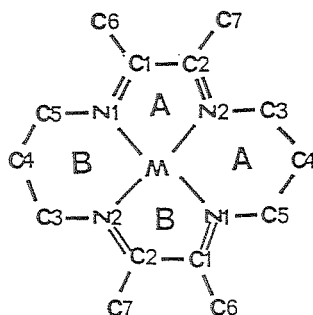


09.4-24 CRYSTAL STRUCTURES OF TWO COPPER(II)-TIM COMPLEXES. A. Elia, E. C. Lingafelter, and V. Schomaker, Department of Chemistry, University of Washington, Seattle, Washington, 98195.

The crystal structures of $\text{Cu}(\text{TIM})\text{Cl}$ (PF6) and $\text{Cu}(\text{TIM})(\text{NCS})(\text{PF}_6)$ have been determined, where TIM is the macrocyclic ligand 2,3,9,10-tetramethyl-1,4,8,11-tetraaza-1,3,8,10-cyclo-tetradecatetraene ($\text{C}_{14}\text{H}_{24}\text{N}_4$). The first complex crystallizes in Pbcu with $a=15.248(5)\text{\AA}$, $b=15.569(5)\text{\AA}$, $c=16.810(7)\text{\AA}$, $Z=8$, and the second in Pnam with $a=12.003(5)\text{\AA}$, $b=15.365(5)\text{\AA}$, $c=11.500(5)\text{\AA}$, $Z=4$. Both complexes are five-coordinate square pyramidal, with the TIM nitrogens forming the basal plane, and the fifth ligand at the apex. In the first case the fifth ligand is Cl^- , in the second case it is a nitrogen bound NCS^- . In the first complex the closest interaction at the sixth coordination site is with the anion, at a distance of $3.38(1)\text{\AA}$, while in the second complex the interaction at the sixth site is with the sulfur of another cation, at a distance of $3.31(6)\text{\AA}$. The two complexes will be compared with each other as well as with a third five-coordinate square pyramidal Copper(II)-TIM complex the $\text{Cu}(\text{TIM})(\text{m-imid})(\text{PF}_6)_2$, where the fifth ligand is a methyl imidazole. The coordination bond distances and geometry, TIM planarity, and the displacement of the copper out of the basal plane will be discussed.



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09.4-25 STRUCTURES OF p-HYDROXYBENZOATE COMPLEXES OF METALS. By A.N. Shnulin, G.N. Nadjafov and Kh.S. Mamedov, Institute of Theoretical problems of Chemical Technology, Institute of Inorganic and Physical Chemistry, The Academy of Sciences of the Azerbaijan SSR, Narimanov prospect 29, Baku 370143, USSR. Structures of p-hydroxybenzoate complexes of bivalent Mg, Co, Ni, Zn, Cu and Cd have been determined by X-ray analysis. It has been shown that complexes of the first four metals are isostructural (space group Pbcu, composition $\text{ML}_2 \cdot 8\text{H}_2\text{O}$). The copper complex forms crystals having cell constants coinciding with those of the previous four complexes (syngony) but with a different space group ($\text{Cmc}2_1$). The cadmium complex ($\text{CdL}_2 \cdot 6\text{H}_2\text{O}$) retains only the largest dimension of the cell ($\sim 24 \text{\AA}$) along which there occurs packing of acid ligands common for all the complexes. It has been estimated that the crystal structures of the first five complexes are affected by H-bonds the role of which is more essential than factors affecting coordination surroundings of the metal. Geometric relations required for formation of hydrogen bonds are dictated by the nature and location of the phenol OH-group. The isostructural complexes have been found to consist of octahedral ions $\text{M}(\text{H}_2\text{O})_6^{2+}$, anions L^- and two crystallization water molecules. The composition of the copper complex is $[\text{CuL}_2 \cdot (\text{H}_2\text{O})_3]5\text{H}_2\text{O}$. There is only one acid anion L^- in the coordination sphere of the cadmium complex.

09.4-26 X-RAY MOLECULAR STRUCTURES OF SOME MACROCYCLIC COMPLEXES. By T.H. Lu, T.J. Lee and C.S. Chung, National Tsing Hua University, Hsinchu, Taiwan 300, Republic of China.

Stereochemical studies (Liang, Margerum and Chung, Inorg. Chem. (1979) 18, 2001) on the complexes with synthetic macrocyclic ligands have received new impetus since the discovery of certain complexes that exhibited distinctive coordination chemistry and biological significance (Busch, Acc. Chem. Res. (1979) 11, 392). Busch pointed out that the structure of a macrocyclic ligand facilitates the ligand's control of chemical and physical properties of metal ions to a remarkable extent. These complexes allow investigation of ways in which different structures of coordinated macrocyclic ligands convey properties on their metal complexes. (Liang and Chung, Inorg. Chem. (1980) 19, 572).

Among all possible macrocyclic complexes (Whimp, Bailey & Curtis, J. Chem. Soc. (A) (1970), 1956), some structures of the isomeric conformations have been solved by the use of Syntex P1 autodiffractometer in the X-ray laboratory of National Tsing Hua University. They are isomeric (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) copper (II) perchlorate (T. H. Lu, T.J. Lee, B.F. Liang & C.S. Chung, to be published in J. Inorg. Nucl. Chem.), and isomeric (5,7,12,14-tetraethyl-7,14-dimethyl-1,4,8,11-tetraazacyclotetradecane) nickel (II) perchlorate. Two isomeric crystals, red (crystal A) and orange (crystal B) in color, are available for the former. Also two isomeric crystals, orange (crystal C) (T.J. Lee, T.H. Lu, B.F. Liang, C.S. Chung & T.Y. Lee, submitted to J. Chinese Chem. Soc.)

and yellow (crystal D), have been obtained for the latter. The space group of crystal D, still under investigation, is probably $I4/m$, which is predicted from intensity statistics. Other crystal data for crystal D are: tetragonal, $a = b = 25.920$, $c = 8.557\text{\AA}$, $Z = 8$, $V = 5744.1\text{\AA}^3$, $D_c = 1.38 \text{ gm cm}^{-3}$, $\mu(\text{MoK}\alpha) = 9.07 \text{ cm}^{-1}$. The structures were mainly solved by the heavy atom method, difference Fourier syntheses and least squares fit. With NH groups, the two perchlorate ions form hydrogen bonds which may contribute to unexpected behavior for the macrocyclic complexes. The two gem-dimethyl groups are on the opposite sides to amine hydrogens relative to the macrocyclic plane for crystal A, and are nearly inverse to each other with Cu atom as inversion center for crystal B. The close packing in crystal C ($8.66 \text{\AA}^3/\text{atom}$) relative to that in crystals A and B is mainly due to the fact that there is an inversion center with Ni at the origin. This causes the whole molecule of crystal C to stay in the more stable state.

Other macrocyclic crystal structures, such as isomeric 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-copper (II) complexes, are in the scope of our studies. We are engaged in systematic research on the macrocyclic complexes in order to deduce the chemical and physical rules that govern not only the synthetic macrocyclic compounds but also the macrocyclic compounds in biological system. (Work supported by the National Science Council Grant 69M-0201-03(0315), the Republic of China).