

09.4-17 ANOTHER AMINOACID COPPER COMPLEX. THE CRYSTAL STRUCTURE OF bis Cu (L-HYDROXYPROLINE).  $4H_2O$ . By M. Teresa L. Duarte, Maria A.A.F. de C.T. Carrondo, Michael B. Hursthouse\*, Centro de Quimica Estrutural, Complexo I, I.S.T., Lisbon Portugal, \*Department of Chemistry, Queen Mary College, London, U.K.

Amino acids are strongly coordinating ligands and in most cases bind as chelating agents. Since it is clear that metals in biological systems exert most of their effect in a bound form, it is especially relevant to make model studies of the metal complexes formed by amino acids.

We have been interested in studying the complexes formed by copper, a metal which has considerable biochemical significance. Previous publications have described the structures of complexes with L-lysine (Author, Inorg. Chimica Acta, 108 (1985) 11-15) and L-arginine (Author, Inorg. Chimica Acta, 124 (1986) 41-47). We now report the structure of a complex with L-hydroxyproline. Blue crystals were obtained by mixing stoichiometric quantities of copper acetate and L-hydroxyproline as aqueous solutions and recrystallising from water. They were characterized by infrared nmr spectroscopy and elemental analysis as  $Cu(L\text{-hydroxyproline})_2 \cdot 4H_2O$ .

X-ray measurements were made using a CAD-4 diffractometer with graphite-monochromatised Mo- $K_\alpha$  radiation, and the structure solved by standard heavy atom methods.

Crystal data:  $C_{10}H_{12}N_2O_6Cu$ , M.W.=395.5, monoclinic, space group  $P2_1$

$a=10.209(6)$ ,  $b=8.071(3)$ ,  $c=8.698(3)\text{\AA}$ ,  $\beta=100.33(4)\text{deg}$

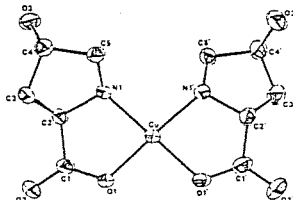
$V=786.1\text{\AA}^3$ ,  $Z=2$ ,  $D_c=1.67\text{ g cm}^{-3}$ ,  $\mu(\text{Mo-}K_\alpha)=14.48\text{ cm}^{-1}$

For 2251 reflections with  $F > 3\sigma(F)$ , the isotropic structure was refined by least squares to an  $R=0.122$ , which decreased to  $R=0.0622$  when anisotropy was permitted. The final  $R$  is 0.0395.

Some bond lengths ( $\text{\AA}$ ) and angles (deg) are as follows:

Cu-O1 ...	1.965(4)	N1-Cu-N1' ...	97.5(2)
Cu-N1 ...	2.034(4)	N1-Cu-O1 ...	84.2(2)
Cu-O1' ...	1.938(3)	O1-Cu-O1' ...	92.9(1)
Cu-N1' ...	1.978(4)	O1'-Cu-N1' ...	86.2(2)

The most important feature of the structure, which has the Cu atom in the usual square-planar configuration, is that the two chelating aminoacid functions are arranged in a cis configuration, rather than the usual trans. Full details of the analysis and geometry will be given in the poster.



09.4-18 CRYSTAL STRUCTURE OF (L-PROLINATO)-(2,2'-BIPYRIDYL)PALLADIUM(II)CHLORIDETRIHYDRATE By R.P.Patel. Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India and, V.M.Padmanabhan, Neutron Physics Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India.

The title complex, a mixed ligand chelate crystallises in orthorhombic space group  $P2_12_12_1$  with  $a=20.814$ ,  $b=25.074$ ,  $c=6.984\text{\AA}$ ,  $Z=8$ . For 1234 reflections collected on Trombay diffractometer  $R=0.099$  at the present stage of refinement. The crystal undergoes radiation damage and crumbles. The loss of water molecules even at room temperature was confirmed by thermogravimetric studies. The coordination of the ligands was confirmed by infrared and electronic absorption spectroscopy. Palladium is four-coordinated having a distorted planar geometry. The two imino-nitrogens of bipyridyl and, the nitrogen and carboxyl oxygen atoms of l-proline are coordinated to palladium resulting in the formation of a bis-chelate. The complex is cationic with chlorine acting as the counter ion. The Pd-O and Pd-N distances are normal. The  $C^\gamma$  of proline shows large thermal vibrations. A network of hydrogen bonds involving the two chlorines and the three water molecules stabilises the structure.

09.4-19 THE PECULIARITIES OF TRIPOD LIGANDS COORDINATION OF SEMI- AND THIOSEMICARBAZIDDIACETIC ACID WITH VANADYL COMPLEXES. By T.I. Malinovsky, I.F. Burshtein, N.V. Gerbeleu and O.A. Bologna, Institute of Applied Physics and Institute of Chemistry, Academy of Sciences MSSR, Kishinev, USSR.

The peculiarities in the arrangement of equal and non-equal branches in coordination compounds of vanadyl with tripod ligands - semicarbazidodiacetic acid ( $H_2Q$ ,  $H_2NC(O)NHN(CH_2COOH)_2$ ) and thiosemicarbazidodiacetic acid ( $H_2L$ ,  $H_2NC(S)NHN(CH_2COOH)_2$ ):  $[VOQH_2O]$  (I)  $a=10.290(5)$ ,  $b=10.100(5)$ ,  $c=9.909(3)\text{\AA}$ , space group  $P2_12_12_1$ ,  $Z=4$  and  $[VOLH_2O] \cdot H_2O$  (II)  $a=15.324(7)$ ,  $b=12.965(6)$ ,  $c=11.271(6)\text{\AA}$ ,  $\gamma=99.56^\circ$ , space group  $P2_1/b$ ,  $z=8$  are discussed.

Each vanadyl ion of such molecular complexes is bound to one molecule of organic ligand and to one molecule of water.

Both tripod ligands are tetradentate. One atom of each three branches together with a hydrazine residue N atom take part in the chelating. Thus the coordination of the central ion is equal to 6 while the coordination polyhedron is the distorted octahedron. Although the coordination polyhedra of I and II are similar in form, the structure of the complexes is different. It should be mentioned that there are two crystallographic independent complexes in II, while in I there is one. The acetate branches are situated in trans-positions in I while the semicarbazide branch is in the cis-position. An analogous structure is observed on one of the II complexes, the structure of the second complex being different. The thiocarbazide and one of the acetated branches are in trans-position. The second branch is in cis-position. In the II compound a new type of geometrical isomer has been found for the coordinated compounds with the tripod ligands. Cis- and trans-isomers exist in the same crystal. In I only the trans-isomer is realized.