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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).

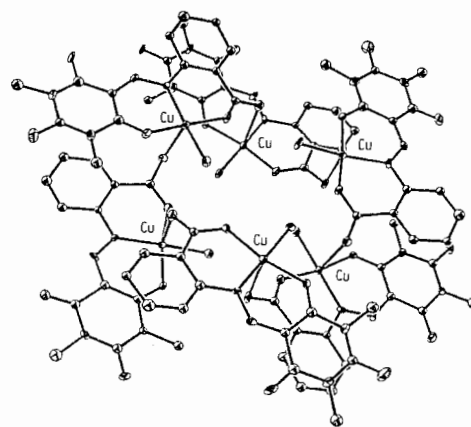


Figure 1. One hexameric unit.

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

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respect to one another. The distance between Pc planes equals 2.57 Å. The tin atom is coordinated by eight isoindole nitrogen atoms forming a square antiprism. The Sn-N distances ranging from 2.312(3) to 2.330(3) Å.

(111) In_2Pc_3 . Crystal Data: $(\text{C}_{32}\text{H}_{16}\text{N}_8)_3\text{In}_2$, $M_r = 589.1$, triclinic, $P1$, $a = 14.492(3)$, $b = 13.179(3)$, $c = 11.493(2)$ Å, $\alpha = 113.96(2)$, $\beta = 97.15(2)$, $\gamma = 66.13(2)^\circ$, $V = 1832.2 \text{ \AA}^3$, $Z = 1$, $D_o = 1.60 \text{ g cm}^{-3}$, $D_c = 1.602 \text{ g cm}^{-3}$, $\lambda(\text{CuK}\alpha)$, $\mu = 56.97 \text{ cm}^{-1}$, $T = 300 \text{ K}$, $F(000) = 890$, $R = 0.028$, $wR = 0.037$ and $S = 1.22$ for 7019 observed ($I > 4\sigma$) reflections. The centrosymmetrical molecule of In_2Pc_3 consists of three Pc ligand plane and two indium anions and forms double sandwich-type complex. The In atoms are located between Pc ligands plane and have six-coordinate geometry. The intramolecular mean distance between Pc planes is about 2.84 Å. The two opposite Pc ligand planes are parallel to each other and the third central Pc plane is rotated about 39.3° in relation to the peripheral Pc. The intramolecular In-In distance is equal 4.036 Å. The shortest intermolecular distance between neighbouring successive Pc planes is 3.477 Å. References

J. Janczak, R. Kubiak, *J. Alloys Comp.*, **190** (1992) 121-124.
R. Kubiak, J. Janczak, *J. Alloys Comp.*, **190** (1992) 117-120.

PS-07.01.20 SIMULTANEOUS BINDING OF BETAININE AND PSEUDOHALIDE TO CADMIUM: CRYSTAL STRUCTURES OF FOUR POLYMERIC MIXED-LIGAND CADMIUM(II) COMPLEXES. By Mok-Yin Chow, Xiao-Ming Chen and Thomas C.W. Mak,* Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong.

Four polymeric cadmium complexes containing betaine and pseudohalide ligands have been synthesized and characterized by single-crystal X-ray analysis. The betaine-azide complex $\text{Cd}_2(\text{Me}_3\text{NCH}_2\text{CO}_2)_2(\text{N}_3)_4(1)$ and betaine-isocyanate complex $\text{Cd}_2(\text{Me}_3\text{NCH}_2\text{CO}_2)_2(\text{NCO})_4(2)$ are isomorphous, crystallizing in the monoclinic space group $C2/c$ with $Z = 4$. The two betaine-thiocyanate complexes $\text{Cd}_3(\text{Me}_3\text{NCH}_2\text{CO}_2)_4(\text{SCN})_6(\text{H}_2\text{O})_2(3)$ and $\text{Cd}(\text{Me}_3\text{NCH}_2\text{CH}_2\text{CO}_2)(\text{SCN})_2(4)$ are both triclinic, space group $P\bar{1}$, with $Z = 1$ and 2, respectively. In this series of complexes the carboxy groups of the betaine ligands act in three coordination modes and the pseudohalide ligands in two typical bridging modes. The structure of 1 or 2 consists of a virtually linear chain in which each pair of adjacent cadmium(II) ions are triply bridged by two $\mu-1,1$ -azido (or -isocyanato) and one μ -carboxy- O,O' ligands. The framework of structure 3 is a one-dimensional chain built of corner-sharing centrosymmetric sixteen-membered $(-\text{N}-\text{C}-\text{S}-\text{Cd})_4$ puckered rings that contain $\mu-1,3$ -bridging thiocyanate groups in both *anti* and skew modes; both unidentate and bidentate chelate modes of the betaine ligands coexist in this complex. The structure of 4 is constructed from an alternate arrangement of two kinds of rings that share corners to form a linear chain: one is an eight-membered chair-like $(-\text{N}-\text{C}-\text{S}-\text{Cd})_2$ ring bridged by a pair of $\mu-1,3$ thiocyanate ligands and the other a four-membered $(-\text{O}-\text{Cd})_2$ ring bridged by two $\eta^2-\mu-O$ carboxylate ligands. The significance of these structural features and the coordination geometries at the cadmium centres are discussed.

