Binuclear Metal Complexes.
L [1]. Synthesis and Magnetic and Spectral Properties of Mononuclear and Binuclear Copper(II) Complexes with 2-[2-(Alkylthio)ethylthio]ethanol

MASAHIRO MIKURIYA, MASAAKI NAKAMURA, HISASHI ŌKAWA and SIGEO KIDA

Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashi-ku, Fukuoka 812, Japan

Received July 30, 1982

Mononuclear copper(II) complexes with 2-[2-(alkylthio)ethylthio]ethanol, Cu($RSCH_2CH_2SCH_2CH_2OH$)Cl_2 and Cu($RSCH_2CH_2SCH_2CH_2OH$)$_2$(ClO_4)$_2$ (R = CH_3 and C_2H_5), and binuclear copper(II) complexes, $Cu_2(RSCH_2CH_2SCH_2CH_2O)_2X_2$ (X = Cl and NO_3), were prepared and characterized by elemental analyses, infrared and electronic spectra, and magnetic susceptibilities. The magnetic data (80–300 K) of $Cu_2(CH_3SCH_2CH_2SCH_2CH_2O)_2Cl_2$ indicate that a strong antiferromagnetic interaction is operating between the copper ions. However, temperature dependence of magnetic susceptibilities of the other binuclear complexes do not obey the equation based on a binuclear model. The binuclear copper(II) complexes exhibit a band at 22–26 × 10^3 cm^{-1} characteristic of alkoxo-bridged structure. These results were compared with those of the complexes with 2-[2-(dialkylamino)ethylthio]ethanol, $Cu_2(R_2NCH_2CH_2SCH_2CH_2O)_2X_2$.

Introduction

As a part of our continuing interest in binuclear copper(II) complexes, we have reported the synthesis, crystal structures, spectra and magnetism of alkoxo-bridged binuclear copper(II) complexes with the tridentate ligands containing a NSO or SNO donor set [2–4]. By comparison of the results with those of the binuclear complexes with the NNO-tridentate ligands, we examined the in-plane coordination effects of thioether sulfur on the structures and properties of binuclear copper(II) complexes.

As an extention of these studies in the present study we prepared binuclear copper(II) complexes with SSO-tridentate ligands, $Cu_2(RSCH_2CH_2SCH_2CH_2O)_2X_2$ (abbreviated as Cu(R-sso)X, where R-ssoH denotes 2-[2-(alkylthio)ethylthio]ethanol, and R = CH_3 and C_2H_5; X = Cl and NO_3) and studied their magnetic and spectral properties. According to our previous papers on the X-ray structure analyses of $Cu_2(R_2NCH_2CH_2SCH_2CH_2O)_2X_2$ (abbreviated as Cu(R-nso)X, where R-nsoH denotes 2-[2-(dialkylamino)ethylthio]ethanol, R = CH_3, C_2H_5, n-C_3H_7, and n-C_4H_9; X = Br, Cl, and NCS), the coordination geometry around the copper ion is a distorted square pyramid formed by the two alkoxo oxygens, thioether sulfur and anion X in the basal plane and the amino nitrogen in the apical position [4]. Thus, in analogy with the Cu(R-nso)X complexes, the terminal alkyl thiogroup of the Cu(R-sso)X complexes was supposed to coordinate to the copper ion from the apical position.

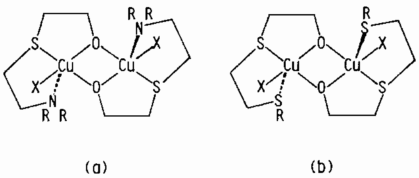

Fig. 1. Structures of complexes. (a) Cu(R-nso)X and (b) Cu(R-sso)X.

Therefore in order to reveal the apical coordination effects of thioether on the spectral and magnetic properties, we have compared in this study the properties of the Cu(R-sso)X complexes with those of the Cu(R-nso)X complexes.

Experimental

Preparation of the Complexes

2-[2-(Alkylthio)ethylthio]ethanol, R-ssoH (R = CH_3 and C_2H_5), were prepared following the method described in the literature [5]. The preparative methods were similar to each other for this series of binuclear complexes. The procedure for the preparation of Cu(CH_3-sso)Cl is shown as an example in the following. A solution of copper(II) chloride (134 mg) in absolute ethanol was added to an absolute ethanol

0020-1693/83/0000-0000/$03.00 © Elsevier Sequoia/Printed in Switzerland

TABLE I. Magnetic Moments (μ_{eff}) of Complexes.

