

## 07-Crystallography of Organometallic and Coordination Compounds

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## PS-07.01.15 CRYSTAL STRUCTURES OF THREE DIASTEREOMERIC COMPLEXES FROM [1-[1-(DIMETHYLAMINO)ETHYL]-2-NAPHTHALENYL-C,N]PALLADIUM(II) AND N,N,N',N'-TETRAMETHYL-2,3-BUTANEDIAMINE.

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It has been shown that the optically active bis-(acetonitrile)[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-C,N]palladium(II) perchlorate is a versatile reagent as an indicator of the enantiomeric excess of optically active diamines. The *S*-isomer of this palladium compound has been reacted with the *R,S*-, *R,R*- and *S,S*- enantiomers of N,N,N',N'-tetramethyl-2,3-butanediamine to produce the three diastereomers the structures of which have been determined using single crystal X-ray diffraction.

Crystal data :  $[(CH_3)_2NCH(CH_3)C_{10}H_6Pd(CH_3)_2NCH(CH_3)CH(CH_3)N(CH_3)_2]ClO_4$

1. (*S,R,S*)-isomer, monoclinic, space group  $P2_1$ ,  $a = 11.661(3)$ ,  $b = 9.982(2)$ ,  $c = 13.227(4)$  Å,  $\beta = 105.29(2)^\circ$ ,  $z = 2$ ,  $R = 0.032$ .
2. (*S,R,R*)-isomer, orthorhombic, space group  $P2_12_12_1$ ,  $a = 7.872(3)$ ,  $b = 15.843(5)$ ,  $c = 20.273(2)$  Å,  $z = 4$ ,  $R = 0.037$ .
3. (*S,S,S*)-isomer, monoclinic, space group  $P2_1$ ,  $a = 7.978(2)$ ,  $b = 20.856(2)$ ,  $c = 15.218(2)$  Å,  $\beta = 92.06(2)$ ,  $z = 4$ ,  $R = 0.036$ .

The unit cell of the (*S,S,S*)-isomer contains 2 pairs of molecules which differ slightly in bond distances and bond angles. The configuration around the palladium atom is distorted square planar in all the three diastereomers.

Simon Y M Chooi, Pak-Hing Leung, Chin Chin Lim, K F Mok, G H Quek, K Y Sim and M K Tan, *Tetrahedron: Asymmetry*, **3**, 529-532, 1992.

## PS-07.01.16 REACTION RATE DEDUCED FROM STRUCTURAL CHANGE IN CRYSTALLINE-STATE PHOTOISOMERIZATION

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It has been found that the  $\beta$ -cyanoethyl ( $\beta$ -ce) group in cobaloxime complexes is transformed to  $\alpha$ -cyanoethyl ( $\alpha$ -ce) group when the complex is exposed to visible light in the solid state. Among the complexes with various base ligands, ( $\beta$ -ce)(3-methylpyridine)cobaloxime forms mixed crystals with the photoproduct  $\alpha$ -ce complex in any composition. A crystal of the  $\beta$ -ce complex was mounted on a Rigaku AFC-5R diffractometer and was irradiated with a Xe lamp. The lattice constants, measured by the diffractometer at a constant interval, showed a gradual change. After about 75h exposure, the change became significantly small. The three-dimensional intensity data were collected. The analyzed structure revealed the disordered form of the  $\beta$ - and  $\alpha$ -ce groups. Figure 1

shows the crystal structures before and after the irradiation. This clearly indicates that the  $\beta$ -ce group is isomerized to the  $\alpha$ -ce group keeping a single crystal form. The reaction rate was estimated from the change of the cell parameters at early stages since the change is well-explained by first-order kinetics. The rate constant is  $1.4 \times 10^{-5} s^{-1}$ .

A similar experiment was performed for the mixed crystal which contains  $\beta$ -ce and  $\alpha$ -ce complexes with a ratio of 6 : 4. The cell dimensions are approximately the same as those of the photo produced crystal with the same ratio. The change of the cell dimensions at early stages are also explained by first-order kinetics and the rate constant was calculated to be  $1.8 \times 10^{-5} s^{-1}$ .

Such a crystalline-state photoisomerization has been examined for the crystals of the  $\beta$ -ce complexes with 3-chloropyridine and 3-bromopyridine as axial base ligands. The results are compared among the three crystals.

