Inorganica Chimica Acta, 35 (1979) 1–4

Tetranuclear Copper(II) Complexes. Copper(II) Complexes of Schiff Bases derived from Histamine and Salicylaldehyde or 2-Pyridinecarbaldehyde

YASUO NAKAO*, WASUKE MORI, NAOKI OKUDA and AKITSUGU NAKAHARA

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

Received October 21, 1978

Reaction of copper(II) ions with the Schiff bases derived from histamine and salicylaldehyde or 2-pyridinecarbaldehyde were investigated in acidic and basic media. The copper(II) complexes obtained from the reactions in acidic solutions were mononuclear complexes I and II, while those from the reactions in basic solutions were tetranuclear complexes III and IV, in which the four copper(II) ions were tetrahedrally arranged. A study on magnetic property (4.2–300 K) of the tetranuclear complexes by the Faraday method suggested the presence of antiferromagnetic interactions between the four copper(II) ions.

Introduction

A great deal of information has been accumulated for the metal complexes containing histidine, histamine and imidazole as ligands, since the histidyl side-chains in protein are important metal-binding groups in biological systems [1]. Of these metal chelates imidazolate bridged complexes are of interest as models for the active site of bovine erythrocyte superoxide dismutase [2], which has a novel histidine-bridged copper(II)–zinc(II) center in the structure.

In this connection Kolks *et al.* [3, 4] studied the preparation and characterization of bi- and tetranuclear copper(II) complexes containing imidazolate and/or its derivatives as bridging ligands. Here we describe the synthesis and the characterization of copper(II) chelates of the Schiff bases derived from histamine and salicylaldehyde or 2-pyridinecarbaldehyde.

Experimental

Preparation of Copper(II) Complexes

Copper(II) complex of the Schiff base derived from salicylaldehyde and histamine, [Cu(Sal=HistamH)Cl]·H_2O, I

To a mixture of 1.2 g (0.01 mol) of salicylaldehyde and 1.8 g (0.01 mol) of histamine dihydrochloride in 20 ml of water was added 3.7 g (0.01 mol) of copper(II) perchlorate hexahydrate. The resulting mixture was adjusted at pH 5–6 by sodium hydroxide solution and stirred at room temperature for 2 h. After it had been filtered off, the precipitate was recrystallized from water to give brown-green crystals. Found: C, 44.04; H, 4.04; N, 12.99%. Calcd. for $[Cu(C_{12}H_{12}ON_3Cl)]\cdot H_2O$: C, 43.50; H, 4.27; N, 12.69%. Magnetic moment, μ_{eff} = 1.84 B.M. (24 °C).

Copper(II) complex of the Schiff base derived from 2-pyridinecarbaldehyde and histamine, [Cu(2-Pyca=HistamH)Cl] ClO_4, II

The complex II was prepared according to the same direction as described for the complex I, by using an equimolar amount of 2-pyridinecarbaldehyde, histamine dihydrochloride and copper(II) perchlorate hexahydrate, and was recrystallized from methanol as green-blue crystals. Found: C, 33.21; H, 3.51; N, 14.25%. Calcd. for $[Cu(C_{11}H_{12}N_4)Cl]\cdot ClO_4$: C, 33.13; H, 3.04; N, 14.06%. Magnetic moment, μ_{eff} = 1.87 B.M. (24 °C). IR(KBr), 1080–1120 cm^{-1} (ClO_4^-).

Tetrameric copper(II) complex of the Schiff base derived from salicylaldehyde and histamine, $[Cu(Sal{=}Histam)]_4$, III

The complex III was prepared also by the same procedure as described for the complex I, except that the pH of the reaction mixture was kept at 12 instead of 5–6. After filtration, the crude product was washed several times with ethanol, being recrystallized from benzene to give dark green-brown crystals. Found: C, 51.98; H, 4.17; N, 14.76% Calcd. for

---

*Present address: Chemical Laboratory, Faculty of Education, Okayama University, Okayama 700.

