

(II) has a distorted square-pyramidal coordination, involving two bridging O and two N atoms from a bisN,N'-(salicylidene)-1,3-propanediaminato (SALPD) ligand as basal plane. One O atom from a dimethylformamide group for (I) and one O atom from a dioxane molecule for (II) complete the coordination number to five. The inner Cu ions have also irregular square-pyramidal environment, consisting of two bridging O atoms from a SALPD ligand, two bridging N atoms from two azido groups and one N atom from the third azido group. The Cu-N-Cu angles in the central azido bridges are 102.5(2)° for (I) and 102.1(3)° for (II). In (I) and (II), Cu-O-Cu angles in the O bridges have values 104.8(2)° and 105.6(2)°, respectively. The Cu-Cu distance in the azido bridge is 3.1462(7) Å for (I) and 3.1156(15) Å for (II). The Cu-Cu distances in the O bridges are 3.1501(7) Å and 3.1582(15) Å in (I) and (II), respectively. Crystal data is given below: (I) [Cu(N₃)₂Cu(C₁₇H₁₆N₂O₂)(C₃H₇NO)], Triclinic *P*-1, 9.211(1), 10.394(2), 12.941(1) Å, 77.831(1), 92.293(2), 71.104(1)°, $I_{obs} > 2\sigma(I) = 3194$, $R = 0.037$; (II) [Cu(N₃)₂Cu(C₁₇H₁₆N₂O₂)(C₄H₈O₂)], Monoclinic *P*2₁/*n*, 11.292(1), 15.413(1), 13.610(1) Å, $\beta = 97.402(5)^\circ$, $I_{obs} > 2\sigma(I) = 2575$, $R = 0.07$. Enraf-Nonius CAD-4, $\omega/2\theta$ scans, MoK α 0.71073 Å

Keywords: copper complexes, copper coordination compounds, structures of tetranuclear copper complexes

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Crystal structure of platinum 2-methyl- and palladium 2,4-dimethyl-8-hydro-selenoquinolate

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In the course of study of complexing activity of 8-hydro-selenoquinoline and comparative investigation of structure of analogous internal complexes platinum 2-methyl-8-hydro-selenoquinolate Pt[C₉H₅(CH₃)SeN]₂ (I) and palladium 2,4-dimethyl-8-hydro-selenoquinolate Pd[C₉H₄(CH₃)₂SeN]₂ (II) have been synthesized. The crystal structure of complex I and II is formed by neutral asymmetric molecules in which central atom is connected bidentatically (Se,N) with two 8-hydro-selenoquinoline ligands. The presence of methyl groups in the position 2 causes the steric hindrance to the formation of planar complexes and gives use both to the changes in the structure of coordination polyhedrons: *trans*-square (2Se+2N) (I) and *cis*-square (2Se+2N) (II). The squares (2Se+2N) occur to be somewhat tetrahedrally distorted: the diagonal angles SePtSe 160.05(5)°, NPtN 178.06(38)° for (I), SePdN 163.08(14)°, 163.14(14)° for (II). Dihedral angles between the SeMN/SeMN coordination planes are 19.67(1)° (I) and 159.82(5)° (II), between quinoline planes - 94° (I) and 102° (II). The bonds M-Se are covalent. The transition of *trans*- to *cis*-coordination causes the weakening of the M-N bond only. The bond strength in the analogous complexes M(C₉H₆NSe)₂, M[C₉H₅(CH₃)SN]₂ (M=Pt, Pd) have been compared. Crystal data: I-Monoclinic, space group *P*2₁/*c*, *a*=12.5661(7), *b*=7.8072(5), *c*=18.6684(12) Å, β =97.328(2)°, *V*=1816.5(2) Å³, *Z*=4, R =0.0629, wR_2 =0.1438 for 4086 reflections; II-Monoclinic, space group *P*2₁/*n*, *a*=9.0092(4), *b*=16.3290(7), *c*=14.1073(6) Å, β =106.710(2)°, *V*=1987.7(2) Å³, R =0.0499, wR_2 =0.1242 for 4495 reflections (diffractometer Bruker-Nonius KappaCCD, λ MoK α).

