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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 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 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 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 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 π - π interactions between the pyridyl rings of the bphd ligands. In compound **4** and **5**, the metal centers are bonded with two 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)¹. 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.

In the case of the bipyridyl ligand (5MeCONHbpy) possessing -NHC(O)Me at 5,5'-positions, of which the orientation is different from -C(O)NH^tBu, the structures of [Ru(5MeCONHbpy)₃]²⁺ drastically depend on the counter ion. The hexafluorophosphate salt, [Ru(5MeCONHbpy)₃](PF₆)₂, yield a bundle structure of one-dimensional chains in which the amide groups connect together with each other via hydrogen bonds. On the other hand, the chloride salt, [Ru(5MeCONHbpy)₃]Cl₂, give layer structures, where the layer of ruthenium complexes link with the chloride layer. Here, the differences in photophysical properties of the ruthenium complexes with amide groups having different orientation will be presented.

Keywords: ruthenium, bipyridine, amide Groups

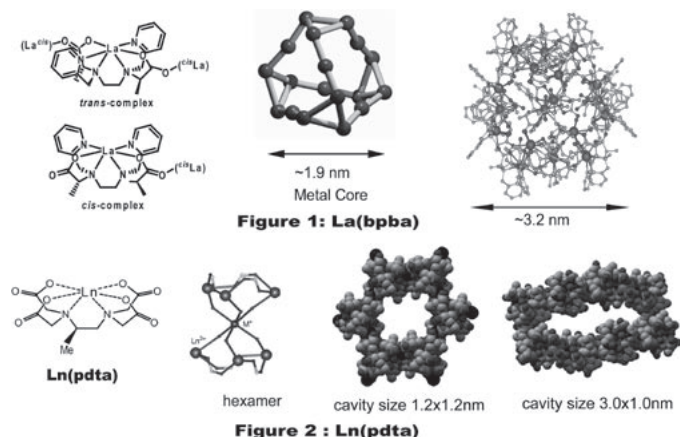
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Supramolecular assemblies of lanthanide clusters with chiral ligands in the crystalline state

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It is well known that the structures of lanthanide-based supramolecular systems are hardly predictable and often quite peculiar. Recently, we found out an unprecedented tetrahedral cage-like lanthanide cluster [La^{III}]₁₈(D-bpba)₁₈(H₂O)₃₆X₁₈ {D-bpba=N,N'-bis(2-pyridylmethyl)-N,N'-1,2-ethanediyl-bis(D-alaninate)} **1**. This octadecameric cluster is built up with twelve cis- and six trans-complexes, including the carboxylate-bridging trinuclear core due to the chiral ligand. Very recently, we found out that the trinuclear core can be easily formed in the chiral M⁺[Ln(pdta)(H₂O)₂]⁻ complexes **2** {pdta=propylenediamine-N,N',N',N'-tetraacetate}, leading to the hexameric unit via a central M⁺ ion. The hexameric unit can generate a two-dimensional porous network via the M⁺ ions in the crystalline state. Especially, supramolecular assemblies with 36 units of **2** (M⁺=K⁺, racemic crystal) and 48 units of **2** (M⁺=Na⁺, chiral crystal) generate large cavities (Figure 2). We wish to present and discuss here the details about the crystal structures of lanthanide complexes **1** (X=Cl⁻, Br⁻) and **2** (M⁺=Na⁺, K⁺; Ln=La^{III}, Pr^{III}, Sm^{III}, Eu^{III}, Gd^{III}, Dy^{III}).



Keywords: cluster in coordination complexes, lanthanide coordination, supramolecular assembly

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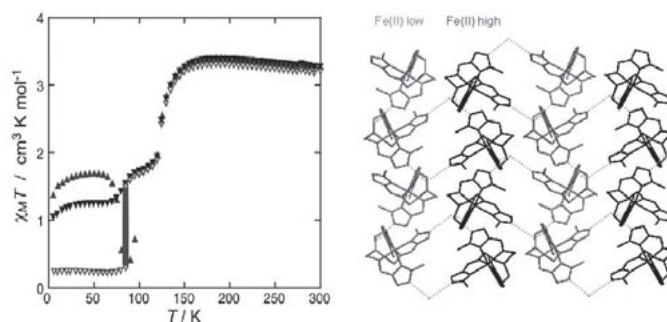
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A problem in the crystal structure of a two-step spin crossover complex

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A spin crossover (SC) complex [Fe^{II}H₃L^{Me}]ClAsF₆ revealed a two-step behavior of HS(High-Spin), (HS + LS)/2, LS(Low-Spin), where H₃L^{Me} denotes the tripod ligand containing three imidazole groups, tris[2-((2-methylimidazol-4-yl)methylidene)amino]ethylamine. The complex exhibited similar cell dimensions at three states. The space group is P₂₁/n at the HS and LS states and P₂₁ at the HS + LS state. The crystal structure consists of a 2D extended network structure constructed by NH...Cl hydrogen bonds, while the anion exists as an isolated counter anion. The complex cation is a chiral species with the C(clockwise) or A(anticlockwise) configuration due to the screw coordination arrangement of the achiral tripod ligand. At 180 and 90 K, there is unique one molecule in the unit cell, in which the A and C enantiomers are related by the symmetry operation to give a racemic crystal. The space group P₂₁ at 110 K is a chiral space group, where either of (a combination of C-HS and A-LS) and (a combination of A-HS and C-LS) should exist in a crystal. However, the Flack parameter calculated was 0.5.



Keywords: iron complex, chirality, spin crossover

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Metallasiloxane complexes: Rings and cages

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Our work is mostly focused on the synthesis of new aluminium and rare earth metallasiloxanes and their structural characterization using X-ray crystallography. Several aluminosiloxanes have been prepared by amine-assisted metathesis and condensation reactions between appropriate aluminium compounds and diphenylsilanediol. The reactions proceeded with the condensation of Ph₂Si(OH)₂ to higher siloxanes containing -OSiPh₂OPh₂SiO- and -OSiPh₂(OSiPh₂)Ph₂SiO- units giving anionic or cyclic aluminosiloxanes. The cyclic complex [AlCl(THF){O(Ph₂SiO)₂}]₂ prepared is the first example of a 12-membered cyclic aluminosiloxane. Interactions of Al(Et)₃