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Binuclear Metal Complexes.
XXVI [1]. Synthesis and Magnetic and Spectral Properties of Binuclear Copper(II) Complexes with N-(2-alkylthioethyl)-3-aminopropanol

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Binuclear copper(II) complexes with N-(2-alkylthioethyl)-3-aminopropanol, $[Cu(RS(CH_2)_2NH(CH_2)_3O)]ClO_4$ *and* $Cu(RS(CH_2)_2NH(CH_2)_3O)CuBr_2$ *(where* $R = CH_3$, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, t-C_4H_9*), were prepared and characterized by elemental analyses, infrared and electronic spectra, and magnetic susceptibilities (78–300 K). Similar to binuclear complexes with the NNO tridentate ligands* ($R_2N(CH_2)_mNH(CH_2)_nOH$ = R-nnoH), [Cu(R-nno)]X (X = ClO_4 *or* $B(C_6H_5)_4$*), all these complexes show subnormal magnetic moments at room temperature and exhibit a band in the near-ultraviolet region* ($\sim 24 \times 10^3$ cm^{-1}) *characteristic of oxo-bridged structures. In the case of the perchlorates, the cryomagnetic data can be interpreted by the equation based on a binuclear structure, and the antiferromagnetic interaction is generally stronger than that of the [Cu(R-nno)]X complexes. However, the temperature dependences of magnetic susceptibilities of the* $Cu(R$-$sno)CuBr_2$ *complexes are unusual and could not be explained by any conventional theoretical formulas.*

Introduction

In some copper proteins, a spin-paired Cu(II)–Cu(II) couple exists as an 'EPR-nondetectable' copper [2–6] at the active site. Such a copper pair acts as a two-electron acceptor in the enzymatic reaction [7–10]. This site has a high redox potential and is associated with the absorption band at 330 nm, which suggests the existence of copper–sulfur bonding [11–13]. Accordingly, binuclear copper(II) complexes with sulfur donor ligands have acquired a considerable research interest. However, little is known about binuclear copper(II) complexes of sulfur-containing ligands [15, 21] in contrast to the great number of binuclear copper(II) complexes with oxygen- and nitrogen-donating ligands, although some binuclear copper(II) complexes with Schiff base derivatives containing sulfur have been reported [14–20].

Recently, Kida *et al.* have reported the preparation and magnetic and spectral properties of binuclear copper(II) complexes with some tridentate diaminoalcohols, $R_2N(CH_2)_mNH(CH_2)_nOH$ (R = alkyl) (R-nnoH) [23–25]. Many of them show antiferromagnetic interaction between the two copper(II) ions and a distinctive absorption band in the near-ultraviolet region. Kida *et al.* attributed the near ultraviolet absorption band to a charge transfer transition from nonbonding orbitals of bridging oxygen atoms to the vacant copper d-orbital [22, 24, 25]. In this study, we have prepared a series of binuclear copper(II) complexes with S-, N-, and O-coordinating tridentate ligands $RS(CH_2)_2NH(CH_2)_3OH$ (R-snoH), and studied their spectral and magnetic properties (Fig. 1). The results were compared with those of the complexes with the NNO tridentate ligands R-nnoH.

Experimental

Preparation of Ligands

2-alkylthioethylamines, $RSCH_2CH_2NH_2$ (where $R = CH_3$, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, t-C_4H_9), were prepared according to the method of Weilend *et al.* [26], by the use of alkylmercaptane and ethyleneimine. The following is a typical example of the procedure for the preparation of the ligand, $RS(CH_2)_2NH(CH_2)_3OH$.

3-(2-n-propylthioethylamino)-1-propanol

2-n-Propylthioethylamine (17.8 g, 0.149 mol) and 3-bromo-1-propanol (20.7 g, 0.149 mol) were dissolved in absolute ethanol and the solution was refluxed for 10 hr. The solvent was removed with a

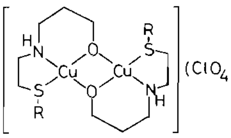

Fig. 1. [Cu(R-sno)]ClO_4.