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Keywords: platinum compounds, palladium compounds, selenium organic compounds

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Indenocorannulene: Molecular geometry, solid state packing, and metal binding

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Nonplanar polyaromatic hydrocarbons are unique molecules in which inside and outside surfaces exhibit different chemical and physical properties. Those include a novel class of bowl-shaped carbon-rich polyarenes that map onto the surfaces of fullerenes and therefore referred to as fullerene fragments or buckybowl. Systematic investigation of their properties is a new area of research that should stimulate the use of curved-surface carbon molecules in materials synthesis. Herein as part of our broad investigation of the structures and reactivity of bowl-shaped polyaromatic hydrocarbons we report the molecular geometry, solid state packing and ligating properties of indenocorannulene, C₂₆H₁₂. The structure of this polyarene will be compared with the parent corannulene and other buckybowl to evaluate effects of bowl size and curvature on the solid state packing. Then the reactivity of the curved unsaturated pi-carbon surface of indenocorannulene toward di- and trinuclear electrophilic metal complexes will be discussed. The structural effects of coordination on the geometry of bowl and metal complexes will be revealed.

Keywords: metal coordination compounds, arenes, intermolecular interactions and packing

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Quaternions, molecular motion and diffuse scattering

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For molecules which may be considered as independent rigid bodies oscillating with large angular amplitudes, the algebra of quaternions offers a neat method for calculating diffuse X-ray scattering [1]. This is because rotations may be combined in a relatively simple way. For an ensemble of independent angular simple harmonic oscillators with a Boltzmann distribution of energies, the probability distribution of angular displacements is Gaussian [2]. The latter distribution may be used to smear the molecular form factor to calculate the influence of librations on the X-ray scattering. The effect of translational vibrations may also be included by applying the well-known Debye-Waller factor, $[1 - \exp(-2M)]$, where *M* is proportional to the mean square displacement. Three globular molecular crystals of increasing molecular size have been chosen as examples to illustrate the method: sulphur hexafluoride (SF₆), adamantane (C₁₀H₁₆) and fullerene (C₆₀). In maps of diffuse X-ray scattering, librations tend to flatten peaks and to raise minima. This quaternion technique can be developed further for anisotropic librations and for larger molecular systems, such as proteins, in which whole assemblies of atoms may be moving through appreciable angles. We thank Dr Sandra Lonie and Dr Lucy MacNay for calculations of thermal motion.

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380-386.

[2] M Moore, PhD Thesis, vol. 2, University of Bristol (1973).

Keywords: diffuse scattering, molecular crystals, rotational disorder

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Photo induced isomerization reaction and phase transition of an organo-dirhodium dithionite complex

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An organo-dirhodium dithionite complex [$\{\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)\}_2(\mu\text{-CH}_2)_2(\mu\text{-O}_2\text{SSO}_2)$] (**1**) shows fully reversible photochromism in which one of four terminal oxygen atoms in the side-on type dithionite $\mu\text{-O}_2\text{SSO}_2$ moiety is converted to a bridged one to produce geometrical isomer form $\mu\text{-OSOSO}_2$ by visible light irradiation in crystalline-state [1]. An analogous dirhodium complex [$\{\text{Rh}(\eta^5\text{-C}_5\text{Me}_4\text{Et})\}_2(\mu\text{-CH}_2)_2(\mu\text{-O}_2\text{SSO}_2)$] (**2**) that contains $\eta^5\text{-C}_5\text{Me}_4\text{Et}$ instead of $\eta^5\text{-C}_5\text{Me}_5$ has similar crystal structure with (**1**). We have tried to analyze the photo-isomerization process of the dirhodium complex (**2**) in single crystals by X-ray structure analyses [2]. The photo-irradiation wavelength, intensity and time dependencies of the photo-generated isomer ratio were measured for (**2**). By using Xeon light passing through band pass filters, it was revealed that the light not on absorption peaks but on absorption tail produced photo-generated isomers. This should be owing to that the light on the absorption peak could not pass through the crystal. At the initial stage of the photo-isomerization process, it was revealed that the cell volume becomes half by the light irradiation. Structure analyses were made for the crystals before and after the photo induced phase transition, indicating that $\eta^5\text{-C}_5\text{Me}_4\text{Et}$ rings are positionally disordered for the original crystals but is ordered for the photo irradiated crystals which is isostructure to (**1**) with space group $P2_1/n$.

