

code: (i)  $-x+1, -y+1, -z$ ]. These structural parameters imply a perfect square-planar geometry around the palladium centre. The Pd-Cl and Pd-C lengths are 2.3052(9) Å and 2.035(2) Å, respectively. These bond lengths are comparable to those observed in literature [3]. In addition, the Pd-Cl bond in the complex is somewhat shorter than the average of 2.33(4) Å calculated for 2151 Pd-Cl lengths in 1306 complexes reported to the Cambridge Structural Database [4,5]. The Pd-Cl lengths in these 1252 complexes span the range 2.222-2.516 Å; therefore, the Pd-Cl separation in the investigated complex is within the expected range. The equivalent Pd-C lengths are consistent with Pd-C single bonds [3].

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Keywords: N-heterocyclic carbenes, palladium, crystal structure

## P07.01.20

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### Structural studies on Ag(I) N-heterocyclic carbene complexes: From monomers to polymers

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N heterocyclic carbenes (NHCs) have shown to equal, if not exceed, phosphines in their ability to bind to many transition metal complexes. Due to this bonding strength, the synthesis of NHC complexes for catalytic applications has received a great deal of interest. Ag(I) carbene complexes are good carbene transfer agents for the synthesis of Ni, Pd, Pt, Cu, Au, Rh, Ir and Ru carbene complexes. A revision of the literature shows that N heterocyclic carbene complexes of silver are able to generate very complex bonding motifs in the solid state, especially with halide anions.[1] In the course of our current studies on group 10 NHC catalysts, we have prepared a series of Ag(I) N-heterocyclic carbenes (NHCs) by reaction of the corresponding N,N disubstituted imidazolium salts with silver oxide in dichloromethane. These carbenes, of general formula (NHC)AgBr, differ in the substituents at the nitrogen atoms. In this report, we will compare three different molecular structures, determined by X ray diffraction methods, of (NHC)AgBr complexes bearing, at the nitrogen atoms, two benzyl groups (1), a benzyl and a mesityl group (2), or two first generation poly(benzyl ether) dendrons (3). Complex 1 is monomeric with an NHC-Ag-Br angle close to the linearity and a Ag-Br distance of 2.51 Å. Complex 2 consists of a dimeric structure, with an asymmetrical bridge and a NHC-Ag-Br angle of 135 deg and Ag-Br distances of 2.61 to 2.77 Å. Complex 3 has an unprecedented polymeric structure constituted by a zigzag chain of alternating silver and bromo atoms (Ag-Br distance = 2.66 Å) with pending carbene ligands coordinated to the Ag centers (NHC-Ag-Br angle of 129.1 deg).

[1] Garrison, J. C., Youngs, W. J., (2005) *Chem. Rev.* 105, 3978-4008.

Keywords: silver compounds, polymer structure, dendrimers

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### Structural analysis of the rare earth metal hydride complexes

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Rare earth metal hydride complexes are fundamental components in a wide range of stoichiometric and catalytic reactions. Heterometallic Mo-Y<sub>4</sub> hydride complex can be proceeded hydrogen addition reaction without degradation of a single crystal form. Moreover, it is thought to exist lattice H<sub>2</sub> in the Mo-Y<sub>4</sub> crystal lattice. In order to clarify the mechanism of the hydrogen addition reaction the determination of the position of lattice H<sub>2</sub> in the crystal lattice is studied by the precise charge density study of Mo-Y<sub>4</sub> complex in SPring-8. The crystals had to be encapsulated in the glass capillary due to the volatile solvent, toluene, being unstable in air, and being exposed in hydrogen gas. Single crystal X-ray diffraction measurements in as high counting statistics as possible were carried out by imaging plate detector to ensure data accuracy in the maximum-entropy method (MEM) analysis. The determined lattice structures are monoclinic  $P2_1/n$ ,  $a = 13.25 \text{ \AA}^3$ ,  $b = 30.41 \text{ \AA}^3$ ,  $c = 18.11 \text{ \AA}^3$ ,  $\beta = 91.9^\circ$  (without hydrogen gas) and  $a = 13.27 \text{ \AA}^3$ ,  $b = 30.79 \text{ \AA}^3$ ,  $c = 17.84 \text{ \AA}^3$ ,  $\beta = 92.3^\circ$  (under hydrogen gas exposure). The reliability factors of structure refinement by SHELXL were  $R = 4.80 \%$  ( $R_{\text{free}} = 4.82 \%$ ) and  $R = 6.59 \%$  ( $R_{\text{free}} = 7.22 \%$ ), respectively. By the MEM charge density, the hydride ligands are clearly identified and the mechanism of the hydrogen addition reaction will be described with a help of the further advanced technique, that is, the MEM electrostatic potential imaging

Keywords: crystallographic analysis, maximum entropy method, metal-hydrogen interactions

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### Structural challenges of giant bismuth oxo-diketonate clusters

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New method for the preparation of polymetallic oxo-diketonates has been developed. Fluorinated bis(gem-diol), 1,1,1,5,5,5-hexafluoropentane-2,2,4,4-tetraol, can be obtained by hydration of hexafluoroacetylacetone (Hhfac). We have shown that in the presence of proton acceptor the tetraol is capable to act as a controlled source of both diketonate and oxo-groups by undergoing a facile cleavage of the two C-O bonds. The first bismuth oxo-diketonate, Bi<sub>9</sub>O<sub>7</sub>(hfac)<sub>13</sub>, has been obtained in quantitative yield using triphenylbismuth as a starting material in reaction with tetraol. The structure of the bismuth oxo-diketonate features metal atoms in two distinctly different chemical and coordination environments: the [Bi<sub>6</sub>O<sub>7</sub>] central oxo-core and three Bi(hfac)<sub>x</sub> arms attached to its periphery. In coordinating solvents, this molecule irreversibly dissociates to give Bi(hfac)<sub>3</sub> and high-nuclearity bismuth oxo-diketonates. A giant oxo-cluster [Bi<sub>38</sub>O<sub>45</sub>(hfac)<sub>24</sub>] has been isolated and fully characterized. Its [Bi<sub>38</sub>O<sub>45</sub>]<sup>24+</sup> core capped by 24 diketonate ligands, has a size larger than 2 nm and may serve as a model for

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  $\text{Pt}_2\text{S}_2$  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  $\text{Pt}_2\text{S}_2$  core in 1.

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

### P07.02.25

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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 <sup>31</sup>P NMR spectroscopy for the CO and PR<sub>3</sub> 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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