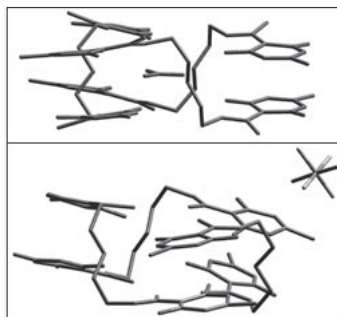


It is very hard to imagine modern supramolecular chemistry without principles of anion binding.¹ Despite all progress in this field, significant anion binding rate in this type of assembly is hard to achieve due to the properties of anions.² Anion binding is interesting because of its potential applications and roles in many biological systems and industrial processes.³ Herein we describe a solid-state study of several supramolecular complexes based on a podand L, containing three potential binding sites, and anions with various geometries and basicities. L adapts its conformation in order to respond to the anion's requests, thus forming two kinds of supramolecular rings with hydrophilic and hydrophobic interiors. Since the assembly is highly anion specific, the occurrence of the complexes in systems with high concentrations of competing anions has been explored. The role of the solvent in structural stabilization will be also discussed.

1) S. O. Kang et al, *Angew. Chem. Int. Ed.* 2006, 45, 7882-7894. 2) P. D. Beer, P. A. Gale, *Angew. Chem. Int. Ed.* 2001, 40, 486-516. 3) J. L. Sessler et al, *Chem. Commun.* 2004, 1276-1277.



Keywords: supramolecular chemistry, template synthesis, anion recognition

P07.04.27

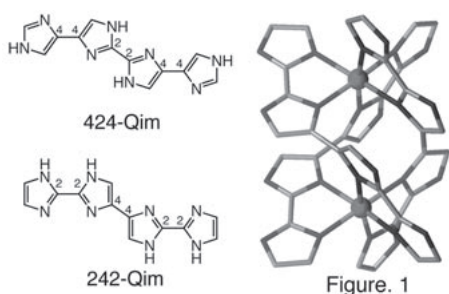
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Triple-stranded helical metal complex of quaterimidazole and its highly-symmetrical network

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In this study, we focused 4,4':2',2'':4'',4'''-quaterimidazole (**424-Qim**), the tetramer of imidazole, and prepared complexes with various metal ions. As a consequence, we have turned out a high potential of **424-Qim** for the versatile and general building block for constructing triple-stranded helical metal complex (triple-helicate) having a multi-dimensional network in the crystal. In this context, we have newly investigated the binding isomer of **424-Qim**, 2,2':4',4'':2'',2'''-quaterimidazole (**242-Qim**) and found that **242-Qim** can also form triple-helicate with two Ni(II) ions (Figure.1). In this presentation, we will report the synthetic method for **242-Qim** and its triple-stranded helical dinuclear Ni(II) complex and highly-symmetrical multi-dimensional network structure of the complex. In the crystal structure, triple-helical structure was constructed by three **242-Qim** molecules that coordinate to two Ni(II) ions with largely twisting structure in the center of their skeletons. Unlike the triple-helicate



composed of **424-Qim**, **242-Qim**-based helicate formed highly-symmetrical two-dimensional sheet structure connected through Hydrogen bonds via counter anions.

Keywords: hydrogen bonding of coordination compounds, supramolecular chemistry, nickel compounds

P07.04.28

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Design of crystalline space for constructing ferroelectric rotators in [Ni(dmit)₂]- salts

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The cation units of aryl ammonium (R-NH₃⁺) - crown ethers in metal dithiolate complex, [Ni(dmit)₂], are one of the useful building blocks to construct supramolecular rotors in crystalline solid. Here, we present the crystal structures, magnetic properties, and ferroelectric properties of (meta-substituted anilinium)(dibenzo[18]crown-6) supramolecular cations associated with the molecular motion in [Ni(dmit)₂] salts (R = F and NH₂). Figure 1 shows the unit cell of (m-F-anilinium⁺)(dibenzo[18]crown-6)[Ni(dmit)₂]-salt viewed along the a-axis. Alternate arrangement of cations and anions was observed along the c-axis. Within the cation layer, the π-plane of m-F-anilinium was interacted with two [Ni(dmit)₂]-anions. The temperature dependent dielectric constant showed a frequency dependent behavior above 240 K, suggesting that the dielectric response was associated with molecular rotation of m-F-anilinium⁺ cations in the crystal. From the electric field - polarization (P - E) measurement at 300 K, a hysteresis behavior was confirmed. The relation between molecular motion and ferroelectric behavior will be mentioned.