$[Cu(C_{12}H_{11}ON_3)]$: C, 52.06; H, 4.01; N, 15.18%. Magnetic moment, $\mu_{eff} = 1.73$ B.M. (24 °C). Molecular weight: *ca.* 900 in benzene. Theoretical values: 1107 for tetramer; 830 for trimer.

Tetrameric copper(II) complex of the Schiff base derived from 2-pyridinecarbaldehyde and histamine, $[Cu(2\text{-}pyca{=}Histam)]_4(ClO_4)_4 \cdot 2H_2O$, IV

Except that the solution was adjusted at pH 12, a similar procedure to that in the preparation of complex II was adopted. Recrystallization was carried out by using methanol to give dark green-brown crystals. Found: C, 35.83; H, 3.52; N, 15.00%. Calcd. for $[Cu(C_{11}H_{11}N_4)]_4(ClO_4)_4 \cdot 2H_2O$: C, 35.58; H, 3.26; N, 15.09%. Magnetic moment, $\mu_{eff} = 1.72$ B.M. (24 °C). IR(KBr), 1080–1120 cm^{-1} (ClO_4^-).

Measurements

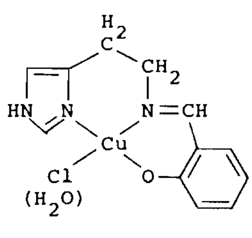
The molecular weight was determined with a Hitachi 117 VPO by employing benzil as the reference. The IR spectra were measured with a Hitachi 215 Grating Infrared Spectrophotometer. Magnetic susceptibility at room temperature was determined by using a Gouy magnetic apparatus. The Faraday method was applied for the measurement of magnetic susceptibility over the range from liquid helium temperature to room temperature.

Results and Discussion

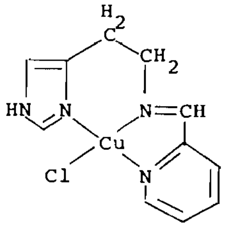
The copper(II) complexes obtained by the reactions of copper(II), histamine, and salicylaldehyde or 2-pyridinecarbaldehyde varied with pH of the solution, as described in the Experimental section.

Copper(II) Complexes Formed in Acidic Solutions

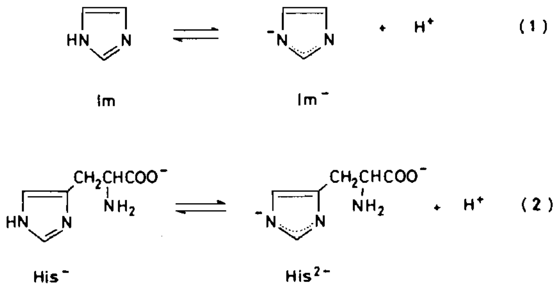
In the light of the results of elemental analysis and the values of effective magnetic moment the complexes isolated from acidic solutions are considered to have the structures shown as I and II. Structures of this type are quite popular, as have been known in many copper(II) Schiff base chelates containing amino acids. However, the coordination of chloride ion in the complex I is a little ambiguous, since the water molecule can be coordinated around copper(II) instead of chloride ion. It may be also possible that both the chloride ion and water molecule are coordinated around copper(II), forming a five-coordinated copper(II) complex. It may be inferred that the proton attached to one nitrogen atom of the imidazole group in histamine would not dissociate with the complex formation under these conditions, since the pK$_a$ values for the concerned equilibria ((1) and (2)) are known to be as high as *ca.* 14 [5].



