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Homo- and Hetero-binuclear Complexes of New Binucleating Ligand *N*,*N'*-Bis(3-methoxycarbonylsalicylidene)ethylenediamine

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Abstract

Dicopper(II), copper(II)–nickel(II), and copper(II)–cobalt(II) complexes of the general formula $[CuM(L)X_2]$ (X = halogeno ion) have been synthesized using *N*,*N'*-bis(3-methoxycarbonylsalicylidene)-ethylenediamine (H_2L). Based on infrared and electronic spectra, it is shown that the copper(II) ion is bound at the N_2O_2-site with the imino nitrogens and the bridging phenolic oxygens and the second metal ion (M(II)) is bound at the O_4-site with the bridging phenolic oxygens and the carbonyl oxygens of the ester groups. In the case of $[CuNi(L)X_2]$ and $[CuCo(L)X_2]$, the configuration around the second metal is pseudo-octahedral with halogeno ions at the apical sites. Cryomagnetic investigations reveal the operation of an antiferromagnetic spin-exchange interaction between the copper(II) and M(II) ions for all the complexes.

Introduction

N,*N'*-Bis(3-carboxysalicylidene)ethylenediamine (H_4fsaen, Fig. 1a) and its homologs [1–3] are binucleating ligands possessing N_2O_2- and O_4-coordination sites. Because of a considerable difference in the ligand field strength between the two sites, this ligand can form discrete hetero-binuclear complexes such as Cu^{2+}–M (M = VO^{2+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}) [1, 4–10], Ni^{2+}–M (M = VO^{2+}, Mn^{2+}, Fe^{3+}, Co^{2+}) [4, 8], and Co^{2+}–M (M = Mn^{2+}, Fe^{2+}) [11]. Magnetic investigations for these complexes have clarified some important factors contributing to antiferromagnetic spin-exchange interactions between metal ions. In order to gain further insight into the mechanism of spin-exchange interaction, it was necessary to develop new ligands capable of forming hetero-binuclear complexes. In this study we prepared *N*,*N'*-bis(3-methoxycarbonylsalicylidene)ethylenediamine (abbreviated as H_2L, Fig. 1b) and examined its complexation behavior. The inside coordination site of this ligand is constituted of two imino-nitrogens and two bridging phenolic oxygens, essentially the same as the inside coordination site of $fsaen^{4-}$. The outside coordination sites of L^{2-} and $fsaen^{4-}$, on the other hand differ from one another, and the site of the former (constituted of two phenolic oxygens and two ester oxygens) is expected to exert a weak ligand field to a metal ion compared with the site of $fsaen^{4-}$ (constituted of two phenolic oxygens and two carboxylate oxygens). Furthermore, H_2L has only two ionizable protons, while H_4fsaen has four. Therefore, it is expected that H_2L will form heterobinuclear complexes differing from those of H_4fsaen. This paper deals with the syntheses and characterization of dicopper(II) and copper(II)–M(II) complexes (M = Co, Ni) of H_2L.

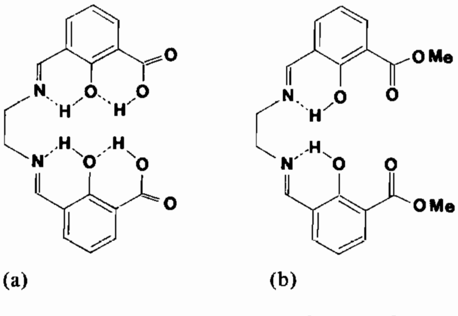

Fig. 1. Chemical structures of (a) H_4fsaen and (b) H_2L.

Experimental

Preparations

3-Formylsalicylic acid was obtained by the literature method [12].

Methyl 3-formylsalicylate

3-Formylsalicylic acid (1×10^{-1} mol) was dissolved in an aqueous solution of sodium carbonate

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(5×10^{-2} mol), and the solution was boiled gently for 30 min to expel carbon dioxide. Addition of an aqueous solution of silver nitrate (1×10^{-1} mol) to this solution resulted in the precipitation of silver 3-formylsalicylate. A mixture of the dried silver salt (5×10^{-2} mol), methyl iodide (5×10^{-2} mol), and dry benzene (200 cm^3) was refluxed for 4 h, and filtered when hot to separate silver iodide. The filtrate was concentrated to *ca.* 100 cm^3, and 3-formylsalicylic acid which crystallized from the solution was separated by filtration. On concentrating the filtrate to dryness, methyl 3-formylsalicylate was obtained as a pale yellow substance. It was crystallized from regloin to form colorless needles melting at 82 °C. *Anal.* Found: C, 59.59; H, 4.42. Calc. for $C_9H_8O_4$: C, 60.00; H, 4.48%.

