CHEMISTRY LETTERS, pp. 1443-1446, 1981. © The Chemical Society of Japan 1981

PREPARATION AND CRYSTAL STRUCTURE OF BIS(L-PHENYLEPHRINATO)COPPER(II) MONOHYDRATE

Hisayoshi NAKAI and Yukinao NODA
Department of Chemistry, Hyogo College of Medicine,
Mukogawa-cho, Nishinomiya, Hyogo 663

The title compound was prepared, and its structure was determined by the X-ray method. The copper environment is trans-square planar and the two phenylephrinato ligands act as bidentate ligands through the N and O(alcolato) atoms.

Since it was suggested by Bouvet$^{1)}$ that the oxidation of adrenaline may go through a copper-adrenaline complex, the copper(II) complexes with adrenaline and its analogous compounds have been biologically very interesting. The structures of these complexes have been discussed on the basis of the potentiometric and spectroscopic studies.$^{2)}$ However, a direct evidence has not yet been reported. L-phenylephrine(=phenyH$_2$, 3-hydroxy-α-[(methylamino)methyl]benzenemethanol) is a well-known adrenergic agent. In order to clarify the copper environment and the conformation of the L-phenylephrine ligand, an X-ray study on bis(L-phenylephrinato)copper(II) monohydrate, [Cu(phenyH)$_2$]H$_2$O, was performed.

By mixing 0.6680 g(4 mmol) of L-phenylephrine(Tokyo Kasei) in 50 ml of 0.16 mol·dm^{-3} aqueous sodium hydroxide solution(8 mmol) with a solution of cupric nitrate(0.4832 g, 2 mmol) in 20 ml of water was obtained a purple solution, which was stirred for 5 h at 40 °C. After filtration, the solution was allowed to stand for 4 d at room temperature. Tiny crystals, plate-like and purple in color, appeared on the surface of the solution. Upon recrystallization from aqueous alkali solutions, larger crystals could not be obtained owing to the decomposition of the compound. Found: C,51.52; H,6.38; N,6.72%. Calcd for [Cu(phenyH)$_2$]H$_2$O: C,52.22; H,6.33; N,6.77%. Crystal data: orthorhombic, a=18.10, b=8.37, c=12.81 Å, Z=4, Dc=1.42, Dm=1.46 g.cm^{-3}, space group $P2_12_12_1$. Attempts to collect the counter data on a Philips PW1100 four-circle diffractometer were unsuccessful because of tiny crystals(0.4×0.3×0.02 mm). Consequently, the integrated intensity data(h0l~h4l and hk0~hk6) were collected by the multiple film equi-inclination techniques using Ni-filtered CuK$_\alpha$ radiation. The intensities were estimated visually and corrected for Lorentz-polarization effects; the intensities of 800 independent reflections were observed, of which 324 were too weak to be measured. No absorption correction was made. The structure was solved by the heavy-atom method, and refined by least-squares calculations. The positions of all the non-hydrogen atoms but not one methyl carbon atom(C(9) in Fig. 1) were obtained from successive Fourier calculations, and were refined by the least-squares calculations with isotropic temperature factors to R=0.19 for 476 non-zero reflections. On the other hand, the difference Fourier map phased with the known atoms revealed two lower peaks at an equatorial position of the N(1) atom. Of these two, one was considered to be unacceptable for the C(9) atom position because of very short contacts(about 2.5 Å) to the O(11) and O(H_2O) atoms, but the other was believed to be a most probable peak, interpreted as the C(9) atom position. However, after two cycles of the least-squares refinement, the isotropic temperature factor of the C(9) atom rose to 17 Å^2. Because of poor intensity data, a further refinement was not performed. Standard deviations were about 0.04 Å in the distances between copper and lighter atoms, and about 0.09 Å in those between lighter atoms.

The crystal is composed of neutral complexes, [Cu(phenyH)$_2$], and uncoordinated water molecules. Figure 1 shows a schematic drawing of the [Cu(phenyH)$_2$].

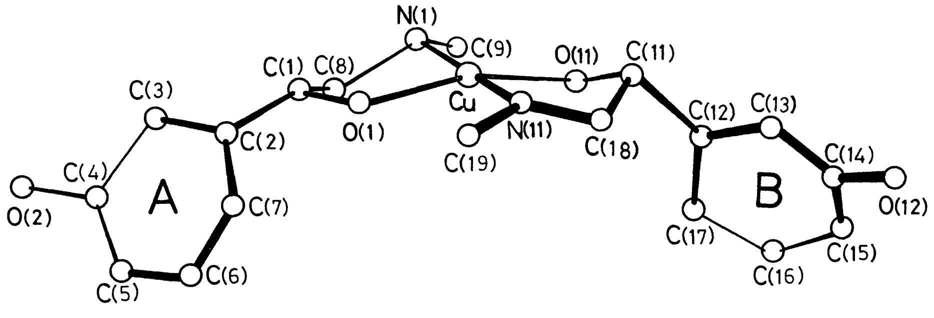

Fig. 1 A schematic drawing of [Cu(phenyH)$_2$], where the C(9) atom position is a most probable one determined by difference Fourier syntheses.