I

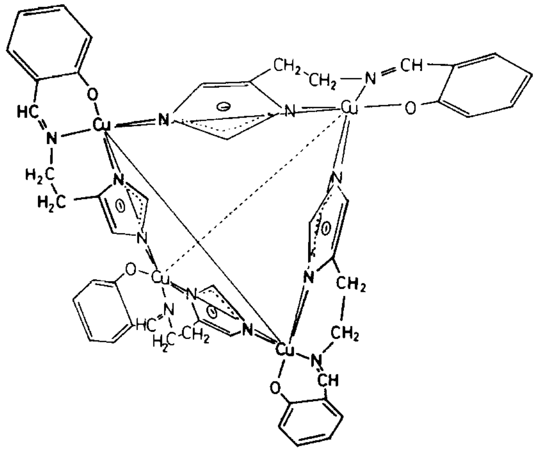


II



Copper(II) Complexes Formed in Basic Solution

The molecular weight determined by means of vapor pressure osmometry apparently indicated that the copper(II) complex of the Schiff base containing the salicylaldehyde moiety is a tetranuclear complex, $[Cu(C_{12}H_{11}ON_3)]_4$ in benzene. Since the magnetic moment of the complex at room temperature was lower than that for the value of copper(II) complex without interaction, it was suggested that the complex is composed of a cluster also in the solid state. In order to obtain detailed information on the structure of this compound, the magnetic susceptibility was measured over the temperature range 4.2–300 K. Figure 1 represents the temperature-dependence of the magnetic susceptibility. There the theoretical susceptibility, χ_A, for bi- and tetranuclear complexes as shown in Figure 3(a) and (b) was depicted by the dotted and solid lines respectively. The calculation of these χ_A values was carried out according to the equations (3) (Bleany–Bowers equation) [6] and (4) [7], respectively.



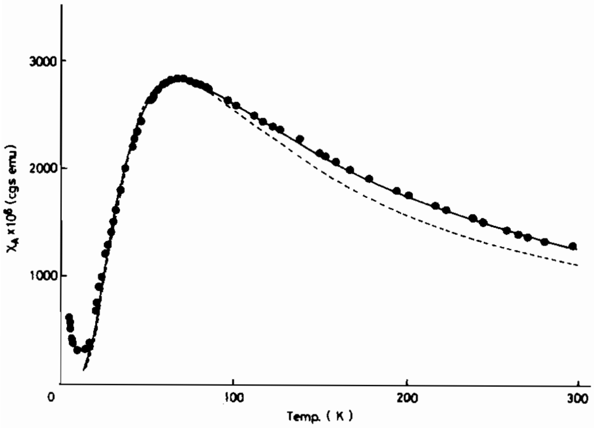


Fig. 1. The temperature-dependence of magnetic susceptibility of copper(II) complex, III. The dotted and solid lines show theoretical susceptibilities calculated by equation (3) with g = 2.00, $-2J/k = 105$ K, $N\alpha = 60 \times 10^{-6}$ cgs emu and (4) with g = 2.13, $-2J/k = 85$ K, $N\alpha = 60 \times 10^{-6}$ cgs emu, respectively.

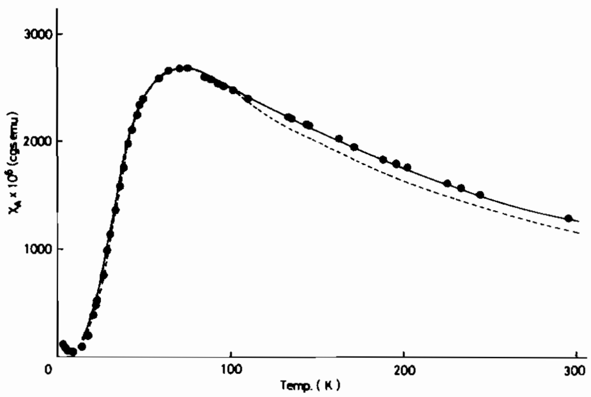


Fig. 2. The temperature-dependence of magnetic susceptibility of the copper(II) complex, IV. The dotted and solid lines represent theoretical susceptibilities calculated by equation (3) with g = 2.00, $-2J/k = 115$ K, $N\alpha = 60 \times 10^{-6}$ cgs emu and (4) with g = 2.14, $-2J/k = 90$ K, $N\alpha = 60 \times 10^{-6}$ cgs emu, respectively.

