

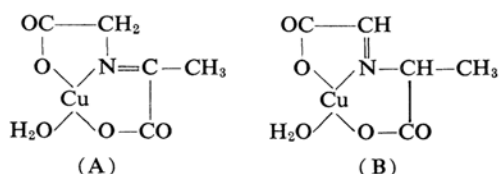
## The Copper(II) Complex of the Schiff Base Derived from Glyoxylic Acid and $\alpha$ -Alanine

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A number of investigations<sup>1)</sup> of non-enzymatic transamination reactions catalyzed by metal ions has resulted in the discovery of the importance of the coordination of metal ions with the Schiff bases produced from aldehydes and amino acids or from keto acids and amines. Comparatively few papers<sup>2)</sup> have, however, been published to report on the isolation of metal Schiff-base chelates as the intermediate compounds in the mechanism of these transamination reactions. We have recently prepared a pair of copper(II) Schiff-base complexes, which are considered to be fairly important in any consideration of the mechanism of the transamination reactions in the metal-pyruvate-glycinate and the metal-glyoxylate-alaninate systems; we therefore investigated their properties and correlations. They are the copper(II) complexes of Schiff bases derived from pyruvic acid and glycine,<sup>3)</sup> A, and glyoxylic acid and  $\alpha$ -alanine. The latter was believed to have the structure B, in the light of many results obtained by other, similar preparations. However, the complex isolated in the crystalline state from the copper(II)-glyoxylate-alaninate system has been proved to be the pyruvideneglycinatoaquocopper(II) (A) instead of glyoxylidenealaninatoaquocopper(II) (B). This finding is understandable only in connection with some kind of rearrangement—a part of the process of the transamination reaction. Although the transaminations of this kind and of the glyoxylate-pyridoxamine system in the presence of metal ions have already been reported,<sup>4)</sup> the previous conclusions were drawn only from the equilibrium studies of solutions; the intermediate complexes were not isolated. The present paper will report on a quite effective transamination based on an investigation of the

isolated intermediate complex. It is also of interest to note that only a chelate of glycine with pyruvate and copper(II), not one of alanine with glyoxylate and copper(II), is isolated.



The method of the preparation of B employed in this work was the same as that of A which has already been reported in a previous paper.<sup>3)</sup> Found: C, 23.03; H, 4.27; N, 5.29; H<sub>2</sub>O, 20.31. Calcd. for CuC<sub>5</sub>H<sub>5</sub>NO<sub>4</sub>·3H<sub>2</sub>O: C, 23.00; H, 4.21; N, 5.36; H<sub>2</sub>O, 20.65%.

The complex began to decompose at 192°C, coinciding precisely with the decomposition temperature of A. A microscopic observation of the two crystals, A and B, revealed that there was no difference in their colors, shapes and habits.

No difference was observed either in their solubilities in water, ethanol and dimethylsulfoxide. The infrared studies and the X-ray powder measurements of the two crystals also verified their identity.

However, an additional decisive proof for the identity of the two compounds and the elimination of the possibility of the structure B was given by a cleavage reaction of the Schiff-base >C=N- double bond of the respective complex. The aqueous solutions of the two complexes were separately treated with hydrogen sulfide in order to give the precipitate of copper sulfide from each solution. The two filtrates were then examined for the amino acids they contained by means of paper chromatography. Both solutions exhibited only one spot corresponding to glycine in the presence of pyruvic acid. No other spots, not even that of alanine were detected on the whole strip. If the real structure of the complex produced from copper(II)-glyoxylate-alaninate system were B, alanine would have been detected instead of glycine. This may

1) E. g., D. E. Metzler and E. E. Snell, *J. Am. Chem. Soc.*, **74**, 979 (1952); D. L. Leussing, *ibid.*, **85**, 231 (1963). Many papers other than these have been published.

2) D. E. Metzler, J. B. Longenecker and E. E. Snell, *J. Am. Chem. Soc.*, **76**, 639 (1954); H. N. Christensen, *ibid.*, **79**, 4073 (1957); G. Baddiley, *Nature*, **170**, 711 (1964).

3) A. Nakahara, H. Yamamoto and H. Matsumoto, *This Bulletin*, **37**, 1137 (1964).

4) D. E. Metzler, J. Olivard and E. E. Snell, *J. Am. Chem. Soc.*, **76**, 644 (1954); H. Mix, *Z. physiol. Chem.*, **325**, 106 (1961).

be one of the most clear-cut examples of effective transamination catalyzed by the copper(II) ion.

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