Complex	μ_{eff}/B.M. (T/K)	
$Cu(CH_3\text{-sso})Cl$	0.16(89)	0.83(299)
$Cu(C_2H_5)\text{-sso})Cl$	0.54(87)	1.30(291)
$Cu(CH_3\text{-sso})NO_3$	0.22(87)	0.80(293)
$Cu(C_2H_5)\text{-sso})NO_3$	0.21(87)	0.86(295)
$Cu(CH_3\text{-ssoH})Cl_2$		1.86(298)
$Cu(C_2H_5\text{-ssoH})Cl_2$		1.78(297)
$Cu(CH_3\text{-ssoH})_2(ClO_4)_2$		1.78(298)
$Cu(C_2H_5\text{-ssoH})_2(ClO_4)_2$		1.77(298)

solution of CH_3-ssoH (609 mg) and triethylamine (143 mg). A dark green precipitate was obtained in the solution. This precipitate was separated by filtration and dried *in vacuo* over P_2O_5. *Anal.* Found: C, 24.06; H, 4.45; Cu, 25.7%. Calcd. for $C_5H_{11}ClCuOS_2$: C, 24.00; H, 4.43; Cu, 25.4%.

$Cu(C_2H_5\text{-sso})Cl$. Found: C, 27.39; H, 5.01; Cu, 24.1%. Calcd. for $C_6H_{13}ClCuOS_2$: C, 27.27; H, 4.96; Cu, 24.0%.

$Cu(CH_3\text{-sso})NO_3$. Found: C, 21.86; H, 4.05; N, 4.98; Cu, 23.1%. Calcd. for $C_5H_{11}CuNO_4S_2$: C, 21.70; H, 4.01; N, 5.06; Cu, 23.0%.

$Cu(C_2H_5\text{-sso})NO_3$. Found: C, 24.91; H, 4.61; N, 4.66; Cu, 22.0%. Calcd. for $C_6H_{13}CuNO_4S_2$: C, 24.78; H, 4.51; N, 4.82; Cu, 21.9%.

In the absence of triethylamine, a mononuclear copper(II) complex was formed. Preparation of the mononuclear complexes is exemplified by that of $Cu(CH_3\text{-ssoH})Cl_2$. A solution of copper(II) chloride (134 mg) in absolute ethanol was added to a solution of CH_3-ssoH (152 mg) in absolute ethanol. The mixture was allowed to stand for several days to give a dark green precipitate, which was collected and dried *in vacuo* over P_2O_5. *Anal.* Found: C, 20.63; H, 4.18; Cu. 21.9%. Calcd. for $C_5H_{12}Cl_2CuOS_2$: C, 20.95; H, 4.22; Cu, 22.2%.

$Cu(C_2H_5\text{-ssoH})Cl_2$. Found: C, 24.09; H, 4.79; Cu, 21.0%. Calcd. for $C_6H_{14}Cl_2CuOS_2$: C, 23.96; H, 4.69; Cu, 21.1%.

$Cu(CH_3\text{-ssoH})_2(ClO_4)_2$. Found: C, 21.20; H, 4.30; Cu, 11.1%. Calcd. for $C_{10}H_{24}Cl_2CuO_{10}S_4$: C, 21.18; H, 4.27; Cu, 11.2%.

$Cu(C_2H_5\text{-ssoH})_2(ClO_4)_2$. Found: C, 24.28; H, 4.84; Cu, 10.3%. Calcd. for $C_{12}H_{28}Cl_2CuO_{10}S_4$: C, 24.22; H, 4.74; Cu, 10.7%.

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. Infrared and electronic spectra were measured with a Hitachi Grating Infrared Spectrophotometer Model 215 and a Shimadzu Multipurpose Spectrophotometer Model MSP-5000, respectively. Magnetic susceptibilities were measured by the Faraday method in the temperature range 80–300 K. 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 B.M. = 9.274×10^{-24} Am^2; 1 cm^3 mol^{-1} (cgs emu) = $4\pi \times 10^{-6}$ m^3 mol^{-1}).

Results and Discussion

The Cu(R-ssoH)Cl$_2$ and Cu(R-ssoH)$_2$(ClO$_4$)$_2$ Complexes

In the infrared spectra of $Cu(R\text{-ssoH})Cl_2$ and $Cu(R\text{-ssoH})_2(ClO_4)_2$, the ν(O–H) band was observed at about 3400 cm^{-1}, indicating that the alcoholic OH group is not deprotonated. For $Cu(R\text{-ssoH})_2(ClO_4)_2$, the band due to the perchlorate ion was observed at 1030–1100 cm^{-1}, and showed no appreciable splitting indicative of the perchlorate coordination [2].

The magnetic moments of $Cu(R\text{-ssoH})Cl_2$ and $Cu(R\text{-ssoH})_2(ClO_4)_2$ at room temperature are 1.77–1.86 B.M. and fall in the range of those for ordinary mononuclear copper(II) complexes (Table I).