TABLE I. Abbreviations of Ligands and Their Boiling Points.

Product	Abbreviation	B.P./mm Hg
$CH_3S(CH_2)_2NH(CH_2)_3OH$	me-snoH	136 °C/23
$CH_3CH_2S(CH_2)_2NH(CH_2)_3OH$	et-snoH	163 °C/20
$CH_3(CH_2)_2S(CH_2)_2NH(CH_2)_3OH$	npr-snoH	184 °C/25
$(CH_3)_2CHS(CH_2)_2NH(CH_2)_3OH$	ipr-snoH	178 °C/18
$CH_3(CH_2)_3S(CH_2)_2NH(CH_2)_3OH$	nbu-snoH	196 °C/23
$(CH_3)_3CS(CH_2)_2NH(CH_2)_3OH$	tbu-snoH	190 °C/35

TABLE II. Elemental Analyses.

Complexes	H(%) Found (Calc.)	C(%) Found (Calc.)	N(%) Found (Calc.)	Cu(%) Found (Calc.)	Br(%) Found (Calc.)
Cu(et-sno)$CuBr_2$	3.63 (3.59)	18.93 (18.72)	3.09 (3.12)	27.91 (28.29)	35.76 (35.58)
Cu(npr-sno)$CuBr_2$	3.88 (3.92)	20.83 (20.74)	3.04 (3.02)	27.27 (27.44)	33.86 (34.50)
Cu(ipr-sno)$CuBr_2$	4.00 (3.92)	21.27 (20.74)	3.24 (3.02)	27.15 (27.44)	34.73 (34.50)
Cu(nbu-sno)$CuBr_2$	4.26 (4.22)	22.90 (22.65)	3.11 (2.94)	26.64 (26.63)	33.80 (33.49)
[Cu(me-sno)]ClO_4	4.53 (4.53)	23.17 (23.15)	4.38 (4.50)		
[Cu(et-sno)]$ClO_4 \cdot 1/2H_2O$	5.14 (5.13)	25.44 (25.15)	4.07 (4.19)		
[Cu(npr-sno)]$ClO_4 \cdot H_2O$	5.53 (5.64)	26.95 (26.89)	3.91 (3.92)		
[Cu(ipr-sno)]$ClO_4 \cdot 1/2H_2O$	5.49 (5.50)	27.63 (27.59)	3.92 (4.02)		
[Cu(nbu-sno)]$ClO_4 \cdot H_2O$	5.78 (5.97)	28.94 (29.11)	3.83 (3.77)		
[Cu(tbu-sno)]ClO_4	5.65 (5.70)	30.30 (30.59)	3.84 (3.96)		

rotary evaporator, and an aqueous solution of sodium hydroxide (7.2 g, 0.18 mol) was added to the residue. The oily layer was separate and fractionally distilled under reduced pressure. B.p. 184 °C/25 mm Hg (Found: C, 53.99; H, 10.80; N, 7.91. Calc. for $C_8H_{19}NOS$: C, 54.19; H, 10.80; N, 7.90%). Table I lists the abbreviation of ligands and their boiling points.

Preparation of the Complexes

[Cu(me-sno)] ClO_4

An ethanol solution (5 ml) of me-snoH (0.149 g) was mixed with a 5 ml ethanol solution containing 0.371 g of $Cu(ClO_4)_2 \cdot 6H_2O$ and 2 ml of 2,2-dimethoxypropane. The solution was allowed to stand for several days at room temperature. Dark green needles were collected by filtration and dried *in vacuo* over P_2O_5. The other perchlorates, [Cu(R-sno)]ClO_4 (R = C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, t-C_4H_9), were prepared by procedures similar to that for [Cu(me-sno)]ClO_4.

Cu(R-sno)$CuBr_2$

This was rapidly precipitated as green-black prisms from an ethanolic solution containing $CuBr_2$ and the ligand R-snoH in a 1:1 molar ratio.

The results of elemental analyses of the new compounds are summarized in Table II.

