

The use of ligands with carboxylate groups makes that the first supramolecular association is organized by the effect of OH...O hydrogen bonds. The π ... π stacking interactions between blocking ligands can cooperate in the formation of the whole crystal structure. All of these interactions can link low-dimensional complexes to give high-dimensional supramolecular structures and further stabilize the crystal structures in the solid state.

Acknowledgments: A.B.L. thanks to Xunta de Galicia for a postdoctoral-fellowship "Ángeles Alvariño". Funding for this work was provided by the Spanish Ministerio de Ciencia e Innovación through projects MAT2007-60660, and "Factoría de Cristalización" (Consolider-Ingenio2010, CSD2006-00015).

[1] D. Braga, *J. Chem. Soc., Dalton Trans.* **2000**, 3705 and references therein.

Keywords: copper complexes; crystal structures; coordination chemistry

FA4-MS06-P06

Crystal Structures of Double Oxygen-bridged Tetranuclear and Polynuclear Metal Complexes.

Dinçer Ülkü^a, Cengiz Arıcı^b, Orhan Atakol^b.
^aHacettepe University Physics Department, Ankara-Turkey. ^bAnkara University Chemistry Department, Ankara-Turkey.

E-mail: dulku@hacettepe.edu.tr

The [N,N'-bis(salicylidene)-1,3-propane-diamine, (SALPD), (C₁₇H₁₆N₂O₂)] ligand forms different complexes with metal salts in nonaqueous media. These compounds are of interest because of their magnetic super-exchange interactions between bridged metal ions[1]. Various combinations of metal ions are possible[2]. Magnetic interactions depend on the immediate environment of the bridge as well as on the ligand arrangement around the metal atoms. Oxygen, nitrogen, acetate or nitrite anions may constitute the μ -bridges. We report here two new structures of this group of compounds:

(I) [Cu₂(SALPD)(C₄H₈O₂)(N₃)₂]_n, P 2₁/n, a=11.2922(12), b=15.4136(11), c=13.6107(13) Å, β =97.402(5)°, Z=2, D_x=1.64 g.cm⁻³, λ =0.71073 Å, I > 2 σ 2575, N_{par}=293, R, R_w→0.07, 0.16, $\Delta\rho_{max}$, $\Delta\rho_{min}$ → 1.2, -1.1 e Å³. Two doubly oxygen-bridged dinuclear Cu complexes are bridged in a head-on fashion via two azido groups to build a centrosymmetrical tetranuclear complex. The terminal Cu ion has a distorted square-pyramidal coordination,

involving two bridging O and two N atoms from a (SALPD) and one O atom from a dioxane molecule. The inner Cu ions also have an irregular square-pyramidal coordination, 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. Whether the coordination sphere around the metal atoms is a trigonal-bipyramide or square-pyramide was decided on the basis of τ value calculations. $\phi_{bridge}(Cu-N-Cu) = 102.1(3)^\circ$, $\phi_{bridge}(Cu-O-Cu) = 105.6(2)^\circ$.

(II) [ZnHg(SALPD)(C₄H₄N₂S₂)_n], P 2₁2₁2₁, a=8.6824(12), b=16.1222(12), c=16.3339(11) Å, Z=4, D_x=2.01 g.cm⁻³, λ =0.71073 Å, I > 2 σ 1951, N_{par}=276, R, R_w→0.031, 0.075, $\Delta\rho_{max}$, $\Delta\rho_{min}$ → 0.80, -0.88 e Å³. Doubly oxygen-bridged dinuclear ZnHg complexes are bridged via SCN groups in an end to end fashion to build a polynuclear chain. The coordination around Zn ion is a distorted square-pyramide involving two O and two N atoms from a SALPD and one N atom from a SCN group. The Hg atom has a tetrahedral environment consisting of two O atoms from a (SALPD) and two S atoms from two SCN groups. The S and N atoms of the SCN bridge between the dinuclear ZnHg complexes are coordinated to Hg and Zn atoms, respectively. This results in a polymeric chain structure. The bridging SCN groups are almost linear. S-C-N angle is 176.5(2)°, $\phi_{bridge}(Zn-O-Hg) = 105.5(2)^\circ$ to 106.5(2)°.

