

**09.4-18** X-RAY STUDY OF THE PROPERTIES OF THE CYANATE ION IN Cu(II) COMPLEXES WITH HETERO-CYCLIC NEUTRAL LIGANDS. By F. Valach and M. Dunaj-Jurčo, Faculty of Chemical Technology, Slovak Technical University, 880 37 Bratislava, Czechoslovakia.

The NCO group in the crystal structure of the  $\text{Cu}(\text{NCO})_2(2,4\text{-lutidine})$  (Valach, Dunaj-Jurčo, Garaj and Hvastijová, Coll. Czech. Chem. Commun. (1974) 39, 380) implements the function of a bridge between two atoms of copper through an atom of nitrogen, while the oxygen atom remains uncoordinated. The crystal structure of  $\text{Cu}(\text{NCO})_2$

$(\text{H}_2\text{O})(3\text{-aminopyridine})_2$ , shows an analogous coordination of one half of the NCO groups to Cu(II) atoms. The remaining NCO groups form the bridges between two atoms of Cu(II) via their end atoms analogous to those found in the structure of  $\text{Cu}(\text{NCO})_2(\text{pyridine})_2$  (Valach, Dunaj-Jurčo and Handlovič, J. Cryst. Mol. Struct. 10 (1980) In press). In the crystal structure of  $\text{Cu}(\text{NCO})_2$

$(\text{H}_2\text{O})(3\text{-aminopyridine})_2$  the copper atoms occupy centrosymmetric sites. Half of them are trans-coordinated by two atoms of nitrogen from the NCO groups and by two atoms of nitrogen from the 3-aminopyridine molecules (the bond lengths Cu-N are 1.94 and 2.03 Å). The coordination is completed by two oxygen atoms from NCO groups (the bond lengths Cu-O are 2.56 Å) to an elongated octahedron. The second half of the Cu(II) atoms has in the axial positions the same coordination of two oxygen atoms from the water molecules (the bond lengths Cu-N and Cu-O are 1.95, 2.03 and 2.67 Å). End-bonded NCO groups have bond lengths N-C, C-O 1.16 and 1.20 Å

respectively and a bond angle N-C-O of  $176.8^\circ$ . The bidentate NCO groups (the lengths N-C, C-O are 1.16, 1.22 Å and the angle N-C-O is  $176.9^\circ$ ) connect the Cu(II) atoms forming endless chains along c (Fig. 1); the chains are connected by hydrogen bonds.

This structure was determined from diffractometric data by the heavy atom method and refined to  $R=0.054$  for 2029 independent reflections. The space group is  $P\bar{1}$  ( $Z=2$ ) and the unit cell parameters are  $a=8.487(3)$ ,  $b=8.349(3)$ ,  $c=12.346(4)$  Å,

$\alpha=102.44(3)$ ,  $\beta=82.69(3)$  and  $\gamma=120.84(3)^\circ$ .

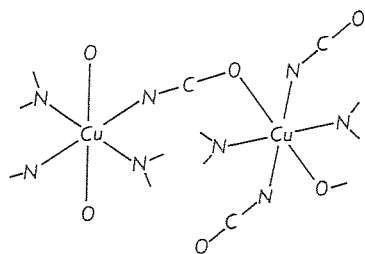


Fig. 1

**09.4-19** STRUCTURES OF COPPER(II)-MERCAPTIDE COMPLEXES. By Oren P. Anderson and C.M. Perkins, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, U.S.A.

Combination of Copper(II) with mercaptans generally results in formation of copper(I) and a disulfide. Application of synthetic guidelines derived from mechanistic studies has allowed us to synthesize and crystallize new, stable copper(II)-mercaptide complexes.

The structure of one such species, the adduct between  $[\text{Cu}(\text{Pre-H})^+]$  (Pre-H = 3,9-dimethyl-4,8-diazamideca-3,4-diene-2-oxime-10-oximate) and the p-chlorothiophenolate anion, has been determined. Dark green crystals of  $[\text{Cu}(\text{Pre-H})(\text{S-Ph-Cl})]$  were monoclinic, space group  $P2_1/c$ , with  $Z=4$  ( $a = 10.530(7)$  Å,  $b = 12.789(8)$  Å,  $c = 15.040(9)$  Å,  $\beta = 105.43(2)^\circ$ ). The structure was refined to  $R = 0.050$ ,  $R_w = 0.051$ .

The coordination geometry about each copper(II) ion is roughly square pyramidal, with nitrogen atoms of the near-macrocylic Pre-H ligand occupying the four basal positions (ave. Cu-N = 1.981(4) Å). The thiolate sulfur atom occupies the apical position, at Cu-S = 2.422(2) Å, and the bond angle at sulfur is surprisingly small (Cu-S-C  $101.0(2)^\circ$ ). Spectroscopic properties of this compound, together with other Cu(II) thiolate complexes in this series, will be discussed.

**09.4-20** THE CRYSTAL STRUCTURE OF DIAQUATETRA ( $\beta$ -PICOLINE)Cu(II)PERCHLORATE,  $[\text{Cu}(\text{H}_2\text{O})_2(\text{C}_6\text{H}_7\text{N})_4](\text{ClO}_4)_2$ . By Shengzhi Hu, Department of Chemistry, University of Amoy (Xiamen), China, Richard J. Barton, Keith E. Johnson and Beverly E. Robertson, Faculty of Science, University of Regina, Regina, Sask., S4S 0A2, Canada.

The picoline complexes of transition metals (Cu, Co, Ni) were obtained as their perchlorates. The compositions as well as coordinations of these compounds suggested an investigation of their crystal and molecular structures.

Crystals of the Cu(II) and Co(II) complexes both showed monoclinic rhombohedral morphology and were shown by diffraction methods to be isomorphous. The structure of the Cu(II) complex has been determined in detail.

	a	b	c	$\beta$	Dm
Cu(II)	15.292(4)	9.672(2)	20.579(5) Å	94.73(2)°	1.46
Co(II)	15.9	9.36	20.5 Å	96.0	1.45

The space group of both compounds is  $C2/c$ . The intensity data were collected with a modified Picker diffractometer. The structure was solved by the heavy atom method and refined by least-squares to a final conventional R factor of 0.10 for the 1918 reflections with  $\sin \theta / \lambda \leq 0.65$  and  $I/\sigma(I) > 2.0$ .

The structure consists of copper coordination polyhedra  $[\text{Cu}(\text{H}_2\text{O})_2(\beta\text{-pic})_4]^{++}$  and perchlorate counterions. The ions are connected by hydrogen bonds of average length 2.81 Å. The four N atoms of the  $\beta$ -picoline ligands form a basal plane with [Cu-N] distances of 2.02(1) and 2.04(1) Å. The water ligands are above and below the basal plane with [Cu-O] distances of 2.47(1) and 2.52(1) Å. The thermal factors suggest that the perchlorate ion undergoes enhanced librational motion which is not unexpected.

Chemical analyses suggest variable water content. Dx with 2 water molecules present is 1.467 g cm<sup>-3</sup>.