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Binuclear Metal Complexes.
59*. Synthesis and Magnetism of Dicopper(II) and Copper(II)–Nickel(II) Complexes with *N,N'*-Ethylenedisalicylamidatocuprate(II)

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Abstract

The complexes [Cu(samen)Cu(L)] and [Cu(samen)Ni(L)$_2$] (L = bpy, phen) have been synthesized by the reaction of sodium *N,N'*-ethylenedisalicylamidatocuprate(II) pentahydrate (Na$_2$[Cu(samen)]·5H$_2$O), a divalent metal ion, and 2,2'-dipyridyl or 1,10-phenanthroline. Cryomagnetic data for the Cu–Cu complexes did not fit the Bleaney–Bowers equation; but the data did fit a modified Bleaney–Bowers equation

$$\chi_A = \frac{Ng^2\beta^2}{3k(T-\theta)}\,[1 + \frac{1}{3}\exp(-2J/kT)]^{1/2} + N\alpha$$

with a large negative J and a significant negative θ, suggesting that a considerable magnetic interaction operates between essentially planar [Cu(samen)Cu(L)] molecules. The magnetisms of the Cu–Ni complexes were well interpreted in terms of the susceptibility equation based on the Heisenberg model. An antiferromagnetic spin-exchange interaction ($J = -13 \sim -14$ cm^{-1}) was suggested between the metal ions.

Introduction

It is known that metal complexes of tetradentate Schiff bases (H$_2$SB) such as *N,N'*-disalicylidene-ethylenediamine (H$_2$salen) act as bidentate chelating agents toward a second metal ion to form binuclear and trinuclear metal complexes [2]. The bridging function of the phenolic oxygens of M(SB) has been revealed by single-crystal X-ray analysis for some of these complexes [3–5]. The use of M(SB) as a chelating agent is now accepted as one of the convenient ways for synthesizing discrete heteronuclear complexes such as [M(SB)M'X$_2$] [6, 7], [M(SB)M'L$_2$] [8], and [M(SB)M'X$_2$M(SB)] [9–11]. Magnetic studies for these complexes demonstrated a significant antiferromagnetic spin-exchange interaction between the metal ions.

In a hope to find a new way to synthesize heterobinuclear complexes, we utilized in this study *N,N'*-ethylenedisalicylamidatocuprate(II), [Cu(samen)]$^{2-}$, as a chelating agent. Because of the structural similarity to [Cu(salen)], [Cu(samen)]$^{2-}$ is expected to act as a bidentate chelating agent through its phenolic oxygens toward a second metal ion. In this paper we present the synthesis and magnetism of [Cu(samen)Cu(L)] and [Cu(samen)Ni(L)$_2$] with 2,2'-dipyridyl (bpy) or 1,10-phenanthroline (phen) as L.

Experimental

Materials

Na$_2$[Cu(samen)]·5H$_2$O was prepared by the literature method [12]. 2,2'-Dipyridyl, 1,10-phenanthroline, CuCl$_2$·2H$_2$O, and NiSO$_4$·6H$_2$O were purchased from Wako Chem. Co.

[Cu(samen)Cu(bpy)]

Copper(II) chloride dihydrate (44 mg) and bpy (40 mg) were stirred in absolute methanol (10 cm^3) to give a pale blue precipitate of [Cu(bpy)Cl$_2$]. To this mixture a methanolic solution of Na$_2$[Cu(samen)]·5H$_2$O (140 mg) was added dropwise with stirring. Reddish brown microcrystals thus formed were separated, washed with small amount of methanol, and dried at 110 °C under reduced pressure.

Anal. Calc. for C$_{26}$H$_{20}$N$_4$O$_4$Cu$_2$·H$_2$O: C, 52.26; H, 3.71; N, 9.38; Cu, 21.27. Found: C, 52.03; H, 3.55; N, 9.30; Cu, 21.13%.

[Cu(samen)Cu(phen)]

This complex was obtained in the same way as that for [Cu(samen)Cu(bpy)] except for the use of phen·H$_2$O instead of bpy.

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Anal. Calc. for $C_{28}H_{20}N_4O_4Cu_2 \cdot 1.5H_2O$: C, 53.64; H, 3.68; N, 8.64; Cu, 20.15. Found: C, 53.24; H, 3.82; N, 8.64; Cu, 20.37%.