H_2L

The reaction of methyl 3-formylsalicylate and ethylenediamine in the 2:1 mole ratio in methanol gave a yellow mass, which was crystallized from methanol to form yellow prisms melting at 180–181 °C. *Anal.* Found: C, 62.26; H, 5.44; N, 6.97. Calc. for $C_{20}H_{20}N_2O_6$: C, 62.49; H, 5.24; N, 7.29%.

[Cu(L)]

A methanolic solution of copper(II) acetate monohydrate (1×10^{-2} mol) was added to a warm methanolic solution of H_2L (1×10^{-2}), and the mixture was heated on a water-bath to give purple crystals. They were collected, washed with a small amount of methanol, and dried over P_2O_5 in a vacuum desiccator. *Anal.* Found: C, 53.67; H, 4.05; N, 6.25. Calc. for $C_{20}H_{18}N_2O_6Cu$: C, 53.87; H, 4.07; N, 6.28%.

[Cu_2(L)Br_2]

[Cu(L)] (192 mg) and $CuBr_2$ (100 mg) were reacted in anhydrous methanol for 2 h. The brown crystalline powder thus formed was separated, washed with methanol, and dried *in vacuo*. *Anal.* Found: C, 36.25; H, 2.89; N, 4.01. Calc. for $C_{20}H_{18}N_2O_6Cu_2Br_2$: C, 35.89; H, 2.71; N, 4.19%.

[CuNi(L)Cl_2]

This complex was obtained as brown prisms by the reaction of [Cu(L)] (192 mg) and nickel(II) chloride hexahydrate (110 mg) in methanol. *Anal.* Found: C, 39.14; H, 3.71; N, 4.38. Calc. for $C_{20}H_{18}N_2O_6CuNiCl_2 \cdot 2H_2O$: C, 39.28; H, 3.63; N, 4.58%.

[CuNi(L)Br_2]

This complex was obtained as dark scarlet prisms in a similar way to that for [CuNi(L)Cl_2]. *Anal.* Found: C, 36.10; H, 3.23; N, 3.82. Calc. for $C_{20}H_{18}N_2O_6CuNiBr_2$: C, 36.15; H, 2.73; N, 4.22%.

[CuCo(L)Cl_2]

This complex was obtained as bluish purple crystals by the reaction of [Cu(L)] (192 mg) and cobalt(II) chloride hexahydrate (110 mg) in methanol. *Anal.* Found: C, 39.23; H, 3.67; N, 4.57. Calc. for $C_{20}H_{18}N_2O_6CuCoCl_2 \cdot 2H_2O$: C, 39.27; H, 3.62; N, 4.58%.

[CuCo(L)Br_2]

This complex was obtained as purple crystals in a similar way to that for [CuCo(L)Cl_2]. *Anal.* Found: C, 34.33; H, 3.17; N, 3.95. Calc. for $C_{20}H_{18}N_2O_6CuCoBr_2 \cdot 2H_2O$: C, 34.28; H, 3.16; N, 4.00%.

Measurements

Elemental analyses were carried out at the Service Center of Elemental Analysis, Kyushu University. Infrared spectra were recorded on a JASCO IR-810 spectrometer on KBr disks. Electronic spectra were recorded on a Shimadzu Multipurpose Spectrophotometer Model MPS-5000 on powder samples. Magnetic susceptibilities were determined by the Faraday method in the temperature range 78–300 K. The apparatus was calibrated by the use of Hg[Co(NCS)$_4$] [13]. Pascal's constants [14] were used for diamagnetic corrections for all the constituent atoms.

Results and Discussion

Infrared (IR) spectral data of the binuclear complexes are given in Table I, together with the data for H_2L and [Cu(L)]. In the case of [Cu(L)], the C=O stretching vibration of the ester group is seen at 1720 cm^{-1}, and the antisymmetric and symmetric ν(OCO) vibrations at 1270 and 1130 cm^{-1}, respectively. This IR spectral feature of [Cu(L)] resembles that of H_2L (ν(CO) 1695, $\nu(\mathrm{OCO})^{as}$ 1300, $\nu(\mathrm{OCO})^{s}$ 1125 cm^{-1}), clearly indicating that the copper(II) ion is bound at the inside coordination site. The azomethine vibration appears at 1640 cm^{-1}. In the binuclear complexes, on the other hand, the C=O stretching band is seen at 1650 cm^{-1}. This band is broad probably because of the superposition with the C=N stretching band. Assignments of the antisymmetric and symmetric ν(OCO) vibrations of the ester group could not be made for the binuclear complexes. These facts suggest that the carbonyl oxygen of the ester group coordinates to the second metal ion.