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Crystal Structures of Alkalides with Mixed Sandwich Crown Ether Cations, a New Type of Complexation Compound

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Crystal structures of several alkalides (ionic compounds with alkali metal anions and complexed alkali metal cations) with mixed sandwich crown ether cations, $\text{K}^+(\text{18C6})(\text{12C4})\text{Na}^-$, $\text{K}^+(\text{18C6})(\text{12C4})\text{K}^-$ and $\text{K}^+(\text{18C6})(\text{12C4})\text{K}^-(\text{18C6})$, have been determined. These structures thus provided evidence of the stability of these mixed sandwich cations over their "parents" with single type of crown ethers. This research project was supported by U. S. National Science Foundation Grant No. DMR 90-17292. The X-ray diffractometer system was provided by NSF Grant No. CHE-84-03823 and CHE89-08088.

PS-07.01.22 STRUCTURES OF INCLUSION COMPOUNDS BETWEEN URANYL / CROWN ETHER AND URANYL / AZACROWN BY M. Nierlich*, L. Deshayes, N. Keller, M. Lance and J.D. Vigner, CEA, CE Saclay - SCM - Bât. 125 - 91191 Gif sur Yvette Cedex - FRANCE.

Complexation of the dioxouranium by macrocycles, particularly by crown-ether, has been widely studied; however the majority of structural studies concerns complexes in which the crown ligand is linked to the uranyl ion via hydrogen bonds (Rogers et al., *Inorg. Chem.*, **30**, 2671, 1991; Deshayes et al. *Acta Cryst.* **C49**, 1, 1993) and few structural studies show a direct uranyl crown coordination (Navaza et al., *Polyhedron*, **3**, 143, 1984; Dejean et al., *Polyhedron*, **6**, L189, 1987). The probability of inclosing UO_2 in the crown cavity is increased by a good choice of the pair solvent-anion which has to be poorly uranyl coordinating. We have chosen as poorly coordinating anion CF_3SO_3^- and the aim of these studies is to correlate the influence of the solvent on the direct uranyl crown coordination.

- In aqueous solution, we have crystallised: $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+} (\text{CF}_3\text{SO}_3)_2^- (\text{18-crown-6})_2$ in which the UO_2^{2+} is coordinated to five water molecules, the CF_3SO_3^- and the crown ether being linked to the uranyl via H bonds. (system triclinic, $P\bar{1}$, $a = 10.411(7)$, $b = 10.760(5)$, $c = 15.801(8)$ Å, $\alpha = 83.52(4)$, $\beta = 89.78(5)$, $\gamma = 61.4(5)^\circ$, $R = 0.045$ for 3459 unique observed reflections).

- In a mixture $\text{H}_2\text{O}-\text{CH}_3\text{CN}$, the complex $\text{UO}_2(\text{H}_2\text{O})_3(\text{CF}_3\text{SO}_3)_2^- (\text{benzo15-crown-5})_2$ crystallise. The linear uranyl is equatorially surrounded by five O atoms from 3 water molecules and 2 CF_3SO_3^- , the crown ether being H bonded to the 3 water molecules (system monoclinic, $P2_1/n$, $a = 15.749(3)$, $b = 14.283(6)$, $c = 19.010(8)$ Å, $\beta = 90.35(5)^\circ$, $R = 0.041$ for 2521 unique observed reflections).

- In organic solution CH_3CN , inclusion compounds crystallise. The uranyl ion is hexacoordinated to the six O atoms of the crown ether or the 6 N atoms of the azacrown.