

07-Crystallography of Organometallic and Coordination Compounds

presence of a halogen bridged polymer in the former and tightly bound *cis* nitrate anions in the latter. Donating solvent molecules can also affect the metal ion's affinity for the macrocyclic cavity. In $[\text{CdI}_2(\text{OH}_2)(\text{THF})]\cdot\text{benzo-15-crown-5}$, the H_2O and THF molecules occupy the equatorial sites of a trigonal bipyramid, leaving the crown ether hydrogen bonded in the secondary sphere. Lastly, trace hard cations present in the reaction effectively compete with Cd^{2+} for polyether coordination, as in $[\text{NH}_4(\text{benzo-15-crown-5})_2]_2[\text{Cd}_2\text{X}_6]$ ($\text{X} = \text{Br}, \text{I}$).

PS-07.01.18 CRYSTAL STRUCTURE OF A Cu_6 CLUSTER WITH SYN-ANTI BRIDGING CARBOXYLATE GROUP. By M. Klinga*, R. Kivekäs, U. Turpeinen, Department of Chemistry, University of Helsinki, Finland, and J.M. García-Ruiz, A. Moreno-Cárcamo, E. Colacio, University of Granada, Spain.

Studies on structural and magnetic properties of polynuclear transition metal complexes aimed at understanding the structural and chemical factors governing electronic exchange coupling mediated by multiatom bridging ligands are of continuous interest.

Among multiatom bridging ligands, carboxylates have been extensively studied. As it is well known, carboxylate group can exhibit different types of bridging modes: monoatomic, triatomic, syn-syn, anti-anti and syn-anti. Generally, the triatomic bridging favours the formation of either chain or layer compound. However, when the carboxylate group is incorporated into a polydentate ligand, it is forced to adopt the syn-anti configuration and a variety of oligomeric copper(II) complexes, dinuclear, trinuclear and tetranuclear, can be obtained (Colacio, Costes, Kivekäs, Laurent & Ruiz, 1990. *Inorg. Chem.* 29, 4240; Colacio, Dominguez-Vera, Moreno, Kivekäs, Romerosa & Ruiz 1993. *Inorg. Chim. Acta*, accepted for publ.). Within this framework, we succeeded in obtaining a hexanuclear copper(II) complex containing six bridging carboxylate groups with syn-anti configuration, $[\text{Cu}_6\text{L}_6(\text{H}_2\text{O})_6]\cdot 4\text{H}_2\text{O}$, where L stands for dideprotonated 1,3-dimethyl-5-((2-carboxyphenyl)azo)barbituric acid.

The coordination of each copper is square-pyramidal (4+1). The barbituric acid derivative is bonded through 3 atoms to copper(II) ion; the square is completed by one water molecule. The 4 short bonds range from 1.86(1) to 1.965(7) Å. The fifth bond from the carboxylate oxygen connects adjacent copper atoms to each other through Cu1-O-C-O-Cu2 pathways (Cu-O 2.60(1) Å), leading to the cyclic hexamer. Water molecules stabilize the structure by filling the gaps.

Crystal data for dark blue crystals of the title compound, $\text{C}_{78}\text{H}_{80}\text{Cu}_6\text{N}_{24}\text{O}_{40}$: FW=2374.9, $F(000)=2420$, hexagonal, sp.gr. P6_3 (no. 173), $a=19.866(8)$, $c=13.216(4)$ Å. $V=4517(2)$ Å³, $Z=2$, $D_x=1.746$ Mg m⁻³, $\mu(\text{MoK}\alpha)=1.50$ mm⁻¹.

The structure was solved by direct methods and refined to $R=0.063$ for 2183 unique observed reflections ($F > 5\sigma(F)$) (Sheldrick, 1990. SHELXTL-Plus. Version 4.2. Siemens Analytical Instrument Inc., Madison, Wisconsin, USA).

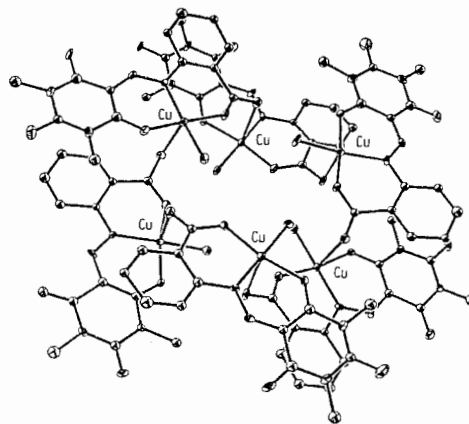


Figure 1. One hexameric unit.

PS-07.01.19 SYNTHESIS, CRYSTAL AND MOLECULAR STRUCTURES OF NEW METALLOPHthalOCYANINES

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New complexes compounds of metallophthalocyanines in crystalline form have been obtained in the reaction of metals and alloys with 1,2-dicyanobenzene at 210°C. In this condition the liquid 1,2-dicyanobenzene undergoes catalytic tetramerisation. Simultaneously the catalytic atom may be coordinated by the forming tetramer. If the catalytic atom is not coordinated by the forming tetramer then two modifications of metal free tetramer - α and β are formed (Janczak and Kubiak, 1992; Kubiak and Janczak, 1992). Here we present the crystal and molecular structures of three new metallophthalocyanines: (I) Tl_2Pc , (II) SnPc_2 and (III) In_2Pc_3 (Pc - phthalocyanine ligand = $\text{C}_{32}\text{H}_{16}\text{N}_8$).

(I) Tl_2Pc . Crystal Data: $\text{C}_{32}\text{H}_{16}\text{N}_8\text{Tl}_2$, $M_r=921.3$, orthorhombic system, space group Cmca , $a=25.173(4)$, $b=7.353(2)$, $c=13.765(3)$ Å, $V=2547.9(7)$ Å³, $Z=4$, $D_0=2.397$ gcm⁻³, $D_c=2.402$ gcm⁻³, $\lambda(\text{MoK}\alpha)=0.71073$, $\mu=128.0$ cm⁻¹, $T=300$ K, $F(000)=1704$. Face-indexed numerical absorption was applied. The crystal was solved by Patterson method and refined by full matrix least squares method with anisotropic temperature factors gave $R=0.043$, $wR=0.040$ and $S=1.75$. The structure consists of discrete dithallium phthalocyanine molecules. The Tl atoms are displaced above and below the Pc skeleton plane. The deviation of Tl from the Pc plane is ± 1.844 Å.

(II) SnPc_2 (β -form). Crystal Data: $(\text{C}_{32}\text{H}_{16}\text{N}_8)_2\text{Sn}$, $M_r=1143.7$, monoclinic, $\text{C}2/c$, $a=18.754(4)$, $b=18.759(4)$, $c=15.357(3)$ Å, $\beta=115.06(3)^\circ$, $V=4894.1(6)$ Å³, $Z=4$, $D_0=1.545$ gcm⁻³, $D_c=1.552$ gcm⁻³, $\lambda(\text{MoK}\alpha)$, $\mu=5.84$ cm⁻¹, $T=300$ K, $F(000)=2312$, $R=0.039$, $wR=0.027$, $S=1.31$ for 3017 reflections with $I > 3\sigma$. The two Pc rings form a sandwich-type complex with the Sn atom in the center of the molecule. The Pc rings are rotated by 37.9° with