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Binuclear Metal Complexes. XL.[1] Synthesis and Magnetic and Spectral Properties of Alkoxo-bridged Copper(II) Complexes with 2-(Alkylthio)ethanols

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Alkoxo-bridged copper(II) complexes with 2-(alkylthio)ethanols, $Cu(RSCH_2CH_2O)X$ ($R=CH_3$, C_2H_5, n-C_3H_7, i-C_3H_7, s-C_4H_9, t-C_4H_9; X=Br, Cl), have been prepared and characterized by elemental analyses, infrared and electronic spectra and magnetic susceptibilities (80—300 K). Based on the magnetic properties, these complexes were divided into three types, A, B, and C. Type A complexes show a strong antiferromagnetic interaction and exhibit a distinct absorption band characteristic of alkoxo-bridged structure in the $22—24\times10^3$ cm^{-1} region. Type B and C complexes follow the Curie-Weiss law. The former complexes show a ferromagnetic behavior, whereas the latter complexes show a weak antiferromagnetism. The results were compared with those of the complexes with 2-(dialkylamino)ethanols, $Cu(R_2NCH_2CH_2O)X$.

A great number of copper(II) complexes with 2-(dialkylamino)ethanols (abbreviated as HR-no) with the general formula Cu(R-no)X were reported and their structures and magnetic properties have been extensively studied.[2-5] However, there has been no study on copper(II) complexes with 2-(alkylthio)ethanols so far. This may partly be due to the poor coordinating ability of both thioether sulfur and alcoholic oxygen atoms.[6] As a continuing project for binuclear copper(II) complexes of sulfur-containing ligands, we recently reported the synthesis, crystal structures and spectral and magnetic properties of alkoxo-bridged copper(II) complexes with tridentate ligands having sulfur, nitrogen and oxygen as donor atoms (SNO and NSO donor sets)· The results were discussed in relation to those of the alkoxo-bridged copper(II) complexes with NNO tridentate ligands.[7,8] In this study, we have prepared a series of alkoxo-bridged copper(II) complexes with 2-(alkylthio)ethanols, $Cu(RSCH_2CH_2O)X$ (abbreviated as Cu(R-so)X, $R=CH_3$, C_2H_5, n-C_3H_7, i-C_3H_7, s-C_4H_9, t-C_4H_9; X=Br, Cl), and investigated their magnetic and spectral properties in comparison with those of the complexes with 2-(dialkylamino)ethanols, Cu(R-no)X (Fig. 1).

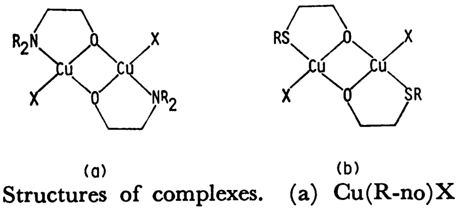

Fig. 1. Structures of complexes. (a) Cu(R-no)X, (b) Cu(R-so)X.

Experimental

Preparation of the Complexes. The ligands, $RSCH_2CH_2OH$ ($R=CH_3$, C_2H_5, n-C_3H_7, i-C_3H_7, s-C_4H_9, t-C_4H_9), were prepared after the method described in the literature.[9] Preparation of the complexes is exemplified by $Cu(CH_3$-so)Cl. To an absolute ethanol solution of 2-(methylthio)ethanol (370 mg) and triethylamine (143 mg) was added an absolute ethanol solution of copper(II) chloride (135 mg). A dark green precipitate was yielded in the solution. This precipitate was separated by filtration, washed with ethanol and dried *in vacuo* over P_2O_5. Yield: 125 mg.

