

The disulfonate anions can be used as versatile ligands in the design of metallorganic frameworks, when they are used in combination with metals with variable coordination number. In this way, by using anthraquinone-2,6-disulfonate (AQDS) anions and rare-earth cations, ytterbium in this case, two different structural types have been obtained. The first of them, named layered rare-earth hydroxide, is a new type of crystalline material, very related to the LDH family of compounds. In the compound, cationic layers of ytterbium hydroxides are created, with molecular formula $[\text{Yb}_4(\text{OH})_{10}(\text{H}_2\text{O})_4]^{2+}$. These layers are separated by the AQDS²⁻ anions, which are not coordinated to the rare-earth cations and neutralize the charge. The SO_3^- groups of the ligand are directed towards the sheets, being connected to them by H bonds. The second type is a 3D polymeric structure. Its molecular formula is $[\text{Yb}(\text{OH})(\text{H}_2\text{O})\text{AQDS}]$, with the sulfonate groups covalently coordinated to the metallic atoms. In this structure, a completely inorganic layer is formed, with the ytterbium atoms connected between them through hydroxyl groups, or by OSO bridges, giving rise to a (6,3) honeycomb layer. The layers are joined through the whole ligand molecules, giving rise to a binodal three dimensional network, three- and penta- connected. The two types of materials have been tested as heterogeneous catalysts, showing excellent results in the reactions of oxidation of sulphides and hydrodesulphurization of thiophene.

Keywords: metalloorganic frameworks, heterogeneous catalysis, layered structures

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A new 2D germanate formed by selective coordination of the *trans* 1,2-diaminocyclohexane to Ge atoms

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ICMM9 is a new germanate, with formula $[\text{C}_6\text{H}_{10}(\text{NH}_2)_2\text{Ge}_3\text{O}_6]$. A mixture of *cis/trans* 1,2-diaminocyclohexane has been employed in the synthesis, giving rise to a layered compound in which only the *trans* molecule is present, with the nitrogen atoms covalently bonded to a germanium atom. Double layers are formed, with two different Ge atoms: one is in tetrahedral environment, and the other situated in a two-fold axis, in octahedral coordination. Tetrahedra are forming sharing vertex chains, which give rise, also by sharing vertexes with the octahedral germanium atom, to GeO_2 infinite eight-R containing layers. Every two of them are connected, in a double one, which is a new 2D binodal 4-c net, with Schläfli symbol: $(3.5^3.6^2)_2(3.5^4.8)$. Looking at the inorganic part of the structure, a correlation is established among ICMM9, pyroxene and amphibole structure types, all them having chains of sharing vertex tetrahedra and octahedral atoms. The ability of ICMM9 as heterogeneous catalyst has been examined by using it in different reactions known to be catalyzed by acid sites or basic sites. ICMM9 has proven to possess both centres and due to this bifunctional acid-base character, its activity has been examined in the synthesis of jasminaldehyde, which is usually obtained with the condensation reaction between benzaldehyde and heptanal. ICMM9 achieves 85 % conversion after 24 h of reaction time with selectivity to jasminaldehyde of > 75%.

Keywords: germanate, heterogeneous catalysis, layered compounds

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Structural characterizations of nanoporous In(III)-MOFs

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We prepared a new series of In(III)-based metal-organic frameworks and characterized them using single crystal X-ray diffraction technique. The permanent porosity of these new materials was also confirmed via N_2 and H_2 sorption analysis. Because of the unique eight coordination ability of the central In(III) ions with four polycarboxylate ligands, the new In-MOFs with various aromatic polycarboxylic acids exhibit interesting topological structures revealed by single crystal X-ray diffraction. The polycarboxylic acids such as 4,4'-biphenyldicarboxylic acid (BPDC), 2,6-naphthalenedicarboxylic acid (NDC), and 1,3,5-benzenetricarboxylic acid (BTC) could form multidimensional frameworks. For example, the In-MOF with BPDC formed a doubly-interpenetrated infinite 3D structure with 54% of solvent accessible void. The In-MOFs containing NDC and BTC exhibited catenation-free extended 3D structures having high void volumes estimated by the PLATON software, 60% and 66%, respectively. The NDC-containing In-MOF showed well-defined three independent 1D rectangular channels. The largest channel was solely occupied by water molecules which can be easily replaced by other volatile solvents. Detailed structural properties and gas storage ability of these nanoporous materials will be discussed.

Keywords: framework structures, porous materials, indium compounds

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In situ X-ray diffraction studies of host-guest properties in nanoporous spin crossover frameworks

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The targeted development of functional metal-organic frameworks, is not only a synthetic challenge, but requires parallel characterization of their often complex structure-property relationships. Among strategic efforts to introduce specific function, the incorporation of spin crossover switching centers allows for the development of new advanced functional materials for molecular-scale electronic switching and sensing devices. Recent work has shown that such spin crossover framework materials (SCOFs) can incorporate an additional level of functionality associated with their often porous natures; guest sorption/desorption in such systems, and the associated perturbation of the iron(II) coordination environment and framework structure, provide a unique avenue for investigating the spin crossover phenomenon in the solid state. To this end we have developed *in situ* synchrotron-based powder X-ray diffraction methods to simultaneously probe their guest-dependent structural and magnetic properties.

