Crystal and Molecular Structures of Bis-(*N*-benzylprolinato)copper(2+) Complexes

By G. G. ALEKSANDROV, YU. T. STRUCHKOV, A. A. KURGANOV, S. V. ROGOZHIN, and V. A. DAVANKOV*
(*Institute of Organo-Element Compounds of the Academy of Sciences, Vavilov, 28, Moscow, U.S.S.R.*)

Summary In the symmetrical *trans*-complex (*N*-Bz-L-Pro)-Cu(*N*-Bz-D-Pro) both benzyl groups are directed towards the apical positions, whereas in *trans*-Cu(*N*-Bz-L-Pro)$_2$ one benzyl radical is twisted in the opposite direction, distorting the chelate ring from planarity.

BIS-(*N*-BENZYLPROLINATO)COPPER(2+) shows considerable stereoselectivity.[1,2] In order to display the stereochemical difference between (*N*-benzyl-L-prolinato)(*N*-benzyl-D-prolinato)copper(2+) (I) and bis(*N*-benzyl-L-prolinato)copper-(2+) (II) whose thermodynamic stabilities in solution are unequal,[1] *X*-ray investigations of their crystal structures were carried out.

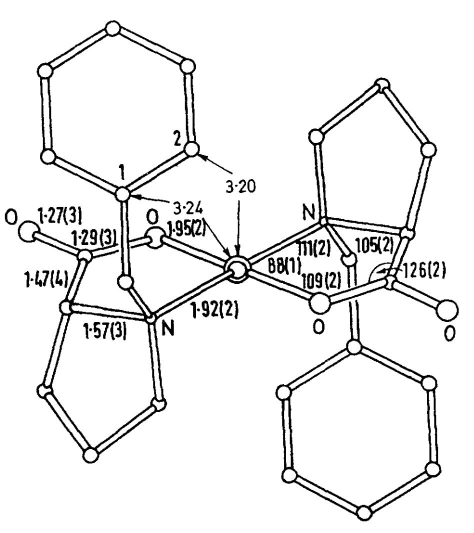

FIGURE 1. *Structure of* (*N*-Bz-L-Pro)(*N*-Bz-D-Pro)Cu(2+) (I).

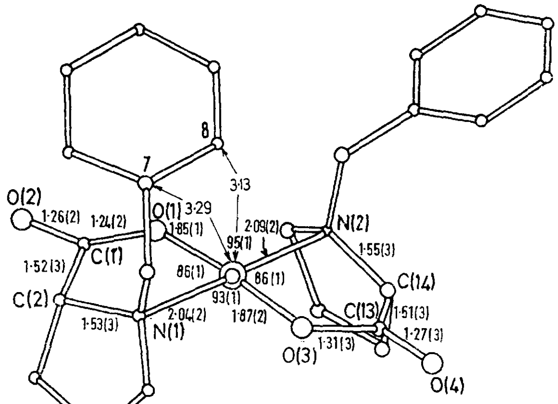

FIGURE 2. *Structure of* bis(*N*-Bz-L-Pro)Cu(2+) (II).

Crystals of (I) are monoclinic, $a = 8{\cdot}857$, $b = 12{\cdot}379$, $c = 10{\cdot}061$ Å, $\gamma = 97{\cdot}1°$, $D_m = 1{\cdot}46$, $D_c = 1{\cdot}44$ g/cm^3 for $Z = 2$, space group $P2_1/b$. Crystals of (II) are orthorhombic, $a = 24{\cdot}031$, $b = 8{\cdot}679$, $c = 10{\cdot}580$ Å, $D_m = 1{\cdot}39$, $D_c = 1{\cdot}43$ g/cm^3 for $Z = 4$, space group $P2_12_12_1$.

The structures were determined by the heavy-atom method and refined by least-squares (full-matrix, isotropic temperature factors). At the present stage of refinement $R = 0{\cdot}17$ for (I) (equi-inclination Weissenberg goniometer, unfiltered copper radiation, 800 independent reflections) and $R = 0{\cdot}10$ for (II) (intensity data were collected on automatic Hilger-Watts diffractometer using graphite-monochromatized Mo-K_α radiation and a θ—2θ scanning procedure, a total of 1100 independent data were collected with $2\theta \leqslant 44°$).

Crystals of (I) and (II) are built up of discrete molecules [(I) is in the centre of symmetry] which have no specific interaction between each other. The geometry of the molecules (I) and (II) is shown in Figures 1 and 2 respectively. Both complexes are *trans*, though in (II) one could expect the *cis*-configuration as in bis-(L-prolinato)-palladium(2+).[3]

The average Cu–N and Cu–O bond lengths are comparable with the average bond lengths in other bis(amino-acid)copper(2+) complexes (Cu–N 1·99, Cu–O 1·96 Å). The other bond lengths and bond angles in the five-membered chelate rings in (I) and (II) are normal. The five-membered pyrrolidine rings with an average value for the ring angles of 106° for (I) and 105° for (II) and the deviation of the γ-carbon atom from the plane of the other four atoms of 0·3 Å in (I) and 0·6 Å in (II) have the conformation typical for complexes with proline ligands.[3,5,6]

A significant feature of the stereochemistry of the *N*-substituted α-amino-acid complexes is the orientation of the *N*-benzyl radicals. If the configuration of the complex is *trans*, the *N*-radicals in the bis-proline complexes are on the same side [as in (II)] or on opposite sides [as in (I)] of the main co-ordination plane. The distances Cu . . . C(2)(Ph) and Cu . . . C(1)(Ph) are 3·20 and 3·24 Å respectively. Similar intramolecular contacts Cu . . . C(Ph) (3·01—3·34 Å) were found earlier in copper complexes with aromatic amino-acids.[7,8] In (II) only one of the benzyl groups has such an orientation: Cu . . . C(7) 3·29 Å and Cu . . . C(8) 3·13 Å. The different orientation of the benzyl groups in (II) apparently results from steric interaction. In (II) the deviation of the Cu and N(1) atoms from the plane O(1)-C(1)O(2)C(2) is 0·03 and 0·25 Å respectively, and that of atoms Cu and N(2) from the plane O(3)C(13)O(4)C(14) is −0·13 and 0·47 Å respectively. In (I) both five-membered metal-containing rings are planar. Possibly the difference in the conformation of the chelate rings in (I) and (II) increases the stereoselectivity in this system, whilst in bis(prolinato)copper(2+) complexes the stereoselective effects are considerably weakened.[2]

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