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The polymeric isomorphous hybrid inorganic-organic vanadium oxide compounds:  $[M(\text{Im})_4\text{V}_2\text{O}_6]$ ,  $M = \text{Mn}(\text{I}), \text{Co}(\text{II}), \text{Ni}(\text{III})$ , Im = imidazole, were investigated between 100 (2) and 295 (2) K by single crystal X-ray diffraction. The compounds contain 2-D sheets packed perpendicular to  $c^*$  and undergo a reversible order-disorder phase transitions. The room temperature  $P4_2/n$  disordered phase ( $Z = 8$ ) is reversibly transformed to the  $I4_1/a$  ordered phase ( $Z = 32$ ) below 281 (2) K for **I** and 175 (2) K for **II**, requiring a change of the hydrogen bond connectivity for two of the eight imidazoles per asymmetric unit of the  $I4_1/a$  structure. The structure of **I** has a well defined phase transition but **II** shows a large hysteresis and it was necessary to include stacking faults in the modelling of **II** at low temperatures. The structure of **III** was shown to be partially twinned but ordered in space group  $P2/n$  ( $Z = 8$ ) at 100 (2) K, with two different localised regions each containing four pairs of inversion related imidazoles hydrogen bonding to framework oxygen atoms involving eight imidazoles in one region and six imidazoles in the other. Models for the phase transition mechanisms are considered.

Keywords: hydrogen bonds, order-disorder structure, phase transitions and structure

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#### Structural diversity of $[\text{M}(\text{SCN})_2]$ fragment with BPHD(2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene)

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Six metal coordination polymers with interesting supramolecular architectures,  $\{[\text{Zn}(\text{bphd})_2(\text{NCS})_2][\text{Zn}_{0.5}(\text{bphd})(\text{NCS})(\text{H}_2\text{O})]\}_n$  (**1**),  $[\text{Mn}(\text{bphd})_2(\text{NCS})_2]_n$  (**2**),  $\{[\text{Mn}_{0.5}(\text{bphd})_{0.5}(\text{NCS})(\text{H}_2\text{O})(\text{bphd})]\}_n$  (**3**),  $\{[\text{Fe}(\text{bphd})_2(\text{NCS})_2] \cdot 2\text{EtOH}\}_n$  (**4**), and  $\{[\text{Co}(\text{bphd})_2(\text{NCS})_2] \cdot 2\text{EtOH}\}_n$  (**5**),  $[\text{Mn}(\text{bphd})_2(\text{NCS})_2]_n$  (**6**), have been synthesized and structurally determined by X-ray diffraction method, each of them adopting a different structural metal-organic frameworks (MOFs). Compound **1** is divided into two parts, the first part is a hexa-coordinated Zn(II) center bonded with two  $\text{NCS}^-$  and four bridging bphd ligands. A 2D layered MOF is constructed by a square-grid as the basic building unit. The second part is a five-coordinated Zn(II) center bonded with two bridging bphd, two  $\text{NCS}^-$  and one water molecule forming a 1D chain-like MOF. Adjacent 2D layered MOFs are then parallel arranged and penetrated by 1D chains. In compound **2** and **6**, the metal center is hexacoordinated by two  $\text{NCS}^-$  and four bphd ligands. The bphd acts a bridging ligand to connect the metal ions forming a 2D square-grid wave-liked layer. Three identical but independent layers are mutually interpenetrated. In compound **3**, the Mn(II) ion is hexa-coordinated bonded with two  $\text{NCS}^-$ , two water molecules and two bridging bphd ligands forming 1D chains. A 3D supramolecular architecture is constructed by hydrogen-bonds among the free bphd ligand and water molecules and  $\pi$ - $\pi$  interactions between the pyridyl rings of the bphd ligands. In compound **4** and **5**, the metal centers are bonded with two  $\text{NCS}^-$  and four bridging bphd ligands to afford a 2D non-interpenetrating square-grid layered MOF. These 2D layered MOFs adopt an ABAB arrangement forming a 3D network with two 1D channels intercalated with solvent molecules.

Keywords: metal-organic framework, coordination polymer, pi-pi interactions

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#### Synthetic strategies and structural aspects of metal-mediated multi-porphyrin assemblies

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Porphyrins play a major role as active chromophores in artificial systems mimicking the natural photoinduced processes. The formation of coordination bonds between peripheral donor sites on the porphyrins and external metal fragments has proved to be an efficient alternative to covalent synthesis for the construction of multi-porphyrin assemblies, whose complexity and beauty gradually approach those of the multichromophore systems found in Nature. In a modular approach, relatively simple metal-mediated porphyrin adducts, owing to their thermodynamic and kinetic stability, can be exploited as building blocks in the construction of higher order architectures. Thus multichromophore systems become accessible on demand, with a limited synthetic effort. The collection of solid state structures reported here demonstrates that the flexibility of the porphyrins and of the metal junctions, combined with the conformational freedom of the coordination bonds, may lead to assemblies with hardly predictable architectures. In previous years we have focussed our attention on the synthesis and structural characterization of metallacycles of pyridylporphyrins obtained by self assembly of two Ru(II) complexes bearing two labile ligands in cis position and two molecules of cis-4'-dipyridylporphyrin (4' cisDPYP)<sup>1</sup>. Examples in which X-ray structural determination was essential for establishing the real composition and geometry of the multiporphyrin assemblies are highlighted.

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Keywords: porphyrins, metal complexes, supramolecular systems

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#### Crystallographic structures of ruthenium tris(2,2'-bipyridine) having amide groups at 5,5'-positions

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We have synthesized ruthenium tris(2,2'-bipyridine) complexes bearing amide groups at 5,5'-positions and analyzed their crystallographic structures. It has been found that the different orientation of amide groups ( $-\text{C}(\text{O})\text{NHR}$  or  $-\text{NHC}(\text{O})\text{R}$ ) leads to different crystallographic structures depending on differences in inter-ligands interaction such as hydrogen bondings and hydrophobic interaction. Especially, ruthenium tris(bipyridine) complex with  $-\text{C}(\text{O})\text{NH}^t\text{Bu}$  at 5,5'-positions affords an amphiphilic channel structure due to hydrophobic interaction among tert-butyl groups.