Measurements

Carbon, hydrogen, and nitrogen analyses were carried out at the Service Center of Elemental Analysis, Kyushu University. Copper analysis was carried out with a Shimadzu Atomic Absorption-Flame Spectrophotometer Model AA-610. Bromine was determined by the colorimetric method of Utsumi [27] using a Hirama Photo-electric Spectrophotometer Model 6B. Infrared spectra were measured with a Hitachi 215 Grating Spectrophotometer on a KBr disk. Electronic spectra were measured with a Shimdazu Multipurpose Spectrophotometer Model MSP-5000. Magnetic susceptibilities were measured by the Faraday method. All the susceptibilities were corrected for the diamagnetism of the constituting atoms by the use of Pascal's constants [28].

Results and Discussion

[Cu(R-sno)] ClO_4

The O–H stretching vibration band at 3350 cm^{-1} of the free ligands is absent in the spectra of the

TABLE III. Electronic Spectral Data of [Cu(R-sno)]ClO_4.

Complexes	Reflectance Spectra		Absorption Spectra (in MeOH), $\tilde{\nu}_{max}$ (10^3 cm^{-1}) (ϵ)				
[Cu(me-sno)]ClO_4	17.3	24.5	16.8 (140)	24.8 (2280)		33.1 (4270)	37.6(sh) (2580)
[Cu(et-sno)]$ClO_4 \cdot 1/2H_2O$	16.9	24.3	16.8 (147)	24.8 (2400)		33.2 (4230)	37.5(sh) (2570)
[Cu(npr-sno)]$ClO_4 \cdot H_2O$	17.0	23.5	16.8 (163)	24.8 (2500)		33.0 (4520)	37.6(sh) (2680)
[Cu(ipr-sno)]$ClO_4 \cdot 1/2H_2O$	17.3	24.1	16.8 (181)	24.6 (2560)	29.6(sh) (2870)	33.2 (4240)	37.3(sh) (2710)
[Cu(nbu-sno)]$ClO_4 \cdot H_2O$	17.2	24.5	16.9(171)	24.8 (2800)		33.1 (4630)	37.3(sh) (2780)
[Cu(tbu-sno)]ClO_4	16.1	24.0	16.9 (225)	24.0 (1400)	29.6 (4940)	33.9 (3880)	37.2(sh) (2800)
[Cu(et-nno)]$ClO_4 \cdot 1/2CH_3OH$			16.3 (109)	26.2 (1540)		32.1(sh) (2570)	36.9 (4900)

copper(II) complexes. This indicates that the alcoholic proton is lost upon complexation. The ν(N–H) (~3300 cm^{-1}) and δ(N–H) (~1640 cm^{-1}) of the free ligands are shifted to lower frequencies (~3200 and ~1620 cm^{-1}, respectively) upon complexation, suggesting that the amino nitrogen is coordinated to copper ion. In the spectra of the complexes containing water molecule, ν(O–H) band appears at 3545 cm^{-1} and δ(H–O–H) band at 1595 cm^{-1} overlapping the δ(N–H) band. These bands are attributable to latice water [29]. The ν(Cl–O) bands of perchlorate ion appear at 1085–1110 cm^{-1}. No coordination of perchlorate ion to copper is supposed, since splitting of the band around 1100 cm^{-1} is small [30].

The electronic absorption spectra in methanol solutions and the diffuse reflectance spectra are similar to each other as shown in Table III, indicating that coordination geometry of the complexes is essentially the same in solid and in solution. The bands around 17 X 10^3 cm^{-1} are undoubtedly assigned to d–d transitions. These d–d bands are slightly higher in intensity compared with those of the complexes with the diaminoalcohols [23, 25]. The bands around 24 X 10^3 cm^{-1} should correspond to the bands observed at 24–29 X 10^3 cm^{-1} in the binuclear copper(II) complexes with the NNO tridentate ligands (= R-nnoH) [22–25]. Hence, these bands are assigned to the $P_\pi(O) \rightarrow d_{x^2-y^2}(Cu)$ charge transfer transitions. The frequencies of the bands of the present complexes are a little lower than those for the NNO complexes. This red shift may be interpreted in the following way. Since the donation of thioether sulfur is less than that of amine nitrogen, the copper atom of Cu(R-sno) has a higher "optical electronegativity" [31, 32] than Cu(R-nno). Therefore, the $P_\pi(O) \rightarrow d_{x^2-y^2}(Cu)$ charge transfer transitions may be shifted to a lower frequency by the substitution of the sulfur donor for nitrogen donor.