TABLE 1. ANALYTICAL DATA OF Cu(R-so)X

Complex R	X	Found(Calcd) (%) C	H
CH_3	Cl	19.45(18.95)	3.89(3.71)
C_2H_5	Cl	23.43(23.53)	4.47(4.44)
n-C_3H_7	Cl	27.03(27.52)	5.09(5.08)
i-C_3H_7	Cl	27.62(27.52)	5.18(5.08)
s-C_4H_9	Cl	30.99(31.03)	5.64(5.64)
t-C_4H_9	Cl	30.81(31.03)	5.72(5.64)
CH_3	Br	15.59(15.36)	3.03(3.01)
C_2H_5	Br	19.44(19.32)	3.76(3.65)
n-C_3H_7	Br	22.88(22.86)	4.20(4.22)
i-C_3H_7	Br	22.98(22.86)	4.31(4.22)
s-C_4H_9	Br	25.88(26.05)	4.68(4.74)
t-C_4H_9	Br	25.85(26.05)	4.81(4.74)

The bromides, Cu(R-so)Br, were prepared by a method similar to that for the chlorides except for using copper(II) bromide instead of copper(II) chloride.

Carbon and hydrogen analyses were carried out at the Service Center of Elemental Analysis, Kyushu University. The results of elemental analyses are listed in Table 1.

Measurements. Infrared spectra were measured with a Hitachi Grating Infrared Spectrophotometer Model 215 in the region 4000—650 cm^{-1} on a KBr disk. Electronic spectra were measured with a Shimadzu Multipurpose Spectrophotometer Model MSP-5000 at room temperature. Magnetic susceptibilities were measured by the Faraday method over the range 80—300 K. The apparatus was callibrated by the use of $[Ni(en)_3]S_2O_3$.[10] All the susceptibilities were corrected for the diamagnetism of the constituting atoms by the use of Pascal's constants.[11] Effective magnetic moments were calculated from the equation, $\mu_{eff}=2.828\sqrt{(\chi_A-N\alpha)T}$, where χ_A is atomic magnetic susceptibility and $N\alpha$ is temperature-independent paramagnetism in cgs emu. (1 BM$=9.274\times10^{-24}$ A m^2, 1 cm^3 mol^{-1} (cgs emu)$=4\pi\times10^{-6}$ m^3 mol^{-1}.)

Results and Discussion

Infrared spectra of the free ligands show a strong band around 3370 cm^{-1}, which is attributed to the OH stretching vibration. In the case of 2-(methylthio)-ethanol, the OH deformation vibration was assigned

TABLE 2. MAGNETIC DATA OF Cu(R-so)X

Type	Complex R	X	μ_{eff}/BM (T/K)	θ/K	$2J$/cm^{-1} [a]	$N\alpha\times10^6$/cgs emu	P
A	CH_3	Cl	0.60 (293)		−745	57	0
	C_2H_5	Cl	0.50 (298)		−865	41	0.96×10^{-2}
	t-C_4H_9	Cl	0.72 (292)		−665	36	1.7×10^{-2}
	CH_3	Br	0.57 (298)		−780	54	0
	C_2H_5	Br	0.38 (294)		−930	56	0
	s-C_4H_9	Br	0.62 (297)		−735	60	0.78×10^{-2}
	t-C_4H_9	Br	0.56 (298)		−820	47	1.7×10^{-2}
B	i-C_3H_7	Cl	1.85 (294)	13		60	
	n-C_3H_7	Br	1.84 (295)	22		60	
	i-C_3H_7	Br	1.84 (294)	16		60	
C	n-C_3H_7	Cl	1.72 (298)	−55		60	
	s-C_4H_9	Cl	1.70 (298)	−45		60	

a) For all the complexes $g=2.10$ was assumed.

to the band at 1160 or 1010 cm^{-1}.[12] All these bands are absent in the spectra of the copper(II) complexes. This indicates that the alcoholic proton is lost upon complexation.

Based on the temperature dependence of the magnetic susceptibilities, we classified the complexes into three types: type A; complexes whose magnetic behavior can be interpreted in terms of the Bleaney-Bowers equation[13] with considerably large J values, type B; complexes which obey the Curie-Weiss law with positive Weiss constants in the temperature range studied, and type C; complexes which obey the Curie-Weiss law with negative Weiss constants. These types exactly correspond to the types A, B, and C(a) of Nishida and Kida's classification,[5] respectively.

