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An hybrid organic-inorganic chain compound of the family Mn(II)bpa-(NCO) is presented: $[Mn_4(NCO)_8(\mu-bpa)_4(bpa)_4(H_2O)_4]_n 2n(bpa)$ nH₂O (1). It contains, unusually, five different dispositions for the bpa [1,2-bis(4-pyridyl)ethane] ligand. Water molecules and free bpa ligands ocupy 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) $[O(3) \cdots C(8): 3.414(4) Å]$. Besides, the C(11) (bridging bpa) establish intermolecular connection with the O(2) (cyanate oxygen) $[C(11)\cdots O(2): 3.324(3) \text{ Å}]$. 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

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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 $BaMn^{4+}_{6}Mn^{3+}_{2}O_{16}$; ankangite, ideally $BaTi^{4+}_{6}V^{3+}_{2}O_{16}$) 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 2×2 outline [1]. The ideal topological symmetry of 2×2 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 β 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, $\frac{1}{2}$ 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].

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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^{3+} [2, 3].