A Novel Copper(II) Complex of Diketopiperazine

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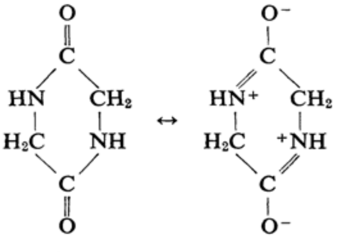
The molecular structure of diketopiperazine has been extensively studied[1-3] and as a result, it is regarded as a resonance hybrid of I and II. X-Ray study has shown that the molecule is nearly planar and has a center of symmetry.[2] Since there are two peptide linkages in the molecule, diketopiperazine is expected to form several types of complexes with metal ions according to the way functional groups are used as donor atoms. No paper has, however, been published to report on the formation of any type of complex, even in solutions.



(I) (II)

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1) A. M. Buswell, J. R. Dowing and W. H. Rodebush, *J. Am. Chem. Soc.*, **62**, 2759 (1940); M. Tsuboi, This Bulletin, **22**, 255 (1949). Many papers other than these have also been published.

2) R. B. Corey, *J. Am. Chem. Soc.*, **60**, 1598 (1938); R. Degeilh and E. Marsh, *Acta Cryst.*, **12**, 1007 (1959).

3) F. A. Bovey and G. V. D. Tiers, *J. Am. Chem. Soc.*, **81**, 2870 (1959).

Recently we have succeeded in preparing one of these diketopiperazine complexes in the crystalline state. The new complex is potassium bis(diketopiperazinato)cuprate(II); on the basis of spectroscopic investigations, it is considered to have a very interesting structure. In this paper we will report on the preparation and on the properties of this new compound, and we will also consider its peculiar structure.

A one-to-two mixture of diketopiperazine and potassium hydroxide in an aqueous solution was treated at room temperature with an excess of freshly precipitated copper(II) oxide to give an intense blue solution as a result of the complex formation. The solution was then gently evaporated in a vacuum. The new complex is obtained as beautiful purple prisms, the color of which is fairly sensitive to moisture. In a humid atmosphere, it appears blue-purple, while in a comparatively dry atmosphere it is red-purple.

Judged from this color of the crystal, it is conceivable that all the four donor atoms around copper(II) are nitrogen, as in the bis(ethylenediamine)copper(II) complex. In fact, the wavelength for the maximum absorption in the visible region obtained by the reflection method strongly supports this theory. On the other hand, elemental analyses indicate that the ratio of copper(II) to diketopiperazine is one-to-two. Thus, the structure of the complex has been supposed to be a kind such as is illustrated in Fig. 1, in which two considerably-bent diketopiperazinato ions are coordinated around copper(II) through peptide nitrogens. The validity of this kind of structure is supported not only by the Stuart model but also by the infrared study. The spectrum of diketopiperazine in the fingerprint region is very simple, while that of the complex differs in many respects and has a number of additional bands of a weak or medium intensity. These changes are consistent with the change in the conformation of the diketopiperazine molecule from the centrosymmetric to the boat configuration, a change caused by chelation with the copper(II) ion.

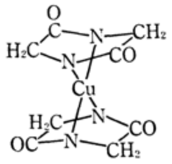

Fig. 1. The sandwich type structure of bis(diketopiperazinato)cuprate(II) ion.

This may be a novel type of complex, having a structure of sandwich-type like ferrocene and other so-called π-complexes. However, the nature of the bondings between nitrogen and copper(II) may be supposed to be, rather, the σ-type on the basis of spectroscopic and stereochemical considerations. In this respect, the new complex bears a strong resemblance to the palladium(II) and platinum(II) complexes of piperazine reported by Mann and Watson.4)

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4) F. G. Mann and H. R. Watson, *J. Chem. Soc.*, **1958**, 2772.