

09.4-21 CRYSTAL STRUCTURE OF (L-ASPARTATE) (IMIDAZOLE) COPPER(II) DIHYDRATE. By L. Antolini, L. Menabue, G.C. Pellacani and M. Saladini, Istituto di Chimica Generale e Inorganica, University of Modena, 41100 Modena, and G. Marcotrigiano and P. Morini, Istituto di Chimica, Facoltà di Medicina-Veterinaria, University of Bari, 70126 Bari, Italy.

This complex which contains ligating moieties found in proteins and enzymes, such as aspartate and imidazole, may be considered a realistic model system of many naturally enzyme-metal ion-substrate complexes.

Crystal Data: $C_7H_{13}CuN_2O_8$, $M=298.7$, orthorhombic, $a=16.049(2)$ Å, $b=9.622(1)$ Å, $c=7.465(1)$ Å, $U=1152.7$ Å³, $D=1.68$ g·cm⁻³, $Z=4$, $D=1.72$ g·cm⁻³, Mo K α radiation, $\lambda=0.71069$, space group $P2_12_12_1$. The structure was refined to $R=0.083$ for 594 "observed" reflections.

The copper atom shows a distorted square-pyramidal environment being linked to three different aspartate ions (one acting as bidentate ligand through the N(amino) and O(α -carboxylate) and the other as monodentate through the O of different carboxylate groups) and one imidazole molecule, resulting in a very unusual arrangement (E. Evans, R. Guevremont and D.L. Rabenstein, in "Metal Ions in Biological Systems", Ed. H. Sigel, Marcel Dekker Inc., New York, Vol. 9, p.41). Each aspartate ion is bonded to three different copper ions giving rise to a polymeric layer structure.

09.4-22 BINUCLEAR COPPER (II) INCLUSION COMPLEXES: BINUCLEAR COPPER (II) CRYPTATES WITH MACROMONO- AND MACROPOLYCYCLIC LIGANDS; INSERTION OF SUBSTRATE BETWEEN THE TWO METAL CATIONS. By R. Louis, Y. Agnus and R. Weiss, Institut Le Bel, 4 rue B. Pascal, Université Louis Pasteur, 67070 Strasbourg Cedex, France.

X-Ray structures of bimetallic copper (II) inclusion complexes with several macromono- and macropolycyclic ligands have been determined. The stoichiometry of all these complexes may be schematically represented by $Cu_2^{II}C^L$ where L symbolizes the macrocyclic ligand. The inclusion of the two Cu^{II} cations is carried out by complex formation with two NS_2 , N_2O_2 , N_3 or NO_2 sets of donor atoms. The two metal ions are separated by a distance of 4-8 Å according to the geometry of the macrocyclic ligand. The later insertion of a substrate molecule between the two cations may become possible.

X-Ray structures, physical and chemical properties will be presented.

09.4-23 THE STRUCTURES OF SALICYLALDIMINATES OF CU(II). By A.N. Shnulin 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.

On the basis of X-ray structural data we have studied the possibilities of directional control of the structural parameters, the energy levels and the coordination of the copper atom in its N-phenyl salicyl(SA)- and naphthaldiminate(NA) complexes by introducing certain groups into the ligand (A.N. Shnulin, Kh.S. Mamedov, Yu. Struchkov, J. Struct. Chem., 18(5), 707; 18(6), 799; 806(1977) (Engl. trans.) 17(5), 866 (1976); 19(4), 688; 19(6) 1088(1978) (Russ.orig.)). The factors have been determined which are responsible for formation of a particular molecular and crystal configuration of these complexes. The competition of steric and π -effects between the aromatic group and the remainder of the ligand is of first rate importance. Domination of one of these effects may be strengthened or weakened by including appropriate donor or acceptor groups into the phenyl ring and by elongation of the π -electronic system of the ligand (SA-NA) as well. This changes the result of the competition on which realization of a particular coordination of Cu depends. In case of the N-hydroxypyrrrolidine- and the 3-Br, 3-Cl and 3-NO₂ substituted salicylaldiminate complexes an unusual interaction with chlorocontaining solvents takes place, namely, abstraction of Cl and its coordination to copper. The presence of an OCH₃-group in position 5 results in formation of the familiar bischelate complex without participation of chlorine. The square planar coordination of Cu must be realized in all the SA-complexes provided that the donor groups occupy the p-position of the phenyl group. The substitution of acceptor for donor has to result in a distorted tetrahedral coordination. The coordination must be analogous in all the NA-complexes, where the p-position of the phenyl group is occupied by an acceptor or strong donor like $N(CH_3)_2$. The lower donors must result in square planar geometry. These two statements are only predictions.