

P07.04.33

Acta Cryst. (2008). A64, C409

Concerted aryl interactions in zinc-imidazole – Oxovanadate hybrid organic-inorganic materialsSamroeng Krachodnok¹, Kenneth J. Haller¹, Ian D. Williams²¹Science, Suranaree University of Technology, Chemistry, 111 University Avenue, Muang, Nakhon Ratchasima, 30000, Thailand, ²Department of Chemistry, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong, China, E-mail: roengkra@hotmail.com

Noncovalent interactions involving aromatic sections of molecules are common and ubiquitous, and particularly when acting in concert, rival the robustness of hydrogen bonds. Herein, we report the ability of an imidazole and its derivatives capable of both hydrogen bonding and aromatic interactions in four zinc-imidazole – oxovanadate compounds, namely [ImH]₂[{Zn(Im)₃}₂V₁₀O₂₈]·2H₂O (1), [2-MeImH]₂[Zn(2-MeIm)₄]₂[V₁₀O₂₈] (2), Zn(2-MeIm)₃V₂O₆·H₂O (3), and [Zn(Im)₄]₂[V₄O₁₂] (4), to form extended concerted aryl interaction motifs. The tetrahedral zinc complexes in 1 to form two edge-to-face (EF) C – H···π hydrogen bond interactions in 1D herringbone fashion along the a axis and interact with organic cations acting as guest molecules to construct concerted (OFF)₂ embraces as well as in 2 to form 1D chains of –[Zn(2-MeIm)₄] – (OFF)(EF)₂ – [Zn(2-MeIm)₄] – (EF)₄ – along diagonal axis. In contrast the tetrahedral zinc complexes in 3 engage in concerted (EF)₆ embrace motifs and further bind through four tilted offset aryl rings to generate 2D nets perpendicular to the a axis, and in 4 to form 1D chains of –[Zn(Im)₄] – (EF)₆ – [Zn(Im)₄] – (EF)₂ – [Zn(Im)₄] – (EF)₆ – [Zn(Im)₄] – (EF)₄ – along the c axis with adjacent chains held together by two pairs of N – H···π face-to-face (FF) hydrogen bond interactions to form 2D nets perpendicular to the a axis.

Keywords: concerted aryl interactions, zinc-imidazole-oxovanadate, hybrid organic-inorganic materials

P07.04.34

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Assemblies of three mixed-ligands coordination polymers with novel 3D metal-organic frameworksChing-Chun Yang¹, Chih-Chieh Wang^{1,2}, Gene-Hsiang Lee³¹Soochow University, Chemistry, No 70, LinShih Rd., Shih-Lin., Taipei, Taiwan, 11102, Taiwan, ²E-mail: ccwang@scu.edu.tw, Tel: +886-2-28819471 ext 6824, ³Instrumentation Center, National Taiwan University, Taipei, Taiwan., E-mail: acvb.yang@msa.hinet.net

Three metal coordination polymers having formulas, [Co(dpe)(BDC)·H₂O]_n (1), [Ni(dpe)(BDC)·H₂O]_n (2) and [Zn(dpe)(BDC)·4H₂O]_n (3) (dpe=1,2-bis(4-pyridyl)ethane, BDC= terephthalic acid), have been synthesized and structurally characterized by using single-crystal X-ray diffraction, elemental analysis, infrared spectroscopy and thermogravimetry (TG). Compound (1) and (2) are isostructural and the metal centers (Co(II) and Ni(II)) are distorted octahedral geometric environment bonded to two nitrogen donors of two bridging dpe ligands with *anti*-conformation and four oxygen donors of two bridging BDC²⁻ ligands with bis-chelating coordination mode forming a three-dimensional (3D) interpenetrating diamond-like metal-organic framework (MOF), which exhibit high thermo-stability and keep their crystalline forms up to about 390 °C. In compound (3), the Zn(II) ions is tetrahedral geometric environment bonded with two nitrogen donors of two bridging dpe ligands with *gauche*-conformation and two oxygen donors of two BDC²⁻ ligands with bis-monodentate coordination mode forming a novel extended 3D architecture. The 1D helical chains are constructed through the

connectivity between the Zn(II) ions and *gauche*-dpe ligands, which are intercalated guest water molecules. Adjacent chains are then linked via the bridges of BDC²⁻ ligands adopting a zigzag pattern to complete the 3D MOF. The TG measurement of (3) reveals that the 3D networks exhibit high thermo-stability and keep their crystalline forms up to about 300 °C. The cyclic de- and ab-sorption procedures of water molecules are observed.

