

## 09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

09.4-39 STRUCTURE MOTIVES OF CuCl IN THE NEW MONO- AND DIOLEFINE COPPER(I)  $\pi$ -COMPLEXES. By E.I.Hladyshesky, M.G.Mys'kiv, P.Yu.Zavalij, V.V.Oliynyk, Lviv State University, Lviv, USSR.

The crystal structures of the new  $\pi$ -complexes of copper(I) chloride with some simple olefine derivatives: acrylamide -  $(CuCl \cdot L)_n$  /A/; acrylic acid -  $(CuCl \cdot L)_n$  /B/; allylic alcohol -  $Cu_4Cl_4 \cdot 4L$  /C/; allyl cyanide -  $(Cu_4Cl_4 \cdot 2L)_n$  /D/; trans-1-cyano-1,3-butadiene -  $(Cu_2Cl_2 \cdot 2L)_n$  /E/ and p-divinylbenzene -  $(Cu_6Cl_6 \cdot 3L)_n$  /F/ have been determined.

	a	b	c	$\gamma$	S.g.
A	6,472(1)	7,957(1)	21,139(4)		Pbca
B	8,153(2)	6,223(1)	20,620(3)		Pbca
C	8,698(1)	16,436(1)	7,189(1)	101,31(2)	P2 <sub>1</sub> /b
D	8,359(3)	7,457(2)	11,851(3)	98,77(3)	P2 <sub>1</sub> /b
E	6,834(1)	13,717(4)	7,450(2)	111,62(2)	P2 <sub>1</sub> /b
F	12,226(4)		6,276(2)		P $\bar{3}$

The distinctive feature of copper(I) halogenide complexes is the ability to form with copper and halogen atoms a large variety of the fragments: di-, tri-, tetra- and hexameric cores, polymeric chains, layers etc. The obtained structure data and not so numerous literature ones (3 compounds with substituted and 4 - with cyclic olefines) allowed to define some construction relationships of those formations in  $\pi$ -complexes discussed.

The homologous connexion of  $\pi$ -complexes fragments with itself and the copper(I) chloride structure (ZnS-sphalerite) has been established. A cyclic core  $Cu_2Cl_2$  or some parts of CuCl structure (hexagon  $Cu_3Cl_3$ , chain -Cu-Cl- along [211] direction) may be considered as the constructive units.

The peculiarity of CuCl motives in copper(I)  $\pi$ -complexes with regard to those in  $\delta$ -ones is a presence of prolonged Cu-Cl bonds. Such a distinction is caused by the structure specificity of  $\pi$ - and  $\delta$ -coordinated copper(I) atoms: trigonal prism with outer chlorine atom at an apex in the first case and the tetrahedron with the equal Cu-Cl bonds in the  $\delta$ -complexes.

Owing to the obtained results there is a strong possibility to predict the coordination character ( $\pi$  or  $\delta$ ) of copper(I) atom on the basis of the structure of CuCl-fragment, and for the polynuclear complexes - using the lattice parameters only.

09.4-40 THE CRYSTAL STRUCTURES OF SOME ZINC(II) COMPLEXES WITH BENZOIC ACID AND ITS p-SUBSTITUTED DERIVATIVES. By F.N.Musayev, B.T.Usubaliev, G.A.Guseynov, Kh.S.Mamedov, Institute of Inorganic and Physical Chemistry, Academy of Sciences of Azerbaijan SSR, Narimanov prospect, 29, Baku, 370143, USSR.

The structures of compounds  $Zn(C_6H_5COO)_2$  (I),  $Zn(C_6H_5COO)(OH) \cdot C_5H_5N$  (II),  $Zn(C_6H_5COS)_2 \cdot 2C_5H_5N$  (III),  $Zn(p-O_2NC_6H_4COO)_2 \cdot 2H_2O$  (IV),  $Na/Zn(p-H_2NSO_2C_6H_4COO)_3 \cdot H_2O$  (V) have been determined by the X-ray diffraction analysis. The Zn atoms in all compounds have a distorted tetrahedral environment of ligands via the donor atoms of O, N, S. The structure of (I) consists of infinite chain molecules of the type:  $-Zn \equiv Zn - Zn \equiv Zn -$ , i.e. the Zn atoms are bridged by the carboxylic groups. The Zn-O bond lengths lie in the range 1.926-1.980 Å, the Zn.....Zn distance is 3.269 Å.

The complex (II) is a polymeric structure as well as (I). The OH groups are linked to Zn atoms (1.945; 1.978 Å), forming  $-Zn-OH-Zn-OH-Zn-$  bridges. The Zn.....Zn distance is 3.458 Å. The Zn atom is coordinated to carboxylic oxygen atoms (1.966 Å) and pyridine nitrogen atoms (2.110 Å). No other oxygen in carboxylic group is coordinated to the metal (Zn.....O 2.733 Å).

The complex (III) is crystallized in two modifications (triclinic and orthorhombic) from 1:1 pyridine-water solution. The two modifications have a *cis* configurations. The structures are built up from discrete neutral molecules. The tetrahedral surrounding about Zn consists of two pyridine molecules (2.079-2.112 Å) and two monothiobenzoate groups bonding as unidentate ligands through sulphur with a shortest Zn-S distance (2.280-2.320 Å).

In the structure (IV) the Zn atoms are coordinated with two water molecules (1.996; 1.994 Å) and two carboxylic oxygen atoms (2.002; 2.010 Å). The crystal structure of (IV) is molecular. The second oxygen in each carboxylic group non-coordinated to the metals (Zn.....O 2.522 Å). The water molecules are situated so as to permit hydrogen bonding to coordinating oxygen atoms of carboxylic group of the neighbouring molecule (along *a*) and non-coordinating oxygen atoms of carboxylic group along *b*. The crystal structure of (V) is polymeric. The sodium atom is in octahedral coordination formed by the oxygen atoms from the carboxylic and sulfamid groups (the Na-O distance varies from 2.295 to 2.622 Å). The distances around Zn atom are  $Zn-O_w = 2.050$  Å,  $Zn-O_{carbox.} = 2.003$ ; 2.006; 2.009 Å. The two carboxylic and one sulfamid groups are bonded to different metal atoms, forming  $-Na-O-Zn-O-Na-$  bridges. These bridges are linked in polymeric chains, running along *c* axis. These chains are interconnected with two types of hydrogen bonds N-H.....O and O-H.....O in three-dimensional net.