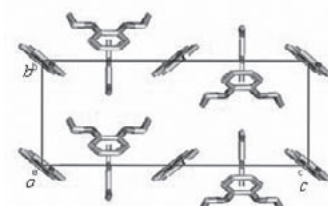


Fig 1. Molecular structures of (m-F-anilinium⁺)([18]crown-6)[Ni(dmit)₂]. Unit cell viewed along the a-axis.

Keywords: ferroelectric properties, supramolecular structure, metal coordination complex

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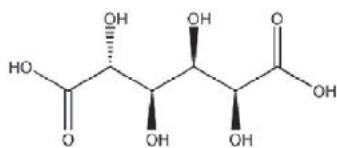
The diabolecules: Some unexpected copper clusters

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Saccharic acid (sacc, I) is a chiral dicarboxylic acid which, when deprotonated, has the ability to bridge metal centres, which can lead to the formation of chiral coordination networks¹. In efforts to further explore the coordination chemistry of this ion we combined it with metal ions in the presence of co-ligands such as 1,10-phenanthroline. With two coordination sites on the metal centre blocked by the terminal 1,10-phen we hoped that a macrocyclic species may form with a chiral hydrophilic void at the centre and aromatic groups on the outside of a macrocyclic ring. A mixture of Cu(NO₃)₂, KHSaccharate and 1,10-phen afforded blue crystals of

two distinct shapes. X-ray diffraction has shown these two crystals to be different forms (orthorhombic and cubic) of a cationic cluster of composition $[\text{Cu}_{21}(\text{sacc})_6(\text{phen})_{12}]^{12+}$. The penta-anionic saccharate adopts a different binding mode in each of the copper clusters. The spaces between the copper clusters are also of interest. The cubic form has a cell length of 73.7 Å and each unit cell contains a void with an approximate volume of $30,000\text{Å}^3$.

I. Abrahams, B.F.; Moylan, M.D.; Orchard, S.D.; Robson, R., *Angew Chem Int Ed*, 2003, 42, 1848.



Keywords: coordination clusters, X-ray crystallography of coordination compounds, inorganic compounds

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A novel chiral metal-organic framework that catalyses asymmetric reaction in the chiral open space

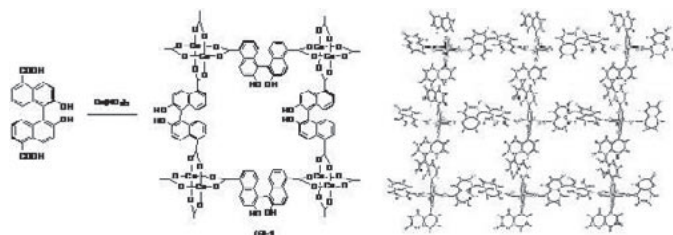
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A novel chiral metal-organic framework, $[\text{Cu}_2(5,5'\text{-BDA})_2]$ (R)-1 was synthesized by treating (R)-2,2'-dihydroxy-1,1'-binaphthalene-5,5'-dicarboxylic acid (5,5'-H2BDA) with Cu(II) ion, in which asymmetric ring opening reaction of epoxide with amine proceeds efficiently under solvent-free conditions.[1] In (R)-1, each Cu (II) ion is coordinated by four carboxylate oxygen atoms of (R)-1 and each pair of Cu(II) ions is bridged by four carboxylate groups to form 2D dinuclear square grid coordination networks with a Cu...Cu distance of 15.62(2) Å; the void space is filled by one MeOH and two H₂O guest molecules through hydrogen bonding.