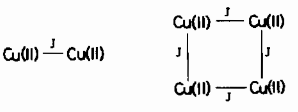


Fig. 3. (a) Spin–spin interaction in binuclear copper(II) complexes. (b) Spin–spin interaction in tetranuclear copper(II) complexes.

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

$$\chi_A = \frac{N\beta^2 g^2}{2kT} \times \frac{2 + 5\exp(2J/kT) + \exp(-2J/kT)}{7 + 5\exp(2J/kT) + 3\exp(-2J/kT) + \exp(-4J/kT)} + N\alpha \qquad (4)$$

where J denotes the exchange integral between copper(II) ions as shown in Figure 3, g is the g-value and Nα is the temperature-independent paramagnetism.

Inspection of Figure 1 reveals that the magnetic susceptibility of the copper(II) complex III conforms to the theoretical susceptibility, χ_A, for the tetranuclear cluster. Accordingly it is suggested that there are antiferromagnetic spin–spin interactions between the four copper(II) ions as shown in Figure 3(b). The molecular structure represented as III is also visualized by use of the CPK models, from which the cluster is expected to be highly symmetric, and the four copper(II) ions are tetrahedrally arranged, being linked together through the deprotonated imidazolate group. At the same time, the possibility of the square planar structure was definitely excluded. The copper(II) complex of the Schiff base containing 2-pyridinecarbaldehyde moiety instead of salicylaldehyde also exhibits a similar magnetic property to the complex III as given in Figure 2. Thus the complex is considered to have the same type of tetrameric structure as described above.

Recently, Kolks *et al.* [3] isolated a tetranuclear complex $[Cu_2(bpim)(im^-)]_2^{4+}$, where bpim represents 4,5-bis-[2-(pyridyl)ethyliminomethyl]imidazolate, and im^- deprotonated imidazolate. In this tetranuclear complex, each copper(II) ion is bridged through each one of deprotonated imidazolate and its derivative, and the copper(II) ions are antiferromagnetically coupled. However, the four copper(II) ions are arranged in a near square planar symmetry, differing from the present tetrahedral arrangement, III. It is known that some copper(II) chelates form a cluster of cubane type structure as represented in Figure 4 [8–10]. The structure of the present tetranuclear copper(II) chelates also differs from the cubane type in that the coordinating ligands are absent in 'L' sites in Figure 4.

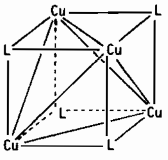


Fig. 4. The structure of cubane-type copper(II) cluster.

Acknowledgments

The authors wish to thank Dr. Yoshio Okamoto of the Faculty of Engineering Science for his measurements of molecular weight. We are also indebted to Miss Teruko Kuroe for the elemental analysis. Expenses for this work were defrayed in part by a grant from the Ministry of Education.

References

1 R. J. Sundberg and R. B. Martin, *Chem. Rev., 74,* 471 (1974).

2 J. S. Richardson, K. A. Thomas, B. H. Rubin and D. C. Richardson, *Proc. Nat. Acad. Sci. USA, 72,* 1349 (1975).

3 G. Kolks, C. R. Frihart, H. N. Rabinowitz and S. J. Lippard, *J. Am. Chem. Soc., 98,* 5720 (1976).

4 G. Kolks and S. J. Lippard, *ibid., 99,* 5804 (1977).

5 G. Yagil, *Tetrahedron, 23,* 2855 (1967).

6 B. Bleany and K. D. Bowers, *Proc. Roy. Soc., A214,* 451 (1952).

7 L. Dubiki, G. A. Kakos and G. Winter, *Aust. J. Chem., 21,* 1461 (1968).

8 J. A. Bertrand, J. A. Kelley and C. E. Kirkwood, *Chem. Commun.,* 1329 (1968).

9 J. A. Bertrand and J. A. Kelley, *Inorg. Chim.Acta, 4,* 203 (1970).

10 W. Mori, H. Ueda, A. Nakahara and M. Kishita, *Proceedings of the 24th Annual Meeting of the Chemical Society of Japan,* Vol. II, p. 762, Osaka, Apr. 1971.