (at 0, 0, 0.65). The occupancy at both sites was allowed to refine freely, the only constraint was to fix the displacement parameters at the same average value for each T run. From 100 K up to RT both sites are partially occupied, with a slight preference for Ba1, whereas at higher temperatures (500 and 700 K) all Ba tends to concentrate in the Ba1 site and Ba2 becomes empty. This may have some effect on the incommensurate structures so far observed in members of the cryptomelane group [4].

- [1] M. Pasero, *Reviews in Mineralogy & Geochemistry* **2005**, 57, 291-305. [2] J.E. Post, R.B. Von Dreele, P.R. Buseck, *Acta Crystallographica* **1982**, B38, 1056-1065. [3] R.W. Cheary, *Acta Crystallographica* **1990**, B46, 599-609. [4] L.A. Bursill, G. Grzinic *Acta Crystallographica* **1980**, B36, 2902-2913.

**Keywords:** X-ray\_diffraction, low\_temperature, high\_temperature.

## MS25.P11

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### Metal-organic frameworks as ion-exchangers

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Porosity and sorption processes represent one of the most stimulating current areas of research activity in the field of materials chemistry, in particular when using metal-organic frameworks (MOFs) [1]. Following our on-going research focused on the development of functional MOFs, we report the synthesis, full structural characterization, porosity measurements and ion exchange properties of a new porous MOF with Ce<sup>3+</sup> [2, 3].

A microporous cationic MOF has been prepared by our research group while investigating the lanthanide/2,5-pyridinedicarboxylic acid system [3]. Large crystals of framework  $[\text{Ce}_2(\text{pydc})_2(\text{Hpydc})(\text{H}_2\text{O})_2]\text{Cl}\cdot(9+y)\text{H}_2\text{O}$  (**1**) (where  $\text{pydc}^{2-}$  is the diprotonated residue of 2,5-pyridinedicarboxylic acid) were directly isolated from the hydrothermal reaction vial via filtration. A second phase was also systematically present and was identified as identical to the structure reported by Huang et al.:  $[\text{Ce}_2(\text{pydc})_3(\text{H}_2\text{O})_2]$  [4].

A systematic change of the reaction conditions to promote the sole preparation of **1** proved to be unsuccessful: we found that we could only improve the ratio between the desired microporous phase **1** and  $[\text{Ce}_2(\text{pydc})_3(\text{H}_2\text{O})_2]$  to 4:1. Nevertheless, the considerable difference in particle size allowed an easy segregation of **1** for further detailed X-ray diffraction studies.

**1** has a single crystallographically independent  $\text{Ce}^{3+}$ . The nine-coordination sphere is composed of one water molecule, six oxygen atoms from *syn*, *skew*- or *syn*, *syn*-bridging carboxylate groups, plus a *N,O*-chelate. The coordination polyhedron resembles a highly distorted dodecahedron. This MOF (*ca.* 43% of accessible volume) contains prominent channels (cross section *ca.*  $12 \times 7 \text{ \AA}^2$ ) running parallel to the [001] direction housing disordered charge-balancing chloride anions and water molecules of crystallization. The BET surface area of the degassed material was calculated as approximately  $106 \text{ m}^2/\text{g}$ . The solvent (water) could be partially exchanged by chloroform or benzyl alcohol by crystal immersion at ambient temperature over a period of several days.

This material (**1**) was treated as an anion exchanger by immersion of the individual crystallites in methanolic solutions of several anions, such as  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ ,  $\text{PF}_6^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{PO}_4^{3-}$ . We note that the presence of the secondary phase,  $[\text{Ce}_2(\text{pydc})_3(\text{H}_2\text{O})_2]$ , is an advantage as it can be used as an internal standard. Structural details of the exchanged materials (solvent and anion), were investigated by using in tandem X-ray diffraction (single-crystal and powder), electron microscopy (SEM and EDS), and FT-IR spectroscopy.