The coordination geometry about the copper atom is trans-square planar: two phenylephrinato ligands coordinate to a copper atom through the N and O(alcolato) atoms and are trans with respect to each other. The Cu-O distances are 1.94 Å on the average and this value is good agreement with the Cu-O(alcolato) distances found in aquabis[L-(+)-threo-2-amino-1-phenyl-1,3-propanediolato-N,O]copper(II) tetrahydrate(1.92 Å on average),3) and cyanato(2-dimethylaminoethanolato)copper(II) (1.94 Å on average),4) rather than the Cu-O(alcohol) one(2.045 Å) found in bis-(benzimidazol-2-ylmethanol-N'O)(nitrato-NO)copper(II) nitrate monohydrate.5) The mean Cu-N distance is 2.09 Å and the bite angles of the chelates are about 88°. The angles of N(1)-Cu-N(11) and O(1)-Cu-O(11) are 178(2) and 162(2)° respectively. The best planes of the two phenol rings, A and B, make angles of 120 and 57° with the plane defined by Cu, O(1), O(11), N(1), and N(11) atoms respectively, and 65° with each other.

Figure 2 shows the c axis projection of the crystal structure. The structure contains the layers of the neutral complexes, [Cu(phenyH)$_2$], each layer being parallel to the ab plane; as a copper atom occupies the position(0.244, 0.011, 0.489) nearly equal to (1/4, 0, 1/2), the arrangement of them can be regarded as a C-centered lattice. In one layer of the neutral complexes, each complex is

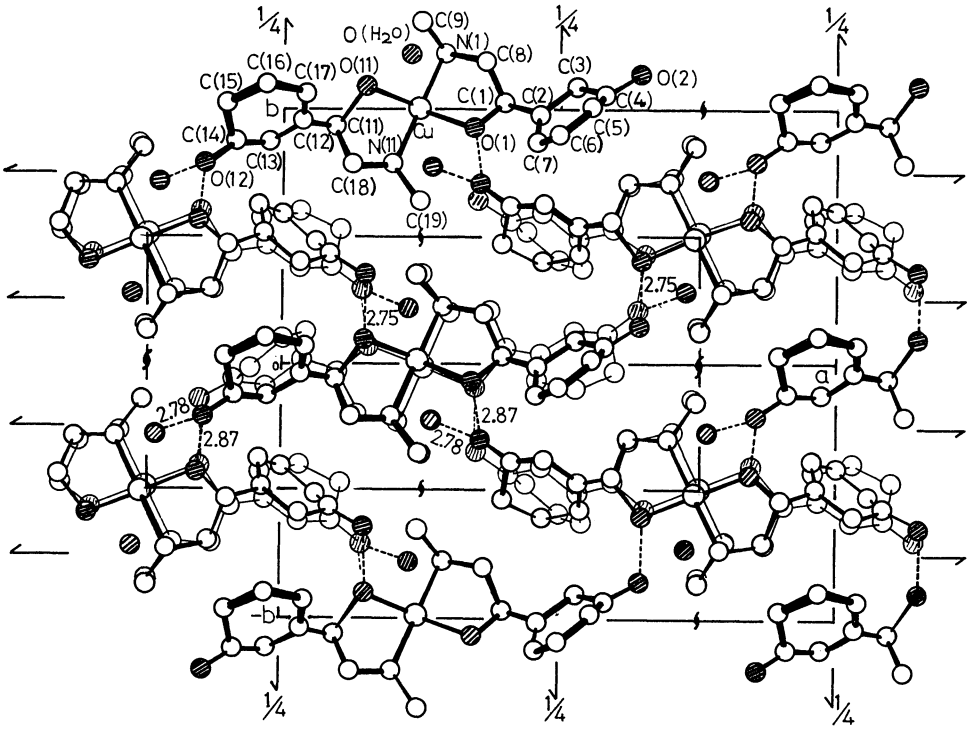

Fig. 2 The crystal structure viewed along the c axis. Dotted lines represent hydrogen bonds and oxygen atoms are shown by ▨ .

linked to four others by four hydrogen bonds(2.75 and 2.87 Å) formed between alcolato and phenolic O atoms and, as its result, two-dimensional networks are built up, while no hydrogen bonding is found between the layers.
The water molecules do not participate in the coordination to the copper atoms but form hydrogen bonds(2.78 Å) with the phenolic oxygen atoms. All the intermolecular distances are normal: fairly short ones are 3.0 Å in N(1)---O(2)[-1/2+x,1/2-y,1-z] and 3.2 Å in C(15)---N(1)[-1/2+x,1/2-y,1-z].

Computations were performed by using the programs(RSSFR-5,⁶⁾ HBLS-V,⁷⁾ and DAPH⁷⁾) on an ACOS Series 77 NEAC System 700 computer at the institute for Protein Research, Osaka University.

References

1) P.Bouvet, Bull. Soc. Chim. Biol., 31, 1301(1949).

2) R.F.Jameson and W.F.S.Neillie, J. Inorg. Nucl. Chem., 27, 2623(1965).

3) A.M.M.Lanfredi, A.Tiripicchio, and M.T.Camellini, Acta Crystallogr., B35, 349-(1979).

4) R.Mergehenn and W.Haase, Acta Crystallogr., B33, 1877(1977).

5) G.J.Hamilton, J.R.Ferraro, and E.Sinn, J. Chem. Soc., Dalton Trans., 1979, 515.

6) T.Sakurai, The Universal Crystallographic Computing System(I), The Crystallographic Society of Japan(1967), p.45.

7) T.Ashida, The Universal Crystallographic Computing System-Osaka, The Computation Center, Osaka University(1973), pp. 55 and 63.

(Received August 3, 1981)