Keywords: powder and single crystal diffraction, microporous

materials, magnetic behaviour

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Insight into the mechanisms of metal ion binding in hexagonal tungsten bronze

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Tungsten trioxides and their alkali-metal-intercalated products $MzWO_3^+$ show potential for application in electrodes, as ion exchangers, catalysts and the treatment of radioactive waste. Hexagonal tungsten bronze (HTB) features hexagonal channels, of diameter ~ 0.54 nm, that may be useful for selective and reversible binding of metal ions. In particular doping of HTB with molybdenum (Mo-HTB) has been reported to enhance the uptake of Cs^+ and Sr^{2+} . We have conducted a powder diffraction study, using both x-rays and neutrons on a series of $MzHTB$ ($M = Na^+, Mn^{2+}, Ba^{2+}, Ce^{3+}, Pb^{2+}$), including some doped with molybdenum (Mo-HTB) synthesized using hydrothermal methods. Rietveld refinement of the diffraction patterns show that doping with Mo rapidly degrades the crystallinity of HTB by creating a high degree of disorder in the a-b planes, suggesting that the presence of Mo retards the hydrothermal crystallization process. The refinements confirm previous reports of an exchangeable metal ion binding site that displays varying degrees of affinity for the various metal ions studied. The solution binding affinity behaviour of the Mo-HTB's was also investigated for selected ions ($M = Co^{2+}, Gd^{3+}, Ce^{3+}, Ce^{4+}, Tl^+, Pb^{2+}$ doped with respective radiotracer) in a range of concentrations of acid and electrolytes solutions. These results show that the optimum condition for metal ion binding depends not only on the Mo doping level, but also the charge and redox chemistry of the exchange cation. In combination, the structure information and the solution chemistry indicate that the loading capacity of the each metal ion is also dependent on the microstructure of the HTB.

Keywords: inorganic ion exchanger, powder diffraction analysis, tungsten bronze

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Dynamics phase transition of water nanotube cluster stabilized in molecular nanoporous crystal

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Moving water molecules in a limited space within a nanometer-scale region, different from the molecular motion of bulk water, have imposed a remarkable nature affected by strong interfacial interactions with a surrounded outer wall. For examples, it has

been theoretically predicted that water molecules impacted on a hydrophobic interface inside carbon nanotube lead to osmotic water transport with a one-dimensional chain hydrate in its internal space instantly, have a critical point of the water-ice phase transition depending on the tube widths, and freeze at a novel ice polymorph with a multi-layered helix structure. Experimentally, it is demonstrated that melting point of each confined tube-like water clusters constructed from 5- to 8-membered rings, which is not supported to decrease melting points in inverse proportion to the pore sizes by theoretical expectation, increases as the widths of single-walled carbon nanotubes. A tube-like three-layered water cluster, called a water nanotube (WNT), forms into each internal channel space and regulates by hydrogen bonds (H-bonds) with the outer wall. In this study, the structure of WNT confined to the channel pores has been investigated by a neutron structure analysis, and revealed to stabilize by an anchor effect of the structural water. Furthermore, by the neutron scattering, a few water molecules around a center of WNT can definitely move about four times faster than those of bulk water, despite of restricting by H-bonds with the surrounded structural water. Investigation of the behavior of the mobile water molecules within WNT would link the elucidation of a mechanism for structural water bearing on vital functions on the cell surface.

Keywords: water cluster, crystal engineering, hydrogen bond

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A fluorescent two-dimensional Zn(II) framework containing 2,2'-bipyridine-5,5'-dicarboxylic acid

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Metal-organic frameworks (MOFs) are interesting nanoporous materials in the material research area because of their large void spaces and unique geometrical structures. These zeotype materials often maintain thermally robust crystalline frameworks with a permanent porosity. The porosity makes MOF potentially useful for catalysis as well as gas storage. Most MOFs are constructed by a unit of a symmetric molecule, which can bridge neighboring metal ions. Choosing a suitable ligand is an important step to prepare functional MOFs because the structural characteristics and physicochemical properties of MOFs primarily depend on the ligand. Multidentate ligands are usually chosen for preparing MOFs. The ligand, 2,2'-bipyridine-5,5'-dicarboxylic acid (bpdca), can work not only as a bridging molecule but also as a chelating ligand. The two nitrogen atoms of the ligand generally chelate to a metal ion, and two carboxylates can connect other metal ions additionally in one of the three possible modes: 1) solely to nitrogen atoms, 2) only to oxygen atoms from carboxylate groups, and 3) to both atoms. These multiple coordination ways of the bpdca ligand would provide interesting structures with a metal ion and apply for preparing the MOFs containing mixed metal ions with selective preference for an oxygen atom or a nitrogen atom. In addition, the ligand is weakly fluorescent. Thus, the corresponding MOF may possess sufficient fluorescence and the resulting materials are valuable for other applications. Herein, we present we present an infinite two dimensional MOF using 2,2'-bipyridine-5,5'-dicarboxylic acid and zinc nitrate. The compound was hydrothermally prepared and characterized by X-ray crystallography. The compound showed fluorescence in solid state at room temperature.