

07-Crystallography of Organometallic and Coordination Compounds

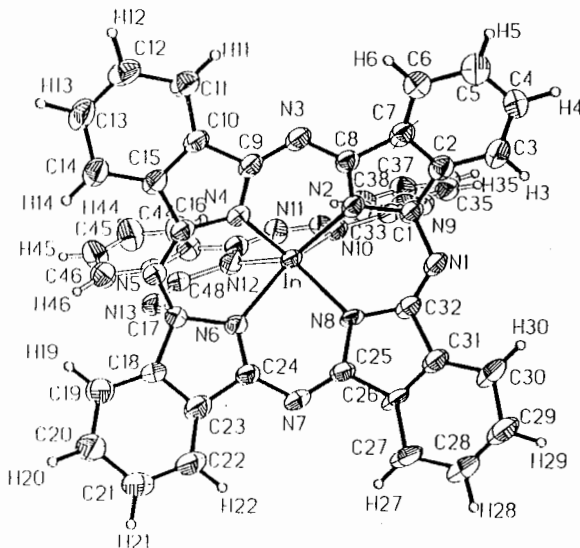
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Two new complexes of bicyclophtalocyanines have been obtained in the crystalline form. Here we present the crystal structures determination of (I) $GdC_{48}H_{24}N_{12}$ and (II) $InC_{48}H_{24}N_{12}$.

Crystal Data: (I) $M_r = 939.3$, triclinic system, space group $P\bar{1}$, $a = 12.388(2)$, $b = 15.978(3)$, $c = 11.683(2)$ Å, $\alpha = 86.00(2)$, $\beta = 65.12(2)$, $\gamma = 75.62(2)^\circ$, $V = 2030.5(7)$ Å³, $Z = 2$, $D_0(\text{floatation}) = 1.53$ gcm⁻³, $D_c = 1.537$ gcm⁻³, $\lambda(\text{MoK}\alpha) = 0.71073$ Å, $\mu = 16.9$ cm⁻¹, $T = 300$ K, $F(000) = 934$. Final $R = 0.047$, $R_w = 0.050$ and $S = 1.31$ for 4749 independent reflections ($I > 4\sigma$) and 655 refined parameters.

(II) $M_r = 896.8$, triclinic system, space group $P\bar{1}$, $a = 12.408(2)$, $b = 15.998(3)$, $c = 11.693(2)$ Å, $\alpha = 85.63(2)$, $\beta = 64.92(2)$, $\gamma = 75.56(2)^\circ$, $V = 2034.7(7)$ Å³, $Z = 2$, $D_0(\text{floatation}) = 1.46$ gcm⁻³, $D_c = 1.465$ gcm⁻³, $\lambda(\text{CuK}\alpha) = 1.54056$ Å, $\mu = 51.5$ cm⁻¹, $T = 300$ K, $F(000) = 904$. Final $R = 0.069$, $R_w = 0.073$ and $S = 1.65$ for 7194 independent reflections ($I > 4\sigma$) and 655 refined parameters.

The molecular geometry and numbering of the atoms is illustrated on Fig.1. The bicyclophtalocyaninato ligand consists of the phtalocyaninato skeleton of four isoindole units bridged by two additional isoindole moieties (see Fig.1). The ligand can also be described as two phtalocyaninato anions having one common half. It can be assumed that the ligand is less stable than phtalocyaninato anion as the conjugation π -electron system of the inner 16-membered C-N ring is interrupted at the two sp^3 -hybridized atoms C1 and C17 of the ring linkage to a bicyclo system. The C-N distances reflect the interruption of the π -electron delocalization system. The bonds at the atoms C1 and C17 average 1.520 Å, and this is close to the expected value for a single bond between sp^3 - and sp^2 - hybridized C atoms. They adjoin shorter bonds of about 1.281 Å which represent double bonds. The other C-N bond distances ranging from 1.315 to 1.440 Å, being typical for a conjugated C-N system.



The six N-isoindole donor atoms of the whole bicyclophtalocyaninato ligand which are coordinated to the central atom (Gd or In) form an irregular octahedron.

PS-07.04.23 THREE CRYSTAL STRUCTURES OF Cu(II) COMPLEXES OF THE DEPROTONATED ANION WITH THE LIGANDS OF DIAZADIAMIDES. By Chung-Sun Chung* and Kelun Shu, Department of Chemistry; Tahir. H. Tahirov, and Tian-huey Lu, Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 300, China

The solution chemistry of diazadiamides and Cu(II) ions forming binuclear and monomer complexes has been extensively studied by potentiometric and spectrophotometric methods (Bai & Martell, J. Amer. Chem. Soc., 1969, 91, 4412-4420; Muir & Rechani, Inorg. Chim. Acta. 1974, 11, 127-136; Armani, Marchelli, Dossena, Casasti & Dallavalle, Helv. Chim. Acta, 1986, 69, 1916-1922). However, in solid state, these complexes containing alkyl groups on carbon or nitrogen have received very little attention. In order to study the steric effect of the N-alkyl or C-alkyl groups on the structure of the C(II) complexes, we have prepared and studied the structures of the three Cu(II) complexes which were determined by X-ray diffraction. Their ligands and crystal data at room temperature are: (A), N,N'-diglycylethylenediamine, $[Cu_2(C_6H_{13}N_4O_2)_2(H_2O)_2][(ClO_4)_2] \cdot 4(H_2O)$, $M_r = 780.47$, monoclinic, $P2_1/n$, $a = 7.321(1)$, $b = 9.786(1)$, $c = 20.803(2)$ Å, $R = 0.038$, $wR = 0.038$ for 1424 observed reflections; (B), N,N'-bis(N-propylglycyl)ethylenediamine, $[Cu_2(C_{12}H_{25}N_4O_2)_2(H_2O)_2][(ClO_4)_2]$, $M_r = 820.708$, monoclinic, $P2_1/n$, $a = 9.454(1)$, $b = 27.61(1)$, $c = 14.762(3)$ Å, $R = 0.058$, $wR = 0.061$ for 7012 observed reflections; (C), (2R, 10R)-N,N'-dialanylethylenediamine, $[Cu(C_9H_{18}N_4O_2)(H_2O)] \cdot 2H_2O$, orthorhombic, $P2_12_12_1$, $a = 7.656(3)$, $b = 12.020(2)$, $c = 15.890(1)$ Å, $R = 0.043$ for 1615 observed reflections. The first two complexes are binuclear. Both Cu(II) ions are five-coordinated, and the geometry about Cu(II) is a distorted square pyramid. Two donor N atoms of one tetradentate ligand and one O atom of the other ligand form a slightly distorted plane and a water O atom occupies the axial position. The last complex is monomeric. The coordination geometry about the Cu(II) ion is distorted square pyramidal with a water O atom in the axial position, and two amine and two deprotonated amide N atoms in equatorial positions. The water molecules, amino groups and carbonyl O atoms participate in forming H-bonds. [Work was supported by National Science Council, Taiwan, China].