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

P07.04.35

Acta Cryst. (2008). A64, C409

Structural characterization and thermal stability of three coordination polymers with 2D MOFsChuan-Yien Liu¹, Gene-Hsiang Lee², Hsin-Ta Wang¹¹National Taipei University of Technology, Department of Molecular Science and Engineering & Institute of Organic and Polymeric Materials, 1, Sec. 3, Chung-hsiao E. Rd., Taipei, Nil, 10608, Taiwan, ²Instrumentation Center, National Taiwan University, Roosevelt Road, Section 4, Taipei, 106, Taiwan, E-mail: cyliu0123@ntu.edu.tw

Three coordination polymers with 2D metal-organic frameworks (MOFs), {[Cd(3-bpd)₂(NCS)₂C₂H₅OH]}_n (1), {[Cd(3-bpd)(dpe)(NO₃)₂](3-bpd)}_n (2), {[Cd(dpe)₂(NCS)₂](3-bpd·H₂O)}_n (3) (3-bpd = 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene), were prepared and fully characterized by infrared spectroscopy, elemental analysis, thermogravimetric analysis, and single-crystal X-ray diffraction. In compound 1, each Cd(II) ion is six-coordinate bonded to six nitrogen donors of four 3-bpd with bis-monodentate coordination mode and two NCS⁻ ligands. The distorted square building blocks connect to each other to generate a 2D non-interpenetrating MOF. Each square unit consists of four Cd(II) atoms and 3-bpd ligands, which form a 4⁴-membered ring structure. In 2, the Cd(II) ion is six-coordinate bonded to six nitrogen donors of two 3-bpd, two dpe and two NO₃⁻ ligands. Both the 3-bpd and dpe ligands adopt bis-monodentate coordination mode to connect the Cd(II) ions forming a 2D, non-interpenetrating parallelogram MOF. Each parallelogram unit consists of four Cd(II) atoms and two 3-bpd ligands, two dpe, which also form a 4⁴-membered ring structure. In 3, the Cd(II) ions is coordinated by four pyridine nitrogen donors of dpe ligands in the basal plane and two NCS⁻ nitrogen donors in the axial sites. The dpe acts as a bridging ligand to connect the Cd(II) ions forming a 2D interpenetrating MOFs by using a square-planar node as the basic unit, which also form a 4⁴-membered ring structure. The free 3-bpd ligands shown in 2 and 3 play an important role on the construction of their 3D supramolecular architecture.

Keywords: framework structures, X-ray structure, coordination polymers

P07.04.36

Acta Cryst. (2008). A64, C409–410

Investigation structure and phase transitions of hybrids inorganic-organic metal vanadatesKittipong Chainok¹, Kenneth J. Haller¹, A. David Rae², Anthony C. Willis², Ian D. Williams³¹Suranaree University of Technology, Chemistry, 111 University Avenue, Muang, Nakhon Ratchasima, 30000, Thailand, ²Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia, ³Department of Chemistry, Hong Kong University of Science

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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

P07.04.37

Acta Cryst. (2008). A64, C410

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

P07.04.39

Acta Cryst. (2008). A64, C410

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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E.Iengo, E.Zangrando, E.Alessio, *Acc.Chem.Res.*, 39, 841-851, 2006.

Keywords: porphyrins, metal complexes, supramolecular systems

P07.04.40

Acta Cryst. (2008). A64, C410-411

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.