[Cu(samen)Ni(bpy)₂]

Nickel(II) sulfate hexahydrate (66 mg) and bpy (80 mg) were dissolved in water (5 cm^3). To the resulting pink solution, an aqueous solution of $Na_2[Cu(samen)] \cdot 5H_2O$ (140 mg) was added dropwise to give brownish purple microcrystals. They were washed with water by decantation several times and dried at 110 °C *in vacuo*.

Anal. Calc. for $C_{36}H_{28}N_6O_4CuNi \cdot 1.5H_2O$: C, 57.04; H, 4.12; N, 11.08; Cu, 8.38; Ni, 7.75. Found: C, 56.97; H, 3.79; N, 11.08; Cu, 8.10; Ni, 7.62%.

[Cu(samen)Ni(phen)₂]

This complex was obtained by the reaction of $NiSO_4 \cdot 6H_2O$ (66 mg), $phen \cdot H_2O$ (100 mg), and $Na_2[Cu(samen)] \cdot 5H_2O$ (140 mg) in water.

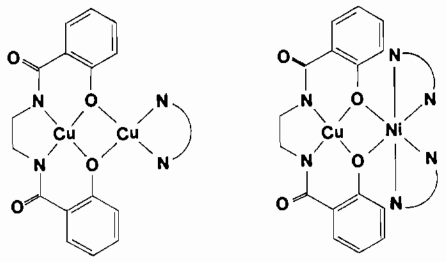
Anal. Calc. for $C_{40}H_{28}N_6O_4CuNi \cdot 1.5H_2O$: C, 59.46; H, 3.87; N, 10.40; Cu, 7.86; Ni, 7.27. Found: C, 59.25; H, 3.55; N, 10.36; Cu, 7.63; Ni, 7.44%.

Measurements

Infrared spectra were recorded on a Hitachi infrared spectrometer Model 215 on KBr disks or nujol mulls. Reflectance spectra were recorded on a Shimadzu multipurpose spectrophotometer Model MPS-5000 on powder samples. Magnetic susceptibilities were measured by the Faraday method. The apparatus was calibrated with $[Ni(en)_3]S_2O_3$ [13]. Diamagnetic corrections were made with Pascal's constants [14] for all the constituent atoms, and the magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_A T)^{1/2}$.

Results and Discussion

The reaction of $Na_2[Cu(samen)] \cdot 5H_2O$ with a metal ion (Cu^{II}, Ni^{II}) and bpy or phen yielded the complexes [Cu(samen)Cu(L)] and $[Cu(samen)Ni(L)_2]$ (L = bpy, phen), which were presumed as the phenoxo-bridged binuclear complexes shown in Fig. 1.



(a) (b)

Fig. 1. Supposed chemical structures of (a) [Cu(samen)-Cu(L)] and (b) $[Cu(samen)Ni(L)_2]$ (L = bpy, phen).

The Cu–Cu complexes readily dissociated in dilute methanol solution, especially in the presence of water. Thus, the synthesis was carried out in small amounts of absolute methanol to improve the yield of the complexes. On the other hand, the Cu–Ni complexes were relatively stable toward dissociation even in water. Patel and Bhattacharya [15] reported the synthesis of $[Cu(SB)Cu(L)]^{2+}$ (L = bpy, phen). However, our reinvestigation has revealed that the products are not binuclear but trinuclear ($[Cu(SB)Cu(L)Cu(SB)]^{2+}$) [16]. Further, the synthesis of $[Cu(SB)Ni(L)_2]^{2+}$ complexes with L = bpy or phen were unsuccessful. Therefore, $[Cu(samen)]^{2-}$ differs from [Cu(SB)] in the complexing behavior. Color, selected IR band, d–d transition bands, and effective magnetic moment at room temperature are given in Table I.