[1] Fukuhara C., Tsuneyoshi K., Matsumoto N., Kida S., Mikuriya M., Mori M. *J.Chem.Soc.Dalton Trans.* **1990**, 3473. [2] Arıcı C., Ülkü D., Tahir M.N., Atakol O. *Acta Cryst.* **2001**, E57,m283-285.

Keywords: organometallic crystal structures; metalloorganic structures; coordination compounds

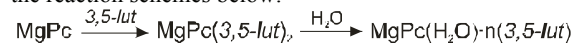
FA4-MS06-P07

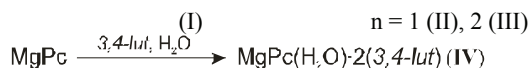
Magnesium(II) phthalocyanine Coordination Compounds with 3,4- and 3,5-lutidines.

Vasył Kinzhybal^a, Jan Janczak^a.
^aInstitute of Low Temperature and Structure Research, Polish Academy of Sciences, POBox. 1410, 50-950 Wrocław, Poland
E-mail: V.Kinzhybalo@int.pan.wroc.pl

Magnesium phthalocyanine (MgPc) and its MgPcL and MgPcL₂ coordination complexes (4+1 and 4+2) with N and O donor ligands deserve attention because of similarity with chlorophyll, thus being its synthetic models. Due to their electrochemical properties they find application in solar energy conversion, are used as pigments in optical disks, laser printers, display devices and chemical sensors. As a continuation of the series of works concerned with MgPc coordination with N- and O- donor ligands we present the results of syntheses and structural investigation of a number of coordination compounds of MgPc with 3,5-lutidine (3,5-lut) and 3,4-lutidine (3,4-lut).

All of the compounds were obtained by recrystallization of purified MgPc (Sigma) from solution of the appropriate lutidine. Four compounds were obtained, as presented on the reaction schemes below:





Structure of compound I ($\text{MgPc}(3,5\text{-lut})_2$) is built of MgPc moieties axially coordinated with two ligand molecules (4+2 type). These fragments are stacked together with π - π interactions to form layered structure. Mg atom lies in the plane of four N isoindole atoms of Pc aromatic ring, it occupies the special position lying in the center of inversion.

Contrary to compound I, compounds II, III and IV are characterized by 4+1 type of Mg metal center coordination site. Water molecule is introduced in closest coordination sphere of Mg atom, replacing the lutidine molecules from Mg environment. Compound II is characterized by the hydrogen bond between one of water molecule H atoms and lutidine N aromatic ring atom as an acceptor. Another H atom of coordinated water molecules form hydrogen bond with the azamethine N atom of the adjacent MgPc molecule, so that the chains going in the *a* axis direction are formed. 3,5-Lutidine molecules are π - π stacked between the neighboring MgPc moieties. The characteristic feature of this compound is the absence of back-to-back type dimers in its structure. Up-to-date all of MgPc coordination compounds with 4+1 type Mg atom environment possessed this kind of dimers.

Compounds III and IV are built of $\text{MgPc}(\text{H}_2\text{O})$ moieties and two lutidine molecules hydrogen bonded with them. These $\text{MgPc}(\text{H}_2\text{O})\cdot 2\text{L}$ moieties are stacked in the structure to form back-to-back type dimers. The deviation of Mg atom from the mean plane of four isoindole N atoms is equal to 0.553(2), 0.510(1) and, 0.464(1) Å, respectively for II, III and IV. Saucer-shaped geometry of MgPc molecule is flattered by the back-to-back type dimers formation in the case of compounds III and IV. The highest Mg atom off-plane deviation value in the compound II correlates well with the absence of back-to-back type dimers.

The tendency to form 4+2 type coordination compounds with N-donor ligands and 4+1 – with O-donor ones is observed.

