FA4-MS08-P01

Powder Diffraction Studies of the Ferrocene@ [Al(OH)(bdc)]₆, and Ferrocene@[VO(bdc)].*  
Kirill Yusenko*, Mikhail Meilikhov*, Roland A. Fischer*.  
*Inorganic Chemistry II - Organometallic and Materials, Ruhr-University Bochum, Germany. 
E-mail: roland.fischer@rub.de

The Coordination Polymers (CPs) with permanent porosity and high thermal stability are a unique class of hybrid solid-state materials with bright future [1]. The use of these materials ranges from gas storage, separation and catalysis, to a number of diverse potential applications, including optoelectronics, sensors, smart membranes etc. Also aiming at applications in catalysis we have introduced the solvent-free gas-phase loading of porous CPs via the adsorption of volatile organometallic all-hydrocarbon precursors [2]. We selected MIL-53(Al), [Al(OH)(bdc)], and MIL-47(V), [VO(bdc)], as members of a huge family of porous CPs based on chains of trans-corner sharing octahedral units [MO₆] cross-linked by bdc (terephthalic acid) which results in a 3D structure exhibiting 1D channels along the a axis. We were able to obtain the absorbate structures for ferrocene [3], ferrocenecarboxylate, 1,1’-ferrocenedi-1,1'-dimethyldiiron and 1,1'-dithiethyldiiron inside MIL-53(Al) and MIL-47(V) based on home powder X-ray diffraction (D8-Advance Bruker AXS diffractometer, Debye–Scherrer geometry) as a model compounds for the further applications. All data were indexed in the Imma and Immm space groups. Positions of the guest molecules were obtained by global optimisation using the FOX software [4] starting from rigid “empty” MIL-53(Al) framework and guest molecules as building blocks. Finally, the model obtained was refined by the Rietveld method with Jana2000 [5]. Our attention here was concentrated on the structure solution strategy, packing of the guest’s molecules inside the 1D channels of the host structure; also structural effects of the substitute group in the guest molecule, guest-host and guest-guest interactions were investigated.


Keywords: X-ray powder diffraction; structure determination; framework structures

FA4-MS08-P02

Synthesis and Crystal structure of [BaCu(H₂O)₆(OOC-C₆H₄-COOH)]₆.*  
Fadila Balegroune*, Aouaouche Benkannounb, Achoura Guerhi-Laidoudi, Slimane Dahaouib, Claude Lecomte*.*  
*Laboratoire de Cristallographie-Thermodynamique, Faculté de Chimie,USTHB, BP32, El-Alia, Alger, Algérie.  
^CRM^, CNRS-UPRESA 7036, Université Henry Poincaré, Faculté des Sciences et Techniques, BP 70239, 54506 Vandoeuvres Les Nancy Cedex, France. 
E-mail: fadilabalegroune@yahoo.fr

Recently, research on the synthesis and characterization of coordination polymers is greatly motivated by substantial interest in their fascinating structures with potential applications [1-2]. We selected 1,2-benzenedicarboxylic acid (H₂BDC) as a bifunctional ligand taking into account its multiple coordination sites that may generate structures of higher dimensions. The heterobimetallic title complex has been synthesized from aqueous solution of a mixture of H₂BDC, barium hydroxyde and copper nitrate. The structure has been reported previously[3], but the positions of the H atoms have not been determined. It has now been refined with new intensity data to significantly higher precision and with all H atoms. Moreover, the compound has been reported as a diaqua, dihydrate complex. Our study shows only coordination water molecules.

The asymmetric unit consists of one Ba(II) cation, one Cu(II) cation, two o-phthalate dianions and four coordination water molecules.

The two independent [BDC]²⁻ ligands adopt different coordination mode. One ligand coordinates to four metal centers with μ₂-η²:n² and μ₂-η²:n² bridging coordination modes. The second ligand is linked to three metal centers with μ₂-η²:n² and μ₂-η²:n²-bridging coordination modes respectively. The Cu(II) cation presents a distorted square pyramidal coordination, which involves a CuO₄ octahedron. The CuO₄ octahedron contains three oxygen phthalate and one oxygen water atom. The axial position is occupied by a coordinated water molecule with a long Cu–O length of 2.277(3)Å due to the Jahn–Teller effect of Cu²⁺ ion.

The coordination geometry around the Ba(II) can be best described as a distorted tricapped trigonal prism. Among all the nine coordinated oxygen atoms, three come from coordinated water molecules and the remaining from five [BDC]²⁻ dianions ligands. The BaO₆ polyhedra share faces to form zigzag chains running along the [010] direction via water bridges, and linking o-phthalate atoms. This results in a Ba....Ba separations of 4.210(1) Å. Consequently, the two-dimensional polymeric structure of the title compound consists of BaO₆ chains and CuO₄ polyhedra linked together through asymmetric o-phthalate bridges, the Ba-Cu distances being 4.340(1) and 6.298(1) Å respectively. There is extensive hydrogen bonding in the structure, involving all the coordinated water molecules and the O atoms of the carboxylate groups.


Keywords: MOFs; bimetallic phthalate; structure