It is generally known that one of the skeletal bands (near 1520 cm^{-1}) of M(SB) shifts to higher frequency in its bi- and oligonuclear complexes [17], and this shift has often been used as a diagnosis for the phenoxo-bridged structures. A similar trend in the skeletal vibration was observed for the present case; *i.e.*, the 1516 cm^{-1} skeletal band of $Na_2[Cu(samen)] \cdot 5H_2O$ [12] shifted to 1522–1526 cm^{-1} in its binuclear complexes. The IR spectra on nujol mull showed a broad band around 3400 cm^{-1}, which is attributed to the lattice water [18]. Each reflectance spectrum of the Cu–Cu complexes showed a d–d band at 19.5×10^3 cm^{-1} with a shoulder at 16.5×10^3 cm^{-1}. The former may be attributed to the copper of $[Cu(samen)]^{2-}$ and the latter to the second

TABLE I. Color and Physical Data for Complexes

	Color	IR ($\tilde{\nu}/cm^{-1}$)	d–d ($\tilde{\nu}/10^3$ cm^{-1})		μ_{eff} (μ_B^{-1})
[Cu(samen)Cu(bpy)]	Red–brown	1525	19.6	16.5	1.49[a]
[Cu(samen)Cu(phen)]	Red–brown	1526	19.4	16.5	1.50[a]
$[Cu(samen)Ni(bpy)_2]$	Brown	1522	18.7	12.5	3.69[b]
$[Cu(samen)Ni(phen)_2]$	Light-brown	1522	18.5	12.4	3.71[b]

[a] Per one copper atom. [b] Per copper and nickel atoms.

copper coordinated by bpy or phen. The configuration around the second copper must be distorted from square plane, judging from its relatively low frequency of the d–d band. Each spectrum of the Cu–Ni complexes showed two d–d bands at ~12.5 × 10^3 and ~18.5 × 10^3 cm^{-1}. The intense 18.5 × 10^3 cm^{-1} band is assigned to the d–d transition of the copper(II). The weaker 12.5 × 10^3 cm^{-1} band is assigned to the $^3T_{2g} \leftarrow {}^3A_{2g}$ transition of six-coordinate nickel(II) [19–21]. The $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ transition must be concealed by the intense d–d band of the copper(II) at ~18.5 × 10^3 cm^{-1}. The electronic spectra of the Cu–Ni complexes are consistent with the structure (b) of Fig. 1, in which $[Cu(samen)]^{2-}$ occupies two coordination sites of the nickel(II) and the remaining four sites are occupied by two molecules of bpy or phen.

Magnetic moments for the Cu–Cu complexes (per Cu atom) are subnormal at room temperature and decrease with lowering of temperature. This suggests the operation of an antiferromagnetic spin-exchange interaction in these complexes. The magnetical analysis for the complexes was carried out with the susceptibility equation (Bleaney–Bowers equation) [22] (eqn. (1)) based on the isotropic spin-exchange operator for a dimer ($\mathcal{H} = -2J\hat{S}_1\hat{S}_2$),

$$\chi_A = \frac{Ng^2\beta^2}{3kT}\left[1 + \frac{1}{3}\exp(-2J/kT)\right]^{-1} + N\alpha \qquad (1)$$

where each symbol has its usual meaning. However, the magnetism of [Cu(samen)Cu(bpy)] and [Cu(samen)Cu(phen)] could not be simulated with eqn. (1). Then, we adopted the modified Bleaney–Bowers equation [23],

$$\chi_A = \frac{Ng^2\beta^2}{3k(T-\theta)}\left[1 + \frac{1}{3}\exp(-2J/kT)\right]^{-1} + N\alpha \qquad (2)$$

which includes a magnetic exchange parameter (θ) between binuclear units. As shown in Figs. 2 and 3, good fits to the experimental data are attained with eqn. (2). Magnetic parameters thus determined are $g = 2.02$, $J = -92$ cm^{-1}, $N\alpha = 50 \times 10^{-6}$ cgs/mol, and $\theta = -10.0$ K for [Cu(samen)Cu(bpy)] and $g = 2.02$, $J = -72$ cm^{-1}, $N\alpha = 40 \times 10^{-6}$ cgs/mol, and $\theta = -17.8$ K for [Cu(samen)Cu(phen)]. The result indicates that the complexes are essentially binuclear and show a strong antiferromagnetic spin-exchange interaction within each molecule. The result also indicates a significant magnetic interaction (antiferromagnetic) between the neighbouring binuclear units. We suppose that the complexes have a discrete oligonuclear structure consisting of the binuclear units, although a definite conclusion on the structure can not be drawn until solved by X-ray analysis.

