

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 Pt₂S₂ 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 Pt₂S₂ core in 1.

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Solid state packing behaviour in pseudo Vaska-type complexes

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Pseudo Vaska-type complexes, $\text{trans-[M(X)(Y)(ZR}_3)_2]$ (M=Rh, Ir if X=CO, NCS, NCO and M=Pt, Pd if X=Cl, Me, Y=halogen, Z=Group 15 atom, R=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 PR₃ 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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Anion directed self-assembly of a flexible ligand into highly porous and symmetrical organic solids

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