Structure of the So-called Tricoordinated Copper Complexes

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We have determined the magnetic moments of a number of tricoordinated copper(II) complexes such as acetylacetone-mono-(*o*-hydroxyanil) copper(II)[1]. From the observed subnormal magnetic moments 0.87~1.37 B.M. per copper atom, it was concluded that binuclear complex molecules are formed in crystals, in which pairs of copper atoms exist: the Cu-Cu distance being so small as to permit exchange interaction between two copper atoms in a pair. Attention was called to the fact that all tricoordinated copper(II) complexes showing a subnormal magnetic moment so far investigated have a planar monomeric structure, because the copper atom is involved in two rings, both of which are either a five-membered ring or a six-membered one having conjugated double bonds[2]. These conclusions have been confirmed by the recent X-ray analysis of a single crystal of acetylacetone-mono-(*o*-hydroxyanil) copper(II) carried out by Barclay et al.[3] It was found that two copper atoms are 3.00 Å distant from each other in a dimer molecule having a planar configuration shown in Fig. 1. In this binuclear complex, each copper atom has one nitrogen and three oxygen atoms as coordinating atoms at the corners of a slightly distorted square.

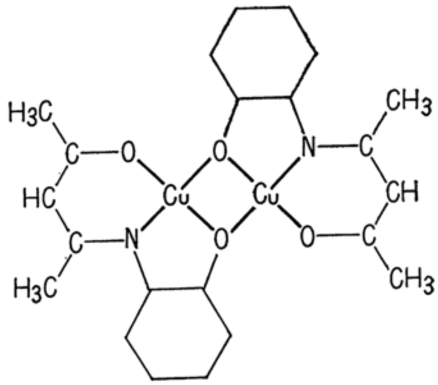

Fig. 1. Binuclear structure of acetylacetone-mono-(*o*-hydroxyanil) copper(II).

We have found[2] that some tricoordinated copper(II) complexes show a normal moment slightly greater than the spin moment for one unpaired electron 1.73 B.M. 5-Nitrosalicylalanthranilic acid copper(II) is an example. It was pointed out that these copper complexes showing a normal magnetic moment have a carbonyl group, the oxygen atom of which is capable of being coordinated on a copper atom and that they contain a six-membered chelate ring possibly having a three-dimensional structure, because only one double bond is involved in the ring[4].

In order to explain the observed moments, we propose a new binuclear structure for the so-called tricoordinated copper(II) complexes having a normal magnetic moment. The structure is shown in Fig. 2 with 5-nitrosalicylalanthranilic acid copper(II) as an example. It is analogous to that shown in Fig. 1 in that the two copper atoms in the binuclear complex have

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[1] M. Kishita, Y. Muto and M. Kubo, *Naturwissenschaften*, **44**, 372 (1957); *Australian J. Chem.*, **10**, 386 (1957).

[2] M. Kishita, Y. Muto and M. Kubo, *Naturwissenschaften*, **44**, 612 (1957); *Australian J. Chem.*, **11**, 309 (1958).

[3] G. A. Barclay, C. M. Harris, B. F. Hoskins and E. Kokot, *Proc. Chem. Soc.*, **1961**, 264.

[4] K. Sakashita, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **74**, 315 (1953).

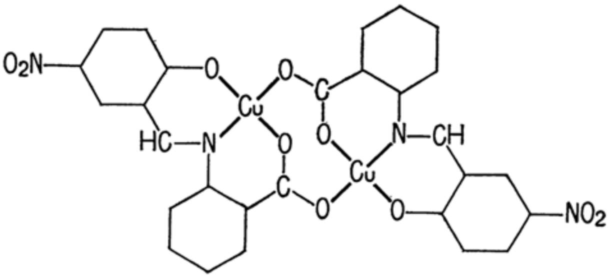

Fig. 2. Binuclear structure of 5-nitrosalicylalanthranilic acid copper(II).

a square coordination of nitrogen and oxygen atoms. It differs from the latter structure in that the copper atoms are involved in an eight-membered ring instead of forming a square with two oxygen atoms and are farther apart from each other than in the structure shown in Fig. 1. Consequently, the direct spin interaction between the two copper atoms is negligible, i.e., the low diamagnetic singlet energy level of the pair of spins practically coincides with the higher paramagnetic triplet level, leading to a situation equivalent to the independent orientation of each spin in the external magnetic field. The eight-membered ring and two six-membered rings adjacent to it are presumably nonplanar for reasons described above. As a result, the distance between two oxygen atoms closest to the center of symmetry of the dimer molecule is of reasonable magnitude as a non-bonded distance between oxygen atoms (ca. 3.0 Å). In fact, the configuration of Cu–O–C–O–Cu links in the eight-membered ring is quite analogous to the anti-syn bridging arrangement determined by X-ray diffraction experiments carried out by Barclay and Kennard⁵⁾ for the royal-blue modification of anhydrous copper(II) formate. The stereochemical requirements such as the normal values for bond lengths and valency angles, the coplanar structure of conjugated systems, the absence of appreciable steric hindrance, etc. are well satisfied and one can construct a plausible molecular model for this structure.

The proposed structure implies that the so-called tricoordinated copper(II) complexes are really binuclear complexes having copper atoms of ligancy 4, regardless of whether they show a subnormal or normal magnetic moment and that "tricoordinated" copper(II) complexes in the literal sense of the word do not exist. It must be recalled that the unusual coordination number 3 for a copper atom has been conceived from the method of synthesis and the chemical analysis of the complexes along with the tridentate nature of the single ligand molecules under a tacit assumption that the complex molecules have only one copper atom. It is evident that the normal magnetic moment of a copper(II) complex does not necessarily lead to the conclusion for the existence of separate monomeric molecules in crystals. Mention should be made here of the cryoscopic determination of the molecular weights of *N*-salicylidene-*N'*-*n*-caprinylhydrazino copper(II) and *N*-salicylidene-*N'*-*n*-palmitylhydrazino copper(II) by Ohta⁶⁾, who found that these tricoordinated copper(II) complexes form dimer molecules. However, Grün and Freiesleben⁷⁾ found monomeric molecular weights for some nickel complexes of formazyls in benzene and are of opinion that the nickel atom has the coordination number 3.

In the monopyridine derivatives of the so-called tricoordinated copper(II) complexes, all of which show a normal magnetic moment, a nitrogen atom of pyridine is presumed to be coordinated on a copper atom to complete the square coordination. As a result, the molecule of these monopyridine derivatives must have a single copper atom.

In short, the coordination number 3 for a copper atom does not afford the only possible interpretation nor the most probable one. On the contrary, with the concept of binuclear complexes, one can dispense with the unusual coordination number 3 in favor of the ligancy 4, irrespective of whether or not the so-called tricoordinated copper(II) complexes show a normal moment.

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7) W. Freiesleben and F. Grün, *Chimia*, **9**, 276 (1957); F. Grün and W. Freiesleben, *Helv. Chim. Acta*, **41**, 574 (1958).