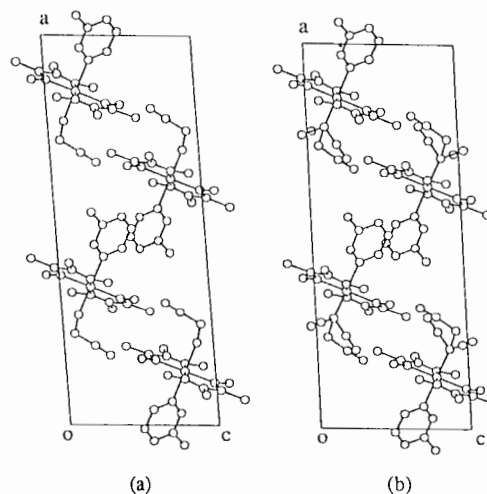


Fig. 1 Crystal structures (a) before and (b) after the irradiation

PS-07.01.17 CRYSTALLOGRAPHIC INVESTIGATION OF 15-CROWN-5 COMPLEXES OF  $CdX_2$  ( $X = Cl, Br, I, NO_3$ ). Andrew H. Bond\* and Robin D. Rogers, Department of Chemistry, Northern Illinois University, DeKalb, IL 60115, USA.

This presentation will focus on factors influencing in-cavity versus out-of-cavity coordination of 15-crown-5 to  $Cd^{2+}$ . The effects of anion type, solvent, and competing cations on metal ion coordination and crown ether conformation will be highlighted.

$Cd^{2+}$  generally adopts a pentagonal bipyramidal geometry when it resides in the 15-crown-5 cavity. This has been observed in  $[(CdCl_2)_2CdCl_2(15-crown-5)]_n$ ,  $[Cd(15-crown-5)(OHMe)(\mu-Br)CdBr_3]$ , and  $[Cd(OH_2)_2(15-crown-5)][CdI_3(OH_2)_2] \cdot 2(15-crown-5) \cdot 2CH_3CN$ . The characteristics of the anion, however, can greatly influence the final metal ion environment. The  $Cd^{2+}$  centers in  $[Cd(15-crown-5)(\mu-Br)_2CdBr(\mu-Br)]_2$  and  $[Cd(NO_3)_2(15-crown-5)]$  are displaced from the cavity of the ether due to the

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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  $\text{H}_2\text{O}$  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  $\text{Cd}^{2+}$  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  $\text{Cu}_6$  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  $\text{Cu1-O-C-O-Cu2}$  pathways ( $\text{Cu-O}$  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.  $\text{P6}_3$  (no. 173),  $a=19.866(8)$ ,  $c=13.216(4)$  Å.  $V=4517(2)$  Å<sup>3</sup>,  $Z=2$ ,  $D_x=1.746$  Mg m<sup>-3</sup>,  $\mu(\text{MoK}\alpha)=1.50$  mm<sup>-1</sup>.

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).

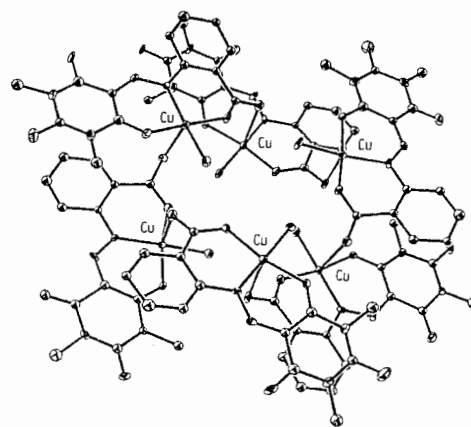


Figure 1. One hexameric unit.

**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 -  $\alpha$  and  $\beta$  are formed (Janczak and Kubiak, 1992; Kubiak and Janczak, 1992). Here we present the crystal and molecular structures of three new metallophthalocyanines: (I)  $\text{Ti}_2\text{Pc}$ , (II)  $\text{SnPc}_2$  and (III)  $\text{In}_2\text{Pc}_3$  (Pc - phthalocyanine ligand =  $\text{C}_{32}\text{H}_{16}\text{N}_8$ ).

(I)  $\text{Ti}_2\text{Pc}$ . Crystal Data:  $\text{C}_{32}\text{H}_{16}\text{N}_8\text{Ti}_2$ ,  $M_r 921.3$ , orthorhombic system, space group  $\text{Cmca}$ ,  $a=25.173(4)$ ,  $b=7.353(2)$ ,  $c=13.765(3)$  Å,  $V=2547.9(7)$  Å<sup>3</sup>,  $Z=4$ ,  $D_0=2.397$  gcm<sup>-3</sup>,  $D_c=2.402$  gcm<sup>-3</sup>,  $\lambda(\text{MoK}\alpha)=0.71073$ ,  $\mu=128.0$  cm<sup>-1</sup>,  $T=300$  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 Ti atoms are displaced above and below the Pc skeleton plane. The deviation of Ti from the Pc plane is  $\pm 1.844$  Å.

(II)  $\text{SnPc}_2$  ( $\beta$ -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,  $\beta=115.06(3)^\circ$ ,  $V=4894.1(6)$  Å<sup>3</sup>,  $Z=4$ ,  $D_0=1.545$  gcm<sup>-3</sup>,  $D_c=1.552$  gcm<sup>-3</sup>,  $\lambda(\text{MoK}\alpha)$ ,  $\mu=5.84$  cm<sup>-1</sup>,  $T=300$  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  $37.9^\circ$  with