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[1] S. Bureekaew, S. Shimomura, S. Kitagawa, *Sci. Technol. Adv. Mater.* **2008**, *9*, 014108. [2] J. Klinowski, F.A.A. Paz, P. Silva, J. Rocha, *Dalton Trans.* **2011**, *40*, 321-330. [3] P. Silva, A.A. Valente, J. Rocha, F.A.A. Paz, *Cryst. Growth Des.*, **2010**, *10*, 2025-2028. [4] Y. Huang, Y. S. Song, B. Yan, M. Shao, *J. Solid State Chem.* **2008**, *181*, 1731-1737.

**Keywords:** metal-organic framework, microporosity, anion-exchange

## MS25.P12

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### 1D systems based on pyrazine-2,5-dicarboxylate linkers and $[\text{Mn}(\text{phen})]^{2+}$ nodes

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In recent years, the area of inorganic crystal engineering [1] has become one of intense research activity because of the growing need for novel solid-state architectures with potential applications as functional materials in fields such as catalysis, conductivity, zeolitic behaviour, and magnetism [2]. The judicious choice of the metal ion, a good understanding of the coordination preferences of the bridging entities, and a careful selection of the terminal ligands are key steps for

the rational design of metal-organic coordination polymers with novel topologies and specific chemical and physical properties [3]. In this context,  $\pi$ -conjugated N-donor bridging ligands, such as pyrazine and its polycarboxylic derivatives, have appeared to be well-suited tools for the construction of extended arrays of metal ions with interesting physical properties in molecular magnetism or selective guest adsorption fields [4].

Two new metal-organic compounds based on the bridging ligand pyrazine-2,5-dicarboxylate (Pzdc) have been synthesized and chemically and crystallographically characterized in the present work:  $\{[\text{Mn}(\mu\text{-Pzdc})(\text{Phen})]\cdot 2\text{DMSO}\}_n$  (**1**) and  $\{[\text{Mn}(\mu\text{-Pzdc})(\text{Phen})]\cdot \text{CH}_3\text{O}\cdot \text{H}\cdot \text{H}_2\text{Pzdc}\}_n$  (**2**), with Phen = 1,10-phenanthroline, DMSO = dimethyl sulphoxide. Compound **1**, obtained using DMSO as solvent, crystallizes in the C2/c space group and it is built up by zig-zag chains in which the metal centers are joined by bisbidentate Pzdc bridging ligands and the phenanthroline molecule acts as blocking ligand avoiding further polymerization. The compound loses crystallinity out of the mother liquors, so the employed solvent was changed to methanol in order to get a more stable structure, obtaining the compound **2**. The complex crystallizes in the P2/c space group and although it is also made up of  $[\text{Mn}(\mu\text{-Pzdc})(\text{Phen})]_n$  chains, the increase of the supramolecular interactions gives rise to a more robust structure. The metal coordination environment in both compounds is similar but not equal as can be observed in figure 1.

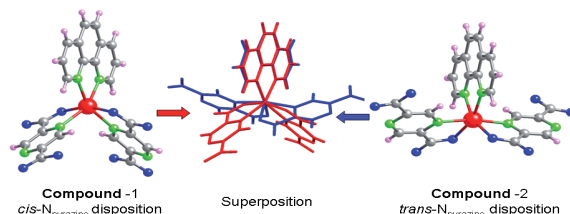


Figure 1. Superposition of the coordination environments of the Mn(II) atoms in compounds **1** and **2**.

[1] D. Braga, L. Brammer, N. R. Champness, *CrystEngComm.* **2005**, *7*, 1-19, [2] S. L. James, *Chem. Soc. Rev.* **2003**, *32*, 276-288, [3] D. Braga, G. R. Desiraju, J. S. Miller, A. G. Orpen, S. L. Price, *CrystEngComm.* **2002**, *4*, 500-509, [4] S. Konar, S. C. Manna, E. Zangrando, N. R. Chaudhuri, *Inorg. Chim. Acta* **2004**, *357*, 1593-1597.

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**Keywords:** coordination-polymer, pyrazine-2,5-dicarboxylate, manganese.

## MS25.P13

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### 3D-copper-adeninate complexes with microchannels tailored by aliphatic acids

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The emerging field of coordination polymers offers a means to a novel class of potentially designable materials because their metrics and chemical functionality can be carefully adjusted for specific applications [1]. In recent times, porous metal organic frameworks (MOFs) have attracted increasing attention because they possess a