The electronic spectra of $Cu(R\text{-ssoH})Cl_2$ and $Cu(R\text{-ssoH})_2(ClO_4)_2$ show a broad band assignable to d–d transitions at 12×10^3 cm^{-1} and 17×10^3 cm^{-1}, respectively. The spectra of $Cu(R\text{-ssoH})Cl_2$ and $Cu(R\text{-ssoH})_2(ClO_4)_2$ are similar to those of $Cu(dth)Cl_2$ and $Cu(dth)_2(ClO_4)_2$ (where dth = 2,5-dithiahexane) [6, 7], respectively (Table II). A more intense band at *ca.* 23×10^3 cm^{-1} of these complexes is assigned to the $\sigma(S) \rightarrow d_\sigma(Cu)$ charge transfer [6–8]. As possible equatorial donor sets, S_2Cl_2 and $SOCl_2$ are considered for the $Cu(R\text{-ssoH})Cl_2$ complexes, and S_4 and S_2O_2 for the $Cu(R\text{-ssoH})_2(ClO_4)_2$ complexes. Considered from the similarity between the electronic spectra of our complexes and those of the dth complexes, it is likely that the $Cu(R\text{-ssoH})Cl_2$ and $Cu(R\text{-ssoH})_2(ClO_4)_2$ complexes have equatorial S_2Cl_2 and S_4 donor sets, respectively.

The Cu(R-sso)X Complexes

The ν(O–H) band around 3400 cm^{-1} of the free ligands, is absent in the spectra of $Cu(R\text{-sso})Cl$ and $Cu(R\text{-sso})NO_3$. This indicates that the alcoholic proton is lost upon complexation. In the case of the nitrates, $Cu(R\text{-sso})NO_3$, the ν(N–O) splits into three (1280, 1420 and 1460 cm^{-1}), suggesting that the nitrate ion coordinates to the copper ion [4].

The magnetic moments per copper atom are subnormal at room temperature and decrease with lower-

TABLE II. Band Maxima ($\tilde{\nu}_{max}$) of Electronic Spectra of Complexes.

Complex	Nujol mull spectra $\tilde{\nu}_{max}/10^3$ cm^{-1}				Absorption spectra (in 1,2-dichloroethane) $\tilde{\nu}_{max}/10^3$ cm^{-1} (logϵ)			
Cu(CH_3-sso)Cl		14.0	23.1		14.6(2.31)	23.6(3.16)	31.4(3.39)	37.7(3.43)
Cu(C_2H_5-sso)Cl		13.6	21.7		13.8(2.10)	23.6(3.13)	31.3(3.42)	37.3(3.47)
Cu(CH_3-sso)NO_3	10.2sh[a]	14.8	23.6		14.2(2.02)	25.6sh(2.91)	32.2(3.35)	
Cu(C_2H_5-sso)NO_3	10.5sh	14.2	25.0sh		14.3(2.07)	25.6sh(3.04)	31.8(3.41)	
Cu(CH_3-ssoH)Cl_2	11.0sh	12.8	22.9	25.2sh				
Cu(C_2H_5-ssoH)Cl_2		12.3	23.0	26.3				
Cu(CH_3-ssoH)$_2$(ClO_4)$_2$		17.2	23.5					
Cu(C_2H_5-ssoH)$_2$(ClO_4)$_2$		17.2	23.5					
Cu(dth)Cl_2		12.4	22.1[b]					
Cu(dth)$_2$(ClO_4)$_2$		16.8	22.2[c]					

[a] sh = shoulder. [b] Data taken from ref. [6]. [c] Data taken from ref. [7].

ing of temperature, indicating the existence of an antiferromagnetic interaction (Table I). In the case of Cu(CH_3-sso)Cl, the susceptibility data (80–300 K) can be interpreted by the modified Bleaney-Bowers equation:

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

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 [2, 4]. The second term in eqn. 1 was added to account for the presence of a small amount of paramagnetic impurity. The $-2J$, g, Nα, and P values obtained by the best fit of the experimental data to eqn. 1 are 585 cm^{-1}, 2.10, 60 × 10^{-6} cgs emu/mol, and 0.007, respectively. On the other hand, the temperature dependence of magnetic susceptibilities of the Cu(R-sso)X complexes except for Cu(CH_3-sso)Cl cannot be interpreted by the equation based on a binuclear structure. A similar magnetic behavior was also observed for the Cu(R-nso)X complexes, except for Cu(n-C_4H_9-nso)Cl [4]. The magnetic moments for the Cu(R-sso)X complexes are generally smaller than those for the corresponding Cu(R-nso)X complexes (1.0–1.2 B.M. at room temperature) [4]. Therefore, antiferromagnetic interaction seems to become stronger upon substitution of the sulfur donor for the nitrogen donor. This trend was already found in the binuclear copper(II) complexes with the SNO- and NSO-tridentate ligands where the sulfur donor takes part in the in-plane coordination [2, 3].