As shown in Table III, a peak at 33 X 10^3 cm^{-1} and a shoulder at 37 X 10^3 cm^{-1} are observed. Since the free ligands show no absorption below 40 X 10^3 cm^{-1}, these ultraviolet bands should be due to charge transfer transitions. Recent spectral studies of copper(II) complexes with sulfur-containing ligands have shown that the $\sigma(S) \rightarrow d_{x^2-y^2}(Cu)$ absorption appears in the 25–30 X 10^3 cm^{-1} region and the $\sigma(N) \rightarrow d_{x^2-y^2}(Cu)$ transition occurs in the 35–43 X 10^3 cm^{-1} region [33–37]. Accordingly, the absorptions at 33 X 10^3 and 37 X 10^3 cm^{-1} are assigned to the $\sigma(S) \rightarrow d_{x^2-y^2}(Cu)$ and the $\sigma(N) \rightarrow d_{x^2-y^2}(Cu)$ transitions, respectively.

The room temperature magnetic moments per copper atom of [Cu(R-sno)]ClO_4 are very low and range from 0.49 to 0.61 B.M. The magnetic susceptibilities were measured over the temperature range 78–300 K. The magnetic susceptibilities decrease with lowering of temperature and are almost constant below 150 K.

TABLE IV. Magnetic Data.

Complexes	μ_{eff} (B.M.) (298K)	$-2J$ (cm^{-1})	Nα	g
[Cu(me-sno)]ClO$_4$	0.61	740	53	2.1
[Cu(et-sno)]ClO$_4$·1/2H$_2$O	0.49	820	53	2.1
[Cu(npr-sno)]ClO$_4$·H$_2$O	0.53	800	50	2.1
[Cu(ipr-sno)]ClO$_4$·1/2H$_2$O	0.51	820	32	2.1
[Cu(nbu-sno)]ClO$_4$·H$_2$O	0.54	800	50	2.1
[Cu(tbu-sno)]ClO$_4$	0.55	780	34	2.1
[Cu(et-nno)]ClO$_4$·1/2CH$_3$OH^a	0.93 (293K)	530	35	2.1
Cu(et-sno)CuBr$_2$	0.98			
Cu(npr-sno)CuBr$_2$	0.73			
Cu(ipr-sno)CuBr$_2$	0.64			
Cu(nbu-sno)CuBr$_2$	0.80			

[a] Data from Ref. 25.

TABLE V. Electronic Spectral Data of Cu(R-sno)CuBr$_2$.

Complexes	Reflectance Spectra		Absorption Spectra (in MeOH), $\tilde{\nu}_{max}$ (10^3 cm^{-1}) (ϵ)^a			
Cu(et-sno)CuBr$_2$	12.5(sh)	17.4(broad) 23.3	15.9 (140)	25.1 (1760)	33.3 (5440)	37.6(sh) (4180)
Cu(npr-sno)CuBr$_2$	12.5(sh)	16.7(broad) 23.3	15.8 (160)	25.1 (1920)	33.2 (5380)	37.2(sh) (4160)
Cu(ipr-sno)CuBr$_{22}$	12.5(sh)	16.1(broad) 23.3	15.6 (180)	25.1 (1920)	33.2 (5060)	37.2(sh) (4100)
Cu(nbu-sno)CuBr$_2$	12.5(sh)	16.7(broad) 23.1	15.8 (180)	25.1 (2000)	33.2 (5800)	37.7(sh) (4640)

[a] ϵ per Cu(R-sno)CuBr$_2$.