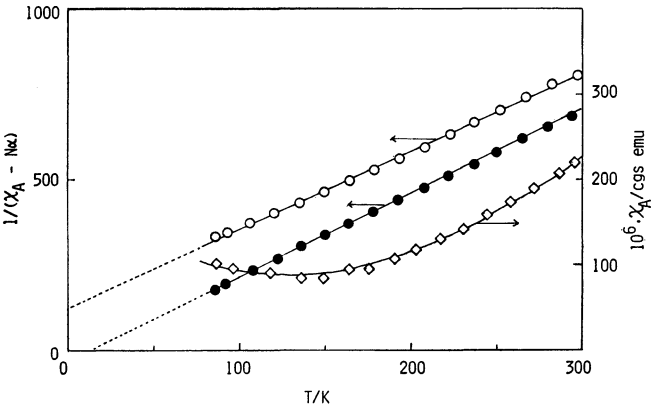

Fig. 2. Temperature dependence of magnetic susceptibilities of Cu(s-C_4H_9-so)Br (type A) (◇), Cu(i-C_3H_7-so)Cl (type B) (●), and Cu(n-C_3H_7-so)Cl (type C) (○). The solid curve was calculated from Eq. 1 using the parameters listed in Table 2.

Type A Complexes. The magnetic moments are very low at room temperature, indicating the existence of a strong antiferromagnetic interaction in these complexes. An example of the temperature dependence of magnetic susceptibilities of type A complexes is shown in Fig. 2. The temperature dependence of magnetic susceptibilities can be interpreted by the modified Bleaney-Bowers equation[14]

$$\chi_A = \frac{Ng^2\beta^2}{3kT}\left[1+\frac{1}{3}\exp(-2J/kT)\right]^{-1}(1-P) + \frac{0.45P}{T} + N\alpha, \qquad (1)$$

where χ_A is susceptibility per copper atom, P is the mole fraction of the mononuclear copper(II) impurity, and other symbols have the usual meanings. The second term in Eq. 1 was added to account for the presence of the small amount of a paramagnetic impurity which was found in some samples of type A complexes. The parameters, $-2J$, $N\alpha$, and P were evaluated from the best fit of the experimental data to Eq. 1 and are listed in Table 2. The $-2J$ values, the energy separation between the spin-singlet ground state and the lowest spin-triplet state, is comparable to those of type A complexes of Cu(R-no)X,[4,5] indicating that a strong antiferromagnetic interaction is operating between the copper(II) ions.

The electronic absorption spectra in nujol mull of type A complexes are shown in Fig. 3. The band maxima of the absorption spectra in nujol mull and in 1,2-dichloroethane solutions are given in Table 3. Both spectra display a broad band centered at about 14—15 × 10^3 cm^{-1} which is attributable to d-d transitions. In the higher frequency region 22—24 × 10^3 cm^{-1}, a

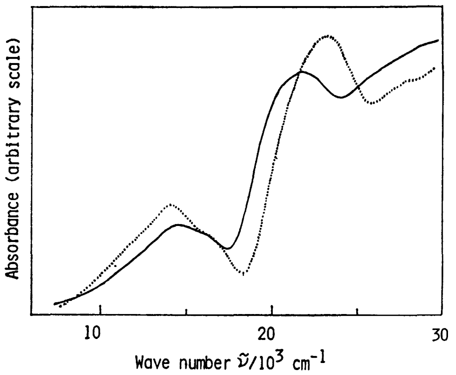

Fig. 3. Mull spectra of Cu(CH_3-so)Br (——) and Cu(C_2H_5-so)Cl (······).