[1]K. Tanaka, S. Oda, M. Shiro, *Chem. Commun.*, 2008, 820-822.



Keywords: inclusion chemistry, host-guest complexes, crystal structures

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The 1-D polymeric dimorphism of copper(I) thiocyanate complexes containing MTA ligand

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Two 1-D polymeric chains of $[\text{Cu}(\mu\text{-MTA})(\mu\text{-1,3-SCN})]_n$ (1) and $[\text{Cu}(\text{MTA})(\mu\text{-1,1,3-SCN})]_n$ (2) complexes (MTA = 3-mercapto-4-

methyl-4H-1,2,4-triazole and n = infinite) have been synthesized and characterized. The structure of complex(1) adopts a 1-D polymeric chain which consists of $[\text{Cu}(\mu\text{-MTA})_2(\mu\text{-SCN})(\mu\text{-NCS})]$ subunits, bridged by pairs of $\mu\text{-S}$ exocyclic thiones of two MTA molecules and by $\mu\text{-S}$ and $\mu\text{-N}$ atoms of thiocyanate groups end-to-end, $\mu\text{-1,3-SCN}$, producing a linear 1-D chain of double MTA and double SCN bridges along the c axis. Each Cu atom has a distorted pseudo-tetrahedral environment. It is coordinated by two $\mu_2\text{-S}$ atoms of the MTA ligands and one $\mu\text{-N}$ atom and one $\mu\text{-S}$ atoms from different thiocyanate groups. The 1-D chain structure of this complex is governed by the weak intra-molecular H-bonding interaction of N(1)-H(1)---N(4) and inter-molecular interactions of S(2)---N(2), generating 2-D network interactions in the ac-plane. The structure of complex(2) adopts a 1-D staircase-like chain containing $[\text{Cu}(\text{MTA})_2(\mu_2\text{-SCN})(\mu\text{-NCS})]$ subunits. Each Cu atom has a pseudo-tetrahedral geometry arising from one terminal thione-S atom of a MTA ligand, two $\mu_2\text{-S}$ atoms from two $\mu\text{-1,1,3-SCN}$ thiocyanato ligands and one $\mu\text{-N}$ atom from a third $\mu\text{-1,1,3-SCN}$ thiocyanate group. Two $\mu_2\text{-S}$ atoms bond to another Cu atom forming the Cu_2S_2 dimeric subunit. A pairs of anti-parallel thiocyanate groups bridges a pairs of Cu atoms to form an eight-membered $\text{Cu}_2(\text{SCN})_2$ parallelogram macrocycle. This macrocycle shares the Cu-S edges with the Cu_2S_2 four-membered ring to form a 1-D staircase-like chain, $[\text{Cu}_2(\text{SCN})_2]_n$ lying parallel to the a-axis. The crystal packing of this complex is governed by inter-molecular H-bonding interactions of N(1)-H(1)---N(2) generating a 2-D network sheet in the ac-plane.

Keywords: copper(I) complexes, dimorphism, 3-mercapto-4-methyl-4H-1,2,4-triazole

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Novel coordination polymers generated from 2,2-dipyridyldisulfide and CuCl_2

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Coordination polymers have infinite frameworks constructed from metal ions and organic ligands. Coordination bonds play an important role in the construction of extended structures as well as other weak chemical bonds such as hydrogen bonds, van der Waals interactions, etc. This synthetic chemistry is like playing with building blocks, where one can control the coordination frameworks by modifying the geometries of the components. Generally, the formation process proceeds automatically and, therefore, is called a self-assembly process. In particular, crystalline coordination polymers are of great use because their structures can be exclusively determined by X-ray crystallographic methods, and have demonstrated that they have unique network motifs, structural diversity, and are available for physical and chemical properties ranging from magnetism, conductivity, and optical properties to porous functions such as adsorption, exchange, separation, and catalysis. We report here the supramolecular structure and thermal properties of two new compounds of copper complexes with 2,2'-Dipyridyldisulfide ligand.

Keywords: coordination polymers, disulfide, supramolecular chemistry