This magnetic behavior can be interpreted with the Bleaney–Bowers equation [38]

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

where χ_A is susceptibility per copper atom, and N, g, J, β, and Nα have the usual meanings. The magnetic data listed in Table IV were evaluated from the best fit of the cryomagnetic data to the Bleaney–Bowers equation. The $-2J$ values, the energy separations between the spin–singlet ground state and the spin–triplet excited state, were all evaluated at about 800 cm^{-1}. In the case of the binuclear complexes with the diaminoalcohols, $-2J$ values are 500 cm^{-1} or slightly above this value [24, 25]. Therefore, the antiferromagnetic interaction seems to become stronger upon substitution of the sulfur donor for the nitrogen donor. This trend has been found in the binuclear copper(II) complexes with the Schiff bases of 2,6-diformyl-4-methylphenol [17–20, 39–42]. For example, binuclear copper(II) complexes with the Schiff bases derived from 2,6-diformyl-4-methylphenol and *o*-aminobenzenethiol or thiosemicarbazide [18] are almost diamagnetic even at room temperature. On the other hand, the complexes with Schiff bases derived from 2,6-diformyl-4-methylphenol and amino acids, N,N-dialkylethylenediamines, or *o*-aminophenol show some paramagnetism at room temperature [39–41].

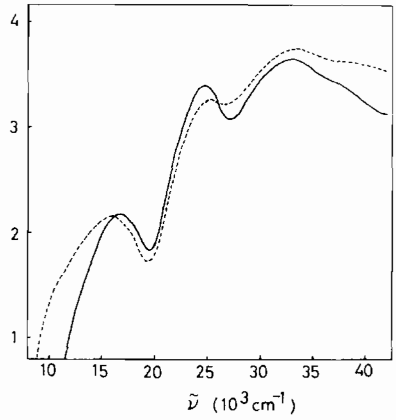

Fig. 2. Electronic absorption spectra of [Cu(et-sno)]ClO$_4$·1/2H$_2$O (——), Cu(et-sno)CuBr$_2$ (-----) in methanol solution.

Cu(R-sno)CuBr$_2$

The electronic spectra of Cu(R-sno)CuBr$_2$ in methanol are similar to those of [Cu(R-sno)]ClO$_4$ except for the low frequency side, as exemplified in Fig. 2. The reflectance spectra are also similar to the solution spectra, as shown in Table V. These

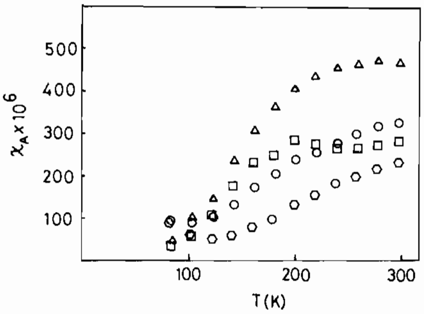

Fig. 3. Temperature dependence of magnetic susceptibilities of Cu(et-sno)CuBr$_2$ (△), Cu(npr-sno)CuBr$_2$ (□), Cu(ipr-sno)CuBr$_2$ (○), and Cu(nbu-sno)CuBr$_2$ (○).

facts suggest that the compounds consist essentially of $[Cu_2(R\text{-sno})_2]^{2+}$ and $2[CuBr_2]^-$ units, although a possibility of weak coordination of $CuBr_2^-$ remains. This view is supported by the fact that the IR spectra of [Cu(R-sno)]ClO$_4$ and Cu(R-sno)CuBr$_2$ in KBr disk are virtually identical except for the perchlorate region (1085–1110 cm^{-1}).

Magnetic moments (per Cu(R-sno)CuBr$_2$) are subnormal (0.64–0.98 B.M.) at room temperature, indicating that a fairly strong antiferromagnetic interaction is operating between copper(II) ions, as in the case of [Cu(R-sno)]ClO$_4$. However, the temperature dependence of magnetic susceptibility of Cu(R-sno)CuBr$_2$ is unusual: some of the examples are shown in Fig. 3. These results could not be interpreted by any theoretical formulas based on the simple Heisenberg or Ising model. A similar magnetic behavior was observed for a binuclear complex Cu($R_2NCH_2CH_2O$)NCS in which weak interaction between the binuclear units through NCS was operating [43–47]. In the present case, however, we can draw no definite conclusion until precise structural data are available.

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