The magnetic moment of the Cu–Ni complexes was temperature-dependent; the moment decreased by *ca.* 0.4 μ_B when the temperature was lowered from room temperature to liquid nitrogen temperature. This should be due to an antiferromagnetic spin-exchange interaction between the metal ions. The susceptibility equations for the ($S = 1/2$)–($S = 1$) system is given by the eqn. (3):

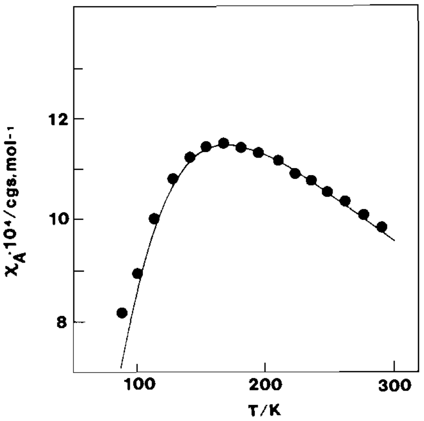


Fig. 2. χ_A *vs.* T plots for [Cu(samen)Cu(bpy)]. The curve is drawn based on eqn. (2) with the magnetic parameters given in the text.

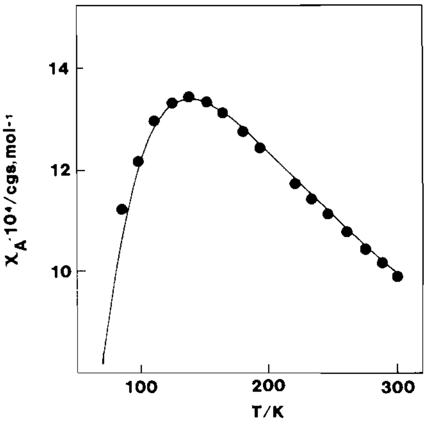


Fig. 3. χ_A *vs.* T plots for [Cu(samen)Cu(phen)]. The curve is drawn based on eqn. (2) with the magnetic parameters given in the text.

$$\chi_M = \frac{Ng^2\beta^2}{4kT} \times \frac{10 + \exp(-3J/kT)}{2 + \exp(-3J/kT)} + N\alpha \qquad (3)$$

In this equation χ_M denotes the susceptibility for the copper and nickel atoms and the remaining symbols have their usual meanings. As shown in Fig. 4, the magnetic behaviors of the Cu–Ni complexes can be well simulated with this equation. The magnetic parameters thus obtained are $g = 2.27$, $J = -14$ cm^{-1}, and $N\alpha = 250 \times 10^{-6}$ cgs/mol for [Cu(samen)Ni(bpy)$_2$] and $g = 2.28$, $J = -13$ cm^{-1}, and $N\alpha = 300 \times 10^{-6}$ cgs/mol for [Cu(samen)Ni(phen)$_2$]. The g values of the present complexes (2.27 and 2.28) are com-

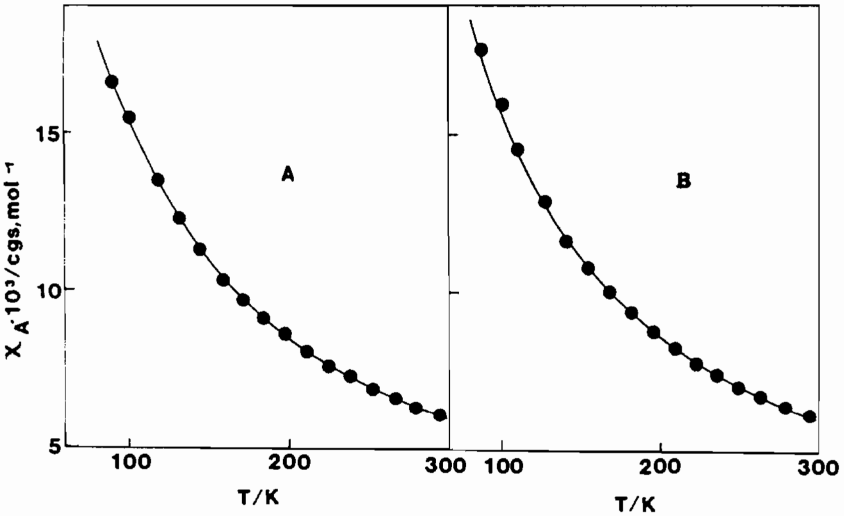


Fig. 4. χ_A *vs.* T plots for (a) [Cu(samen)Ni(bpy)$_2$] and (b) [Cu(samen)Ni(phen)$_2$]. Each solid curve is drawn based on eqn. (3) with the magnetic parameters given in the text.

