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Imidazolate-Bridged Binuclear Copper(II) Complexes with Dipeptides

W. MORI, A. NAKAHARA

Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka 560, Japan

and Y. NAKAO

Chemical Laboratory, Faculty of Education, Okayama University, Okayama 700, Japan

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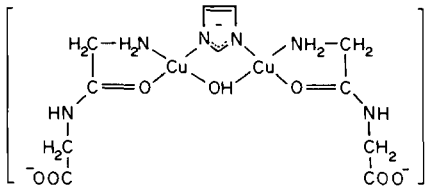
A considerable number of imidazolate-bridged bi- and tetra-nuclear copper(II) complexes have been recently prepared and characterized [1–6] because of their biological importance as models for the active site of bovine erythrocyte superoxide dismutase [7]. Driver and Walker [8] reported earlier than these on the preparation and structure of copper(II) complexes with imidazole and glycylglycine, concluding that the two coppers(II) are bridged by one each of imidazolate and hydroxide ion as represented by structure 1.



However, their proposed structure does not seem feasible in the following respects: (i) glycylglycinate in the complex was considered to be coordinated around copper(II) as a bidentate chelate ligand through the terminal amino nitrogen and amide oxygen, in spite of the fact that the complex was obtained from a basic solution (pH > 10), (ii) the effective magnetic moment per copper(II) ion in the complex was determined to be 1.92 B.M. (22 °C), being contradictory to the μ-hydroxo-bridged structure which may afford the two copper(II) ions a quite strong antiferromagnetic interaction [4, 9–11], hence a considerably subnormal magnetic moment.

Recently we reinvestigated the structure of the same compound, and reached an entirely different conclusion based on both the elemental analysis and a study of magnetic property (4.2–295 K). The preparation of the complex was carried out according to the directions of Driver and Walker [8]. It was confirmed that the same compound is obtainable by using copper(II) acetate monohydrate instead of copper(II) hydroxide in a basic solution (pH ≃ 12). The result of elemental analysis for sodium and copper as well as C, H, and N proved that the experimental formula must be $Na[Cu_2C_{11}H_{15}N_6O_6] \cdot 6H_2O$. The magnetic moment, μ_{eff} value, which was determined at 22 °C by using a Gouy magnetic apparatus, is 1.80 B.M. The temperature-dependence of the magnetic susceptibility is represented in Fig. 1, revealing that there is an antiferromagnetic spin–spin interaction between the two copper(II) ions in the complex. Judged from the coupling constant ($2J/k = -55$ K) and the μ_{eff} value at room temperature the present interaction is, however, definitely weaker than those observed for the hydroxide-bridged copper(II) chelates [4, 9–11]. Accordingly the possibility for the presence of μ-hydroxo-bridge between the two copper(II) ions is safely excluded.

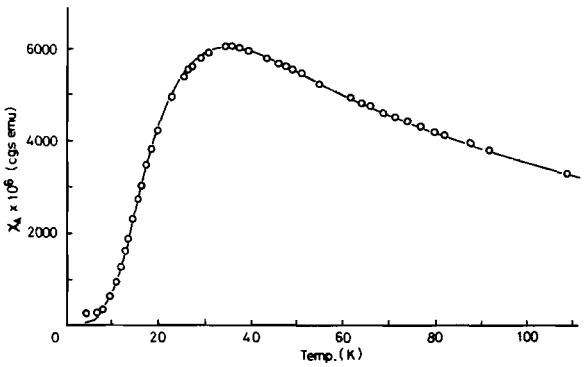
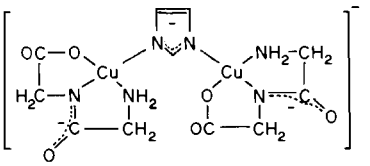


Fig. 1. The temperature-dependence of magnetic susceptibility of copper(II) complex 2. The solid line shows theoretical susceptibility calculated by the Bleany–Bowers equation

$$\chi_A = \frac{Ng^2\beta^2}{kT} \times \frac{1}{3 + \exp(-2J/kT)} + N\alpha$$

with g = 2.08, $2J/k = -55$ K, $N\alpha = 60 \times 10^{-6}$ cgs emu.

Thus we intend to propose structural formula 2 for the present binuclear copper(II) complex. As is visualized there, glycylglycinate is coordinated



around each copper(II) through the terminal amino nitrogen deprotonated amide nitrogen and the carboxylate oxygen, whereas the two coppers(II) are bridged by an imidazolate ion. This mode of coordination may be well accepted in the light of the knowledge established through the investigations of oligopeptide copper(II) chelates [12]. It has also been disclosed that the dimeric structure is maintained even in a 3.1×10^{-2} *M* aqueous solution (μ_{eff}/Cu = 1.8 B.M. at 22 °C).

The same type of binuclear copper(II) complex with glycyl-β-alaninate instead of glycylglycinate has also been obtained, and the complex exhibited a magnetic property similar to that of complex 2.

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