1) H. Nakai, et al., *Angew. Chem. Int. Ed.*, 2006, 45, 6473-6476.

2) K. Toriumi, et al., *AsCA 07*, Taipei, Taiwan, 2007/11.

Keywords: solid state reaction, photo chemical reaction, phase transition

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Atomic displacement parameters and specific heat of α -glycine polymorph between 10 and 298 K

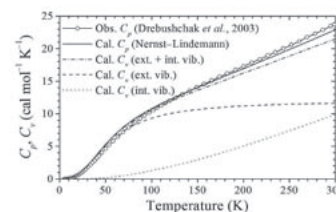
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Synchrotron data to 0.5 Å resolution of the α -polymorph of glycine were collected between 10 and 298 K at the two synchrotron sources in Japan, KEK Photon Factory (PF) and SPring-8. Data from KEK-PF and SPring-8 were processed with RAPID AUTO and DENZO/SCALEPACK and refined with SHELXL-97, yielding comparable data quality. Simultaneous analysis of the multi-temperature atomic displacement parameters (ADPs) were performed to obtain the

libration and translation frequencies [1]. The six external vibration frequencies from normal mode analysis and the intramolecular vibration frequencies from *ab initio* calculations were used together with the molecular Einstein, Debye, and Nernst – Lindemann models to estimate heat capacities C_v , C_p and found to be in fair agreement with C_p from calorimetric measurements [2]. Figure below shows the results obtained from SPring-8.

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Keywords: atomic displacement parameters, specific heat, polymorphs

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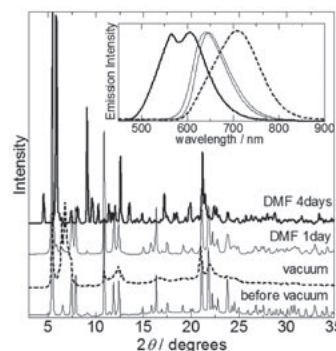
A structural study on a nano-porous vapochromic Pt complex

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One-dimensional stacking Pt-diimine complexes have attracted much attention because of their characteristic luminescence based on the Pt-Pt interaction and potential for a chemical sensors [1,2]. Our attention have been focused on the properties of $\text{Pt}(\text{CN})_2(\text{dcbpy})$ ($\text{dcbpy} = 4,4'$ -dicarboxy-2,2'-bipyridine) which has nano-size pores and exhibits interesting vapochromism [3]. In this paper, we discuss the vapochromism on the basis of powder X-ray diffraction (PXRD). Fig. 1 shows the PXRD patterns in vacuum and DMF (N,N -dimethylformamide) vapor. Observed PXRD patterns indicate that the porous structure could be broke down by removal of crystal water in vacuum and then regenerated on exposure to DMF vapor. The emission peak also shifted from 647 nm to 710 nm and returned to 640 nm. Further exposure to DMF vapor induced the structural phase transition and a new emission peak appeared at 560 nm. These results suggest that the vapochromism of this complex originates from the structural flexibility and nano-sized pore which can absorb various organic vapors.

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Keywords: coordination chemistry compounds, luminescence, crystal synthesis and phase transitions