All the binuclear complexes are considerably stable in the solid state but undergo decomposition in solutions especially in water. Therefore, the electronic spectra were determined on powder samples. The results are also included in Table I. The reflectance spectrum of [Cu_2(L)Br_2] exhibits an intense absorption at 18×10^3 cm^{-1} with a shoulder at 13×10^3 cm^{-1}. It is reasonable to assign the 18×10^3

TABLE I. Infrared and Reflectance Spectral Data for H_2L, [Cu(L)] and [CuM(L)X_2]

	IR (cm^{-1})				Reflectance $\nu(10^3\ cm^{-1})$			
	ν(CO)	ν(CN)	$\nu(OCO)^{as}$	$\nu(OCO)^{s}$				
H_2L	1695	1635	1300	1125				
[Cu(L)]	1720	1640	1270	1130	18.0			
[Cu_2(L)Br_2]	1645				18.0	13.0		
[CuNi(L)Cl_2]	1650				17.8	9.0	~14	~17
[CuNi(L)Br_2]	1645				17.8	8.5	~14	~17
[CuCo(L)Cl_2]	1655				18.0	7.1	~13	~17
[CuCo(L)Br_2]	1650				17.9	7.0	~13	~17

cm^{-1} band to a d–d band of the copper(II) ion at the inside coordination site, because this frequency is essentially the same as that ($18 \times 10^3\ cm^{-1}$) of the mononuclear precursor [Cu(L)]. The $13 \times 10^3\ cm^{-1}$ band can be assigned to a d–d band of the copper(II) ion at the outside coordination site. This frequency is slightly lower than that ($13.5 \times 10^3\ cm^{-1}$) of [$Cu_2$(fsaen)], in accord with our presumption that the ligand field strength of the outside coordination site of L^{2-} is weaker than that of fsaen^{4-}. At the moment we cannot clearly say if the bromide ions coordinate at the apical sites of the second copper(II) ion.

The electronic spectra of [CuNi(L)Cl_2] and [CuNi(L)Br_2] are similar to each other, and show an intense band at $17.8 \times 10^3\ cm^{-1}$ attributable to the inside copper(II) ion and weak bands at 9×10^3, 14×10^3, and $17 \times 10^3\ cm^{-1}$ attributable to the outside nickel(II) ion. The spectral result clearly indicates the configuration around the nickel(II) ion to be pseudo-octahedral, with the phenolic and ester oxygens in the equatorial plane and the halogeno ions at the apical sites. The same configuration is inferred for [CuCo(L)Cl_2] and [CuCo(L)Br_2], based on their electronic spectra showing an intense band at $18 \times 10^3\ cm^{-1}$ and weak bands at 7×10^3, 13×10^3, and $17 \times 10^3\ cm^{-1}$.

Magnetic moment (per metal) of [Cu_2(L)Br_2] at room temperature is subnormal (1.04 μ_B), suggesting the operation of an antiferromagnetic spin-exchange interaction within a molecule. Temperature variation of the magnetic susceptibility determined in the temperature range 80–300 K is shown in Fig. 2. The magnetic susceptibility decreases with lowering of the temperature and reaches a constant value ($60 \times 10^{-6}\ cm^3\ mol^{-1}$) below 90 K. This χ_A *versus* T behavior can be explained by the Bleaney–Bowers equation [15] based on the isotropic spin-exchange operator for a dimer ($\mathcal{H} = -2J\hat{S}_1\hat{S}_2$)

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

where N is the Avogadro number, β the Bohr magneton, k the Boltzmann constant, T the absolute temperature, J the exchange integral, and $N\alpha$ the temperature-independent paramagnetism. By the best fit technique g, J, and $N\alpha$ were estimated at 2.08, $-270\ cm^{-1}$, and $60 \times 10^{-6}\ cm^3\ mol^{-1}$, respectively. The exchange integral is slightly smaller (in absolute value) than that ($-330\ cm^{-1}$) [2] of the dicopper(II) complex with fsaen^{4-}.

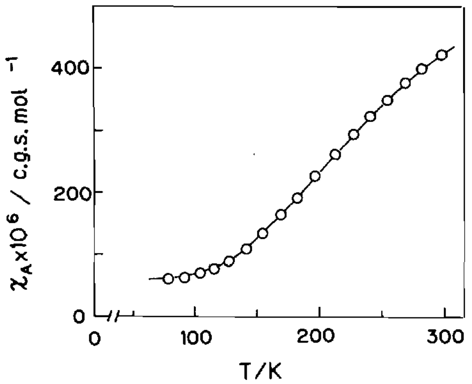

Fig. 2. Temperature variation of magnetic susceptibility of [Cu_2(L)Br_2]. Solid line is drawn based on the Bleaney–Bowers equation with the parameters $g = 2.08$, $J = -270\ cm^{-1}$ and $N\alpha = 60 \times 10^{-6}\ cm^3\ mol^{-1}$.