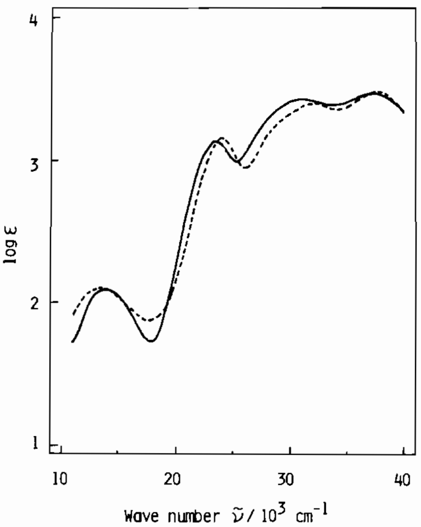

Fig. 2. Electronic spectra of Cu(C_2H_5-sso)Cl (——) and Cu(C_2H_5-nso)Cl (-----) in 1,2-dichloroethane.

As shown in Fig. 2, the Cu(R-sso)X complexes show electronic spectra similar to those of the Cu(R-nso)X complexes [4]. The d–d bands around 14 × 10^3 cm^{-1} are higher in frequency compared with those (12–13 × 10^3 cm^{-1}) of the Cu(R-nso)X complexes. The more intense bands in the 22–38 × 10^3 cm^{-1} region are attributable to charge transfer transitions from ligands to the copper ion. They all shift by *ca.* 0.5 × 10^3 cm^{-1} to lower frequency compared with those of the corresponding Cu(R-nso)X complexes. The band at 23.6 × 10^3 cm^{-1} of Cu(R-sso)Cl corresponds to the 24.0 × 10^3 cm^{-1} band of Cu(R-nso)Cl and the 25.6 × 10^3 cm^{-1} band of Cu(R-sso)NO_3 to the 26.2 × 10^3 cm^{-1} band of

$Cu(R\text{-}nso)NO_3$. These bands seem to be characteristic of an alkoxo-bridged binuclear structure [4]. Thus, they may be assigned to the $p_\pi(O) \rightarrow d_\sigma(Cu)$ transition. It is believed that the degree of donation of thioether sulfur is less than that of amino nitrogen [9]. Therefore, substitution of thioether group for amino group at the apical position would result in the lowering of energy of whole copper 3d orbitals, while as the result of the ligand field change, the d_σ orbital would be relatively lifted in the manifold of the 3d shell. Thus, it is understandable that the blue shift for the d–d bands and the red shift for the CT bands relative to those of the Cu(R-nso)X complexes were observed in the present complexes.

References

1 Part II. H. Ōkawa, M. Kakimoto, T. Izumitani, M. Nakamura and S. Kida, *Bull. Chem. Soc. Jpn., 55,* 149 (1983).

2 M. Mikuriya, H. Okawa and S. Kida, *Inorg. Chim. Acta, 34,* 13 (1979);
ibid., 42, 233 (1980);
Bull. Chem. Soc. Jpn., 53, 3717 (1980).

3 M. Nakamura, M. Mikuriya, H. Okawa and S. Kida, *Bull. Chem. Soc. Jpn., 54,* 1825 (1981);
M. Mikuriya, M. Nakamura, H. Okawa and S. Kida, *Inorg. Chim. Acta, 68,* 111 (1983).

4 M. Mikuriya, H. Okawa and S. Kida, *Bull. Chem. Soc. Jpn., 53,* 2871 (1980);
54, 2979 (1981);
55, 1086 (1982).

5 F. Fehér and K. Vogelbruch, *Chem. Ber., 91,* 996 (1958).

6 E. W. Ainscough, A. M. Brodie and K. C. Palmer, *J. Chem. Soc., Dalton Trans.,* 2375 (1976).

7 M. M. Olmstead, W. K. Musker and R. M. Kessler, *Inorg. Chem., 20,* 151 (1981).

8 V. M. Miskowski, J. A. Thich, R. Solomon and H. J. Schugar, *J. Am. Chem. Soc., 98,* 8344 (1976);
A. R. Amundsen, J. Whelan and B. Bosnich, *ibid., 99,* 6730 (1977);
A. C. Braithwaite, C. E. F. Rickard and T. N. Waters, *Inorg. Chim. Acta, 26,* 23 (1978);
E. W. Ainscough, A. M. Brodie and N. G. Larsen, *Inorg. Chim. Acta, 60,* 25 (1982).

9 C. K. Jørgensen, *J. Inorg. Nucl. Chem., 24,* 1571 (1962);
G. B. Kauffman, J. Tsai, R. C. Fay and C. K. Jørgensen, *Inorg. Chem., 2,* 1233 (1963).