

investigating the chemistry of bismuth oxide nanoparticles.

Keywords: main-group elements, bismuth compounds, clusters in coordination complexes

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Solvent driven association and dissociation of the hydrogen-bonded protonated decavanadate dimer

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When crystallized with tetraalkylammonium cations, the decavanadate anions form monomers, dimers and linearly catenated polymers. The dimers of triprotonated anions, which are linked by six hydrogen-bonds, are observed in the crystals obtained from the mixed solvents of water and aprotic protophobic solvents (e.g. acetone and 3-pentanone). The monomers of tetraprotonated anions, which forms hydrogen-bond complex with solvent molecules, are observed in the crystals precipitated from the mixed solvents of water and aprotic protophilic solvents (e.g. 1,4-dioxane and tetrahydrofuran). In order to examine whether these hydrogen-bond aggregates in the crystals exist also in the solution, we carried out systematic SAXS experiments of tetraamylammonium decavanadate in the mixtures of aprotic protophobic and aprotic protophilic solvents. Solutions of tetra-n-amylammonium decavanadate in the mixtures of acetone and 1,4-dioxane or pyridine were subjected to the SAXS experiment at 12ID-C beamline in APS. Radius of gyration of 100% acetone solution calculated from the Guinier plot was 5.8Å and that of the solution in (20:80) mixture of acetone and 1,4-dioxane was 3.6Å. These values agree well with the values calculated from the crystal structure, 5.1Å for the dimer and 3.5Å for the monomer. The acetone/pyridine system showed a similar trend. These SAXS results clearly demonstrate that the association and dissociation of hydrogen-bonded protonated decavanadate dimer is controlled by the nature of the solvent.

Keywords: polyoxometalates, SAXS, hydrogen bonds

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Is 2.07 Å the record for the shortest Pt-S distance? Two questionable experimental structures

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The available crystal structures of the very similar compounds $(\text{Ph}_3\text{P})_2\text{Pt}(\text{m-S})_2\text{Pt}(\text{PPh}_3)_3$, 1, [1] and $(\text{Ph}_2\text{PyP})_2\text{Pt}(\text{m-S})_2\text{Pt}(\text{PPh}_2\text{Py})_2$, 2, [2] raise intriguing questions about their geometrically different Pt_2S_2 cores. In particular, the independent Pt-S distances in 1 are the shortest ever reported for this kind of bond and also the trans-annular S-S separation of 2.69 Å is dramatically shorter than that in 2 (=3.01 Å). This apparent case of structural isomerism could be in principle due to a different amount of electronic coupling between the sulfido bridges. This topic is part of our ongoing interests [3], hence we decided a careful examination of the problem. The conclusion is that complex 1 has been incorrectly formulated and its actual nature

is $[(\text{Ph}_3\text{P})_2\text{Pt}(\text{m-OH})_2\text{Pt}(\text{PPh}_3)_3](\text{BF}_4)_2$, 3. While the hypothesis was verified, also the available crystal structure of the latter complex [4] was found to be in error. Although suspiciously similar, the unit cells of 1 and 3 are not equal and, in particular, the ratio between the volumes is 2:1. Matrices transforming one cell into the other are readily devised, hence leading to the conclusion that the two compounds are the same but the structure of 3 was determined by using only one half of the collectable diffraction data. The new synthesis, crystallization and X-ray analysis of 3 fully support the working hypothesis and dismiss any further conjecture about the inconsistent Pt_2S_2 core in 1.

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Keywords: S-S coupling, structure revision, geometry-electronic structure relations

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Solid state packing behaviour in pseudo Vaska-type complexes

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Pseudo Vaska-type complexes, $\text{trans-}[M(X)(Y)(\text{ZR}_3)_2]$ ($M=\text{Rh, Ir}$ if $X=\text{CO, NCS, NCO}$ and $M=\text{Pt, Pd}$ if $X=\text{Cl, Me, Y}=\text{halogen, Z}=\text{Group 15 atom, R}=\text{aryl, alkyl}$) can undergo various key step catalytic reactions, e.g. oxidative addition, reductive elimination, substitution, insertion, etc., yielding them as well-behaved model complexes for various catalytic systems. These complexes are easy to synthesize and can be investigated structurally due to their favorable thermal stability. Data obtained from solid-state investigations can then be correlated with solution IR and 31P NMR spectroscopy for the CO and PR_3 ligands to evaluate different ligand effects. However these complexes are also well known for their tendency to be statistically disordered, thus decreasing accuracy of the solid-state data in some cases leading to incorrect correlations. Complexes represented are part of a study to determine which factors govern the packing disorder.

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Keywords: vaska-type complexes, catalysis, disorder

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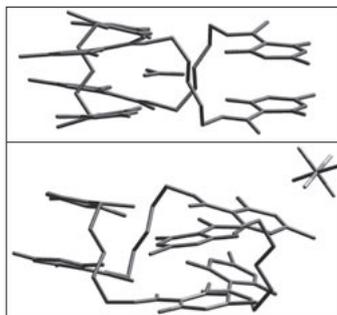
Anion directed self-assembly of a flexible ligand into highly porous and symmetrical organic solids

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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.

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Keywords: supramolecular chemistry, template synthesis, anion recognition

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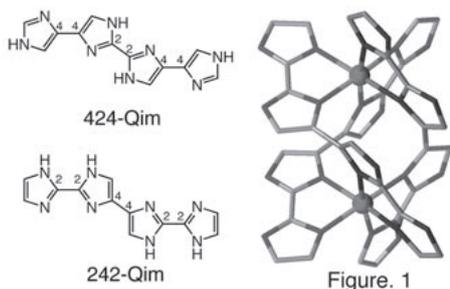
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Triple-stranded helical metal complex of quaterimidazole and its highly-symmetrical network

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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

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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.

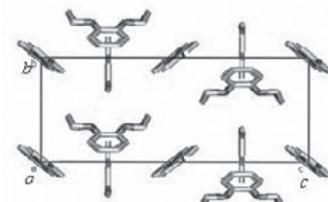


Fig 1. Molecular structures of (m-F-anilinium⁺)([18]crown-6)[Ni(dmit)₂]. Unit cell viewed along the a-axis.

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