Keywords: macrocyclic ligands; coordination compounds; phthalocyanines

FA4-MS06-P08

Spectroscopic and Crystallographic Characterization of Bis(azido) Cobalt(III) Porphyrinates. Bader Bel Haj Ali^a, Mohamed Salah Belkhiria^a, Michel Giorgi^b, Habib Nasri^a. ^a*Laboratoire de Physico-chimie des matériaux, Faculté des Sciences de Monastir, Avenue de l'environnement, 5019 Monastir, Tunisia.* ^b*Spectropole, Faculté des Sciences de St-Jérôme, Université d'Aix-Marseille, Avenue Escadrille Normandie-Niemen, 13397 Marseille Cedex 20, France.*

E-mail : belhaj_bader@yahoo.fr

While iron porphyrins are frequently used as synthetic model systems, cobalt(III) porphyrins exhibit catalase-like activity in the disproportionation of H_2O_2 . Here we present the results of our investigation on new hexacoordinate

bis(azido) cobalt(III) porphyrinates with picket fence porphyrin (TpivPP) and the octaethylporphyrin (OEP). The two derivatives were characterized by UV-vis. IR and ¹H NMR spectroscopies. Both complex ions $[\text{Co}^{\text{III}}(\text{TpivPP})(\text{N}_3)_2]^+$ (**I**) and $[\text{Co}^{\text{III}}(\text{OEP})(\text{N}_3)_2]^+$ (**II**) crystallize in the monoclinic space group P2₁/n.

(**I**): Z = 4, a = 12.9596(2) Å, b = 27.5833(5) Å, c = 23.8539(5) Å, β = 105.134(1)°, at 293 K. R_1 = 0.0942, wR_2 = 0.2489 for 10119 observed reflections [$I \geq 2\sigma(I)$].

(**II**): Z = 4, a = 115.3589(2) Å, b = 17.9122(3) Å, c = 21.276053 Å, β = 101.370(1)°, at 293 K. R_1 = 0.0759, wR_2 = 0.2736 for 12646 observed reflections [$I \geq 2\sigma(I)$].

The average equatorial Fe–Np distance value for the TpivPP derivative which is 1.962(4) Å is quit shorter than the one of the OEP bis(azido) species (Co–Np = 1.984(3) Å). The average value of the Co–N(azido) distance of (**I**) is 1.945(6) Å is shorter than the Co–N(azido) bond length of derivative (**II**) (1.977(3) Å). Both cobalt(III)-azido distances in compounds (**I**) and (**II**) are significantly shorter than the iron(II) monoazido species $[\text{Fe}^{\text{II}}(\text{TpivPP})(\text{N}_3)]^+$ [1]. This indicates that the Co^{III}–N(azido) distance is stronger than the Fe^{II}–N(azido) bond length in metalloporphyrins.

[1] I. Hachem, M.S. Belkhiria, M. Giorgi, C.E. Schulz, H. Nasri accepted for publication in *Polyhedron*, doi:10.1016/j.poly.2008.12.054

Keywords: porphyrin structures; spectroscopy; single-crystal X-rays

FA4-MS06-P09

Extrusion/Uptake of Alcohols by Silver Carboxylate Coordination Networks. Inigo Vitorica Yrezabal^a, Harry Adams^a, Lee Brammer^a. ^a*Department of Chemistry, University of Sheffield.*

Email: Chp08iv@sheffield.ac.uk

Chemical reactions in the organic solid state are uncommon but well-established. They involve the formation of covalent bonds between neighbouring moieties as a result of photochemical or thermal activation [1]. In this work a class of single crystal-single crystal reactions within nonporous crystals of a coordination network will be presented, wherein bonds are broken and formed in a ligand substitution reaction at silver (I) centre. It has been shown that the behaviour of the Ag⁺ ions in these networks show structural similarities to the hydrogen “ions” in the carboxylic acid structures [2]. We have extended this equivalence by inclusion of an alcohol molecule in the $[\text{Ag}_2(\text{O}_2\text{CR})_2]$ dimer [3]. A series of compounds of general formula $[\text{Ag}_4(\text{TMP})_3(\text{O}_2\text{CR})_4(\text{ROH})_2]$ (TMP=2,3,5,6-tetramethylpyridine, R_f=perfluoroalkyl group, ROH=alcohol) have been prepared and crystallographically characterised. The release of the alcohol molecules from the expanded dimer and their extrusion from the crystals of the coordination network material $[\text{Ag}_4(\text{TMP})_3(\text{O}_2\text{CR})_4(\text{ROH})_2]$ yielding the alcohol-free network $[\text{Ag}_4(\text{TMP})_3(\text{O}_2\text{CR})_4]$ has been investigated. Both this process and the reverse reaction involving different alcohol uptake occur in single-crystal-single crystal reactions.