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The Stability of Fused Rings in Metal Chelates. V. Copper(II) Chelates of the Schiff Base Derived from Pyruvic Acid and *n*-Propanolamine

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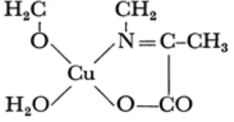
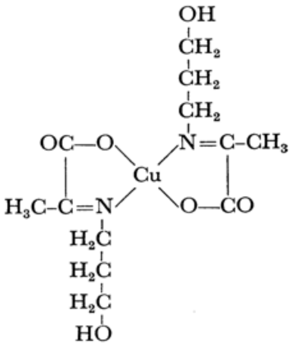
Although ethanolamine molecule is provided with two donor groups for chelation, it cannot always be coordinated as a bidentate ligand around a metal ion. The Schiff base derived from salicylaldehyde and ethanolamine is, for instance, coordinated around copper(II) to produce not only the one-to-one type copper(II)-Schiff base complex but also the one-to-two type complex,[1] in which the hydroxyl groups of the ethanolamine moieties are free from coordination. In addition to that, the Schiff base derived from pyruvic acid and ethanolamine reacts with copper(II) to form exclusively the one-to-two type copper(II)-Schiff base complex; consequently the corresponding one-to-one type complex is hardly obtained regardless of the molar ratio of copper(II) to Schiff base employed in the preparation.[2]

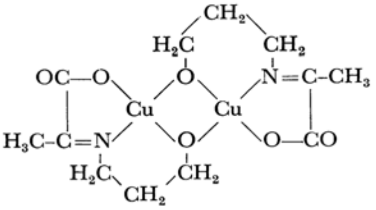
These findings are explainable by taking into account the rather weak binding ability of alcohol oxygen in one hand, and the low stability of the 5-5[3] fused-chelate-ring structure on the other hand.[4] If this interpretation is valid, it may well be suggested that the successful preparation of the one-to-one type copper(II)-Schiff base complex of this kind will become easier by adopting *n*-propanolamine instead of ethanolamine moiety, because of its more stable 5-6 fused-chelate-ring structure as indicated in I. On the basis of this consideration, we have recently succeeded in preparing the one-to-one type copper(II) complex of the Schiff base derived from pyruvic acid and *n*-propanolamine, I, as well as the corresponding one-to-two type chelate, II.



(I)



(II)



(III)

The freshly prepared one-to-one type complex is a blue lath-shaped crystal, and is described by the formula, $[Cu(pyv{=}propam)(H_2O)]\cdot 4H_2O$, where pyv=propam represents the Schiff base derived from pyruvic acid and propanolamine. However, the complex undergoes a gradual dehydration of itself in atmosphere, resulting a purple crystalline powder, to which a binuclear structure as illustrated in III is easily assigned on the basis of its extremely subnormal magnetic moment (0.7 B. M. for copper atom) and magnitude of molcular weight (428.7) in chloroform. The formation of this binuclear complex is even more accelerated by heating *in vacuo*.

Although we do not have any decisive proof for the particular binuclear structure III, the other possible structure, in which two copper(II) atoms are bridged by carboxylate-oxygen, would be less plausible in some respects. For example, there is a fact that similar type complex of *N*-ethanolsalicylaldimine does not give the corresponding binuclear complex,[1] whereas that of *N*-*n*-propanolsalicylaldimine does to produce a brownish

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1) A. Nakahara, H. Yamamoto and H. Matsumoto, *Sci. Rep.* (College of General Education, Osaka Univ.), **12**, 11 (1964).

2) Y. Komiyama and A. Nakahara, to be submitted. The title of paper will be "The Crystal and Molecular Structure of Bis(β-hydroxyethyliminopyruvato)copper-(II) Tetrahydrate."

3) A fused-chelate-ring consisting of two five-membered rings is abbreviated as 5-5 in this paper.

4) A. Nakahara, Y. Yamamoto and Y. Matsumoto, This Bulletin, **37**, 1137 (1964).