parable with the reported values for the trinuclear Cu(II)–Ni(II)–Cu(II) complexes [9] derived from Cu(SB), but the exchange integrals (−13 and −14 cm^{-1}) are lower than those of the trinuclear complexes. The present magnetic investigation clearly demonstrates that [Cu(samen)Ni(L)$_2$] (L = bpy, phen) are discrete heterobinuclear complexes with the structure given in Fig. 1b.

References

1 H. Ōkawa, K. Horiuchi, W. Kanda, H. Oshio and S. Kida, *Bull. Chem. Soc. Jpn.*, in press.
2 E. Sinn and C. M. Harris, *Coord. Chem. Rev., 4,* 391 (1969).
3 C. A. Bear, J. M. Waters and T. N. Waters, *J. Chem. Soc., Chem. Commun.,* 703 (1971).
4 E. Sinn and W. T. Robinson, *J. Chem. Soc., Chem. Commun.,* 359 (1972).
5 R. M. Countryman, W. T. Robinson and E. Sinn, *Inorg. Chem., 13,* 2013 (1974).
6 (a) S. J. Gruber, C. M. Harris and E. Sinn, *Inorg. Nucl. Chem. Lett., 3,* 495 (1967); (b) *4,* 107 (1968); (c) *Inorg. Chem., 7,* 268 (1968); (d) S. Kokot, C. M. Harris and E. Sinn, *Aust. J. Chem., 25,* 45 (1972).
7 H. Ōkawa and S. Kida, *Inorg. Chim. Acta, 23,* 253 (1977); (b) M. Nakamura, H. Ōkawa and S. Kida, *Inorg. Chim. Acta, 62,* 201 (1982).
8 C. J. O'Conner, D. P. Freyberg and E. Sinn, *Inorg. Chem., 18,* 1077 (1979).
9 S. J. Gruber, C. M. Harris and E. Sinn, *J. Chem. Phys., 49,* 2183 (1968).
10 V. Kasempimolporn, H. Ōkawa and S. Kida, *Bull. Chem. Soc. Jpn., 52,* 1982 (1979); *52,* 3459 (1979).
11 M. Handa, H. Ōkawa and S. Kida, *Bull. Chem. Soc. Jpn., 58,* 1835 (1985).
12 H. Ojima, *Nippon Kagaku Kaishi, 88,* 329 (1967).
13 N. F. Curtis, *J. Chem. Soc.,* 3147 (1961).
14 P. W. Selwood, 'Magnetochemistry', Interscience, New York, 1956, pp. 78–91.
15 K. V. Patel and P. K. Bhattacharya, *J. Chem. Soc., Dalton Trans.,* 359 (1982).
16 M. Handa, A. Honda, Z. J. Zhong, H. Ōkawa and S. Kida, *Inorg. Chim. Acta, 101,* 39 (1985).
17 C. M. Harris and E. Sinn, *J. Inorg. Nucl. Chem., 30,* 2723 (1968).
18 K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds', Wiley, New York, 1970, p. 166.
19 H. Itoh, *Nippon Kagaku Zasshi, 77,* 1399 (1956).
20 S. Bunel, L. Gil, E. Moraga and H. Bobadilla, *Inorg. Chim. Acta, 4,* 415 (1970).
21 S. M. Nelson and J. Rodgers, *J. Chem. Soc. A,* 272 (1968).
22 B. Bleaney and K. D. Bowers, *Proc. R. Soc. London, Ser. A, 214,* 451 (1952).
23 M. Inoue, M. Kishita and M. Kubo, *Inorg. Chem., 6,* 900 (1967).