TABLE 3. SPECTRAL DATA OF Cu(R-so)X

Type	Complex		Mull spectra $\tilde{\nu}_{max}/10^3$ cm^{-1}				Solution spectra[a] $\tilde{\nu}_{max}/10^3$ cm^{-1}(ε)	
	R	X						
A	CH_3	Cl		13.9	16.1sh	23.8sh[b]		
	C_2H_5	Cl		14.1	16.4sh	23.2	14.5(120)	23.8(1570)
	t-C_4H_9	Cl		13.9		22.7	14.2(99)	23.5(1260)
	CH_3	Br		14.5		21.7	14.5(160)	22.5(1750)
	C_2H_5	Br		14.2	16.3sh	21.8	14.5(160)	22.4(2220)
	s-C_4H_9	Br		14.4		21.8	14.7(190)	22.4(2420)
	t-C_4H_9	Br		14.7		21.7	14.9(240)	22.3(1790)
B	i-C_3H_7	Cl	12.7sh	15.5			14.6(91)	23.7(1490)
	n-C_3H_7	Br	13.0sh	15.3			14.6(160)	22.4(2220)
	i-C_3H_7	Br	12.8sh	15.3			14.6(170)	22.3(2520)
C	n-C_3H_7	Cl		13.9		21.5	14.5(130)	23.8(1700)
	s-C_4H_9	Cl		15.2		22.2sh	14.7(170)	23.6(2200)

a) 1,2-Dichloroethane solution. b) sh=Shoulder.

distinct absorption band with higher intensity (log ε= *ca.* 3) was observed. This band should correspond to the band in the 24—25×10^3 cm^{-1} region observed for type A complexes of Cu(R-no)X,[4,5] and may be assigned to $p_\pi(O) \rightarrow d(Cu)$ charge transfer transition.[5] The lowering of the transition energy for Cu(R-so)X relative to that of Cu(R-no)X may be interpreted in terms of lowering of optical electronegativity[15] of copper ion of Cu(R-so)X on the assumption that the energies of p_π electrons of alkoxo oxygen are nearly constant.[7]

Type B Complexes. The room-temperature magnetic moments of type B complexes fall in the range of the value generally observed for mononuclear copper(II) complexes. As shown in Fig. 2, the magnetic susceptibilities of type B complexes follow the Curie-Weiss law, $\chi_A = C/(T-\theta) + N\alpha$, in the temperature range 80—300 K. Since the ground states of these complexes are orbitally nondegenerate, the positive Weiss constants indicate that a ferromagnetic interaction is operative between the copper ions (Table 2), as was so in the case of type B complexes of Cu(R-no)X.[4,5] The X-ray structure analyses showed that type B complexes of Cu(R-no)X have tetranuclear structures with a cubane type Cu_4O_4 core.[3] Therefore, it can be presumed that type B complexes of Cu(R-no)X have similar cubane tetranuclear structures.

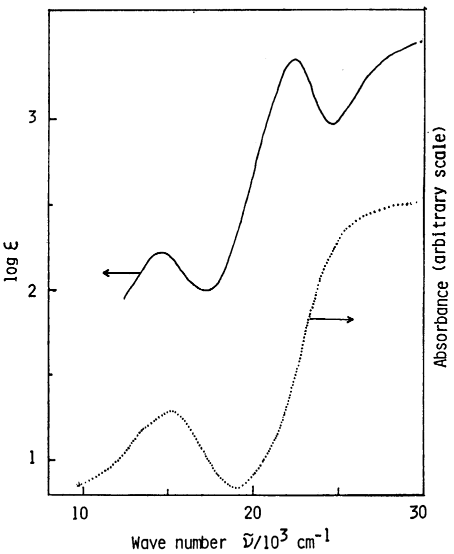

Fig. 4. Absorption spectra of Cu(n-C_3H_7-so)Br in Nujol mull (……) and in 1,2-dichloroethane solution (——).

As shown in Fig. 4, type B complexes show no distinct absorption band at 22—24×10^3 cm^{-1} in the nujol mull spectra, whereas in the solution a distinct absorption in that region. This fact suggests that type B complexes are likely to dissociate in solution to form a binuclear species similar to type A complexes.[16]

Type C Complexes. The effective magnetic moments at room temperature of type C complexes are slightly lower than the spin-only value for one unpaired electron per copper atom. The cryomagnetic data follow the Curie-Weiss law with a negative Weiss constant, indicating the existence of a weak antiferromagnetic interaction in this type of complexes (Fig. 2).

The band maxima of the electronic absorption spectra of type C complexes are given in Table 3. In both the solid state and the solution spectra, type C complexes show a distinct absorption band at 22—24×10^3 cm^{-1}, as observed for type A complexes. These magnetic and spectral properties are similar to those of type C(a) complexes of Cu(R-no)X.[4,5]

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