Table 1. Magnetic susceptibilities per gram and magnetic moments of copper (II) complexes of γ-hydroxypropyliminopyruvate

Complex	Temp. °C	$10^6\chi_g$	μ(B.M.)
$[Cu(pyv{=}propam_2)]\cdot 2H_2O$	16	3.55	1.9
$[Cu_2(pyv{=}propam)_2]$	18	0.45	0.7

purple binuclear complex.[5,6] In other words, the propanol-oxygen seems to take an important role in the formation of binuclear complexes.

The one-to-two type copper(II)-Schiff base complex is a light blue plate, and shows a normal magnetic moment (1.9 B. M. for copper atom). The two alcohol-oxygen atoms must, of course, be free from coordination in the light of the molecular structure of the corresponding chelate with β-hydroxyethyliminopyruvate, determined by X-ray analysis.

Of interest is comparison of the tendency for the formation of binuclear complexes: (1) the one-to-one type complex with salicylideneiminoethanol does not form binuclear complex, (2) the same type complex with salicylideneiminopropanol cannot even be isolated because of high stability of the binuclear complex, (3) similar complex with γ-hydroxypropyliminopyruvate is appropriately stable and, for this reason, complexes of both monomer and dimer structure can be isolated in crystalline state.

Experimental

The Preparation of Copper(II) Complexes of Schiff Base derived from Pyruvic Acid and *n*-Propanolamine. *The One-to-One Type Copper(II)-Schiff Base Complex, I,* $[Cu(pyv{=}propam)(H_2O)]\cdot 4H_2O$. A mixture of 1.76 g (0.02 mol) of pyruvic acid and 1.50 g (0.02 mol) of ethanolamine were dissolved in 200 m*l* of aqueous ethanol (50 vol %). To this was added 1.60 g (0.04 mol) of sodium hydroxide and 4 g (0.02 mol) of copper(II) acetate monohydrate. The mixture was stirred and heated at about 70°C for 1.5 hr; hereupon a blue-green solution was obtained. After it had been filtered, the solution was concentrated until the volume of the solution became one third of the initial state. The resulting solution was allowed to stand overnight in a refrigerator. A large amout of blue-green crystals was obtained, which was recrystallized from a small quantity of water. Found: C, 24.06; H, 6.28; N, 4.84. Calcd for $[Cu(pyv{=}propam)(H_2O)]\cdot 4H_2O$: C, 24.28; H, 6.45; N, 4.72%. Since the compound readily underwent a dehydration in atmosphere, the elemental analysis had to be performed by uisng freshly deposited crystals.

The One-to-Two Type Copper(II)-Schiff Base Complex, II, $[Cu(pyv{=}propam)_2]\cdot 2H_2O$. The almost same procedure as that employed in the above preparation was adopted, but the molar ratio of the reagents was 1 : 2 : 1 copper(II): Schiff base : sodium hydroxide instead of 1 : 1 : 2. mp 188—192°C (decomp). Found: C, 36.51; H, 6.32; N, 7.24%. Calcd for $[Cu(pyv{=}propam)_2]\cdot 2H_2O$: C, 37.16; H, 6.24; N, 7.22%.

The Binuclear form of the One-to-One Type Copper(II)-Schiff Base Complex, III. The complex, I, was dehydrated at 80°C *in vacuo* for several hours until the weight became constant. Found: C, 34.69; H, 4.30; N, 6.79%. Calcd for $[Cu_2(pyv{=}propam)_2]$: C, 34.87; H, 4.39; N, 6.78%. Molecular weight in chloroform: 428.9. Calcd for the above formula: 413.4.

Magnetic Measurements. The magnetic susceptibility was determined at room temperature by using a Gouy magnetic apparatus. The results are shown in Table 1. From the observed susceptibilities, the magnetic moments were evaluated per copper atom. The results are shown in Table 1.

The Molecular Weight of the Complex, III, was determined with a Hitachi Model-115 osmometer by using chloroform solution.

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[5] S. Yamada, Y. Kuge and K. Yamanouchi, *Inorg. Chim. Acta*, **1**, 139 (1967).

[6] M. Kato, Y. Muto, H. B. Jonassen, K. Imai and A. Harano, This Bulletin, **41**, 1864 (1968).