

related problem, the field of Molecular Magnetism is currently shifting towards more complicated systems. One direction has been opened by the observation of slow relaxation of the magnetization in 1D systems (called Single Chain Magnets or SCMs). Synthetic efforts are devoted to the development of new systems SCMs that can help us understanding the physical background that lies beneath this phenomenon. In this contest several groups have developed new tools allowing for the engineering of both magnetic and structural properties. Here we discuss some opportunities offered by the Metal Nitronitroxide strategy. In particular the experimental and theoretical work developed on finite-size effects revealed itself a key point. We describe the rational strategy that allowed creating the first rare-earth based SCMs. We show that we can freely substitute the metallic centres without structural alterations, thus tuning of the magnetic properties. This affords a useful information on the key parameters that rule SCMs.

Keywords: molecular magnets, superparamagnets, synthesis of new materials

### P07.10.61

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#### Synthesis, crystal structure, and magnetic properties of trioxotriangulene stable neutral radical

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Synthesis and elucidations of molecular and electronic-spin structures of novel stable neutral radical derivatives are fundamentally important issues for the development of spin-mediated molecular functional materials. Oxophenalenoxyl derivatives are new persistent neutral radicals with two oxygen-atoms in the phenalenyl skeleton. Importantly, electronic-spin structures of these neutral radicals are intrinsically different in the topological symmetry from that of the phenalenyl. Furthermore, by controlling the redox process, these radicals show the reversible topological switching of the spin-delocalized nature. The electronic features enabled us to investigate the redox-based spin diversity and the molecular crystalline secondary battery. In this work, as the two-dimensional pi-extended derivative of 6-oxophenalenoxyls, we have synthesized and isolated trioxotriangulene neutral radical derivative having C<sub>3</sub>-symmetric and 25pi-conjugated molecular/electronic structures. The electronic-spin structure and redox ability of this neutral radical have been revealed by X-ray crystal structure analysis (Figure), ESR and magnetic measurements, and DFT calculations.



Keywords: ESR, magnetic materials, radicals

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#### Hemidirected novel lead(II) azide complex of 2,6-diacetylpyridine dihydrazone

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The chelating behaviour of 2,6-diacetylpyridinedihydrazone (L) towards lead(II) with azide ion has been characterized by means of elemental analyses, FTIR and determined by single-crystal X-ray analysis. The title compound, Pb(C<sub>9</sub>H<sub>13</sub>N<sub>11</sub>) (I), was crystallized in the monoclinic space group C2/c. Title complex exhibits the expected coordination sphere with five nitrogen atoms coordinated to the central lead(II) and shows distorted trigonal bipyramid coordination geometry. The coordination chemistry of title complex exhibits a gap around the lead(II) ion, occupied possibly by stereochemically active electron lone pair on lead(II) which results in a hemidirected lead complex. It has been obtained from the antimicrobial activities of the free ligand and its lead(II) complex that the antimicrobial activity of the complex is higher than the free ligand.

Keywords: biological activity, X-ray Diffraction, crystal structure

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#### Novel route to synthesis copper halide with Cu<sub>2</sub>S<sub>2</sub> core and its crystal packing

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The novel route to synthesis of [Cu<sub>2</sub>{·-S=C(NH)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>}<sub>2</sub>{S=C(NH)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>}<sub>2</sub>Br<sub>2</sub>] or (I) was simply. Single crystal X-ray structure analysis and FT-IR spectra confirmed its components. The structure revealed a dimeric monobromide bis(ethylenethiourea)copper(I) complex with in the monoclinic space group C2/c. The final residual factor (R) is 0.0285. The Cu<sub>2</sub>S<sub>2</sub> core of the dimer is lozenge with C-S distances of 2.375(1) and 2.408(1) Å, a Cu-S-Cu angle of 70.81(3)°. The crystal packing is stabilized by extensive N-H...Br interactions and weak N-H...S interactions.

Keywords: X-ray crystal structure, Cu<sub>2</sub>S<sub>2</sub> lozenge core, crystal packing

### P07.11.64

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#### Crystal structures of two new tetranuclear copper complexes based on Schiff-base ligands

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Two new double azido-bridged tetranuclear copper complexes were synthesized, namely Bis{μ-[bisN,N'-(salicylidene)-1,3-propanediaminato-N,N'-diformamidocopper(II)]azido(μ-azido)copper(II)} (I) and Bis{μ-[bisN,N'-(salicylidene)-1,3-propanediaminato copper(II)]azido(μ-azido)copper(II)} dioxan (II), and their crystal structures were determined. In both compounds two doubly oxygen-bridged dinuclear Cu complexes are bridged in a head-to-head fashion via two azido groups. The terminal Cu ion in (I) and

(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(N<sub>3</sub>)<sub>2</sub>Cu(C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>)(C<sub>3</sub>H<sub>7</sub>NO)], 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(N<sub>3</sub>)<sub>2</sub>Cu(C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>)(C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>)], Monoclinic *P*2<sub>1</sub>/*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 $\alpha$  0.71073 Å

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

## P07.11.65

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

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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-selenoquinolinate Pt[C<sub>9</sub>H<sub>5</sub>(CH<sub>3</sub>)SeN]<sub>2</sub> (I) and palladium 2,4-dimethyl-8-hydro-selenoquinolinate Pd[C<sub>9</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub>SeN]<sub>2</sub> (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(C<sub>9</sub>H<sub>6</sub>NSe)<sub>2</sub>, M[C<sub>9</sub>H<sub>5</sub>(CH<sub>3</sub>)SN]<sub>2</sub> (M=Pt, Pd) have been compared. Crystal data: I-Monoclinic, space group *P*2<sub>1</sub>/*c*, *a*=12.5661(7), *b*=7.8072(5), *c*=18.6684(12) Å,  $\beta$ =97.328(2)°, *V*=1816.5(2) Å<sup>3</sup>, *Z*=4,  $R=0.0629$ ,  $wR_2=0.1438$  for 4086 reflections; II-Monoclinic, space group *P*2<sub>1</sub>/*n*, *a*=9.0092(4), *b*=16.3290(7), *c*=14.1073(6) Å,  $\beta$ =106.710(2)°, *V*=1987.7(2) Å<sup>3</sup>,  $R=0.0499$ ,  $wR_2=0.1242$  for 4495 reflections (diffractometer Bruker-Nonius KappaCCD,  $\lambda$ MoK $\alpha$ ).

[1] J. Ashaks, Yu. Bankovsky, D. Zaruma, I. Shestakova, I. Domracheva, A. Nesterova, E. Lukevics. *Chem. of Heteroc. Comp.*, 2004, 6, 905.

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, C<sub>26</sub>H<sub>12</sub>. 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 (SF<sub>6</sub>), adamantane (C<sub>10</sub>H<sub>16</sub>) and fullerene (C<sub>60</sub>). 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.

[1] J S Reid, M Moore & L MacNay, *Acta Cryst.* A63 (2007)