Room temperature magnetic moments of [CuNi(L)Cl_2] and [CuNi(L)Br_2] are 3.27 and 3.25 μ_B, respectively. They also decreased when the temperature was lowered. Temperature dependence of the magnetic susceptibility for [CuNi(L)Cl_2] is shown in Fig. 3. The magnetism could be simulated with the magnetic susceptibility equation for the ($S = 1/2$)–($S = 1$) system based on the operator $\mathcal{H} = -J\hat{S}_1\hat{S}_2$

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

with the magnetic parameters, $g = 2.13$, $J = -46.2\ cm^{-1}$ and $N\alpha = 150 \times 10^{-6}\ cm^3\ mol^{-1}$. Similarly, magnetism for [CuNi(L)Br_2] could be simulated by the equation mentioned above, using the parameters, $g = 2.12$, $J = -42.2\ cm^{-1}$ and $N\alpha = 120 \times 10^{-6}\ cm^3\ mol^{-1}$. The exchange integrals of the complexes are considerably smaller than that ($-75\ cm^{-1}$) [1, 4] of the Cu^{II}–Ni^{II} complex with fsaen^{4-}.

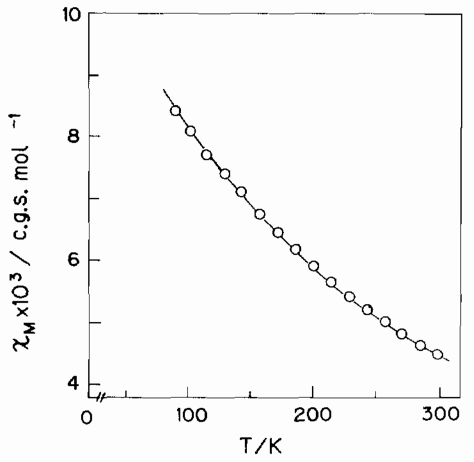

Fig. 3. Temperature variation magnetic susceptibility of $[CuNi(L)Cl_2]$. Solid line is drawn based on the theoretical equation for $(S = 1/2)-(S = 1)$ (see text) with the parameters $g = 2.13, J = -46.2$ cm^{-1} and $N\alpha = 150 \times 10^{-6}$ cm^3 mol^{-1}.

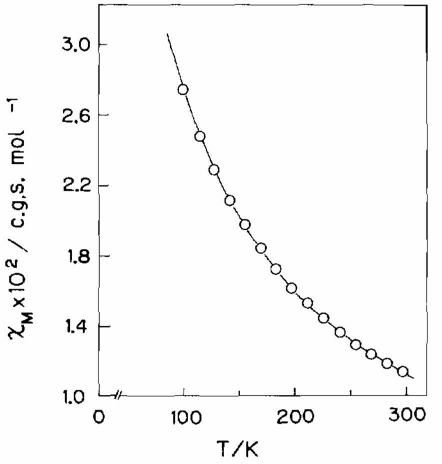

Fig. 4. Temperature variation of magnetic susceptibility of $[CuCo(L)Cl_2]$. Solid line is drawn based on the theoretical equation for $(S = 1/2)-(S = 3/2)$ (see text) with the parameters $g = 2.48$, $J = -17.2$ cm^{-1}, and $N\alpha = 500 \times 10^{-6}$ cm^3 mol^{-1}.

Magnetic moments of $[CuCo(L)Cl_2]$ and $[CuCo(L)Br_2]$ are 5.19 and 5.22 μ_B, respectively at room temperature. The moments decrease monotonously with lowering of the temperature, implying the operation of an antiferromagnetic spin-exchange interaction within each molecule. The temperature dependence of the magnetic susceptibility for $[CuCo(L)Cl_2]$ is given in Fig. 4. This magnetic behavior could be explained by the susceptibility equation for the $(S = 1/2)-(S = 3/2)$ system

$$\chi_M = \left(\frac{Ng^2\beta^2}{kT}\right)\left(\frac{10 + 2\exp(-4J/kT)}{5 + 3\exp(-4J/kT)}\right) + N\alpha$$

with the magnetic parameters, $g = 2.48$, $J = -17.2$ cm^{-1} and $N\alpha = 500 \times 10^{-6}$ cgs/mol. For $[CuCo(L)Br_2]$ the following magnetic parameters were obtained: $g = 2.49$, $J = -17.0$, and $N\alpha = 460 \times 10^{-6}$ cm^3 mol^{-1}. The exchange integrals for the complexes are about one half of that (-35 cm^{-1}) [4] of the $Cu^{II}-Co^{II}$ complex with fsaen^{4-}.

Hence, it is revealed from this study that H_2L can form discrete hetero-binuclear complexes as well as homobinuclear complexes. We believe that this ligand can be applicable to the syntheses of other hetero-binuclear complexes and mixed-spin binuclear complexes such as $Co^{II}(S = 1/2)-Co^{II}(S = 3/2)$.

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