October, 1980] © 1980 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 53, 2871—2877 (1980)

Binuclear Metal Complexes. XXXIII.[1] Synthesis, Structure, Spectra, and Magnetism of Binuclear Copper(II) Complexes with 2-[2-(Dialkylamino)ethylthio]ethanol

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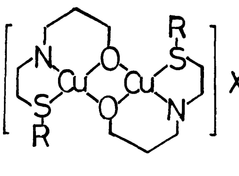
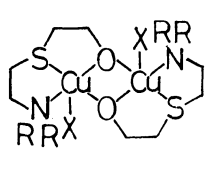
(Received April 10, 1980)

Binuclear copper(II) complexes with 2-[2-(dialkylamino)ethylthio]ethanol, Cu{$R_2N(CH_2)_2S(CH_2)_2O$}X (abbreviated as Cu(R-nso)X, where R=CH_3, C_2H_5, n-C_3H_7, n-C_4H_9; X=Br, Cl, NO_3), were prepared and characterized by elemental analyses, infrared and electronic spectra and magnetic susceptibilities (80—300 K). They exhibit a band at 22—26×10^3 cm^{-1} characteristic of alkoxo-bridged structure. The magnetic data of Cu(n-C_4H_9-nso)Cl indicate that a strong antiferromagnetic interaction is operating between the copper ions. However, temperature dependence of magnetic susceptibilities of the other complexes do not obey the equation based on a binuclear structure. The crystal structure of Cu(CH_3-nso)Br was determined by the single-crystal X-ray diffraction method. The crystals are monoclinic, space group $P2_1/c$, $a=10.133(2)$, $b=7.858(2)$, $c=14.893(3)$ Å, $\beta=118.8(1)°$, and $Z=2$. The structure was solved by the heavy atom method and refined by the block-diagonal least-squares method to an R factor of 0.042. The structure consists of alkoxo-bridged binuclear units, $Cu_2(CH_3\text{-nso})_2Br_2$. The coordination geometry of the copper ion is distorted square pyramid. Since the distances between the binuclear clusters are too long to give rise to an intercluster magnetic interaction, it is suggested that some structural change takes place at low temperature.

In blue copper oxidases (*e.g.*, laccase, ceruloplasmin, and ascorbate oxidase), type III copper is believed to be present as an antiferromagnetically coupled copper(II) dimer.[2] Although no exact information is available yet on the coordination geometry or the nature of the donor atoms for type III copper, models incorporating sulfur donor ligands have attracted a remarkable attention. However, few spectral and magnetic data and almost no structural data are available on binuclear copper(II) complexes with sulfur donor ligands.[3–6]

As a part of the continuing project dealing with binuclear copper(II) complexes of sulfur-containing ligands, we recently reported the synthesis and spectral and magnetic properties of the binuclear copper(II) complexes with N-[2-(alkylthio)ethyl]-3-amino-1-propanol, Cu{$RS(CH_2)_2NH(CH_2)_3O$}X (abbreviated as Cu(R-sno)X, where R=alkyl, X=anion).[1,7] In this study, we have prepared binuclear copper(II) complexes with 2-[2-(dialkylamino)ethylthio]ethanol, Cu{$R_2N(CH_2)_2S(CH_2)_2O$}X (abbreviated as Cu(R-nso)X, where R=CH_3, C_2H_5, n-C_3H_7, n-C_4H_9; X=Br, Cl, NO_3) and investigated their spectral and magnetic properties. In these complexes, the sulfur atom was considered to link two five-membered chelate rings upon complexation. Such a condensed-ring system should bring about a considerable strain, if all donating atoms and copper(II) ions are placed on a plane. Thus, the ligands have the potential to adopt a nonplanar arrangement about the copper ion, promoting stabilization of the copper(I) oxidation state.[8] In order to clarify the detailed molecular structure, the crystal structure of bromo{2-[2-(dimethylamino)ethylthio]ethanolato}copper(II), Cu(CH_3-nso)Br, was determined by the single-crystal X-ray diffraction method.


Cu(R-sno)X


Cu(R-nso)X

Experimental

Preparation of the Ligands. N,N-Dialkyl-2-chloroethylamine hydrochlorides were prepared from 2-(dialkylamino)ethanols and thionyl chloride by the method described in the literature.[9] The ligands, $R_2N(CH_2)_2S(CH_2)_2OH$ (R=CH_3, C_2H_5, n-C_3H_7, n-C_4H_9), were prepared by the reaction of N,N-dialkyl-2-chloroethylamine hydrochlorides and 2-mercaptoethanol by the method of Clinton *et al.*[10]

Preparation of the Complexes. The synthetic methods of the chlorides, Cu(R-nso)Cl (R=CH_3, C_2H_5, n-C_3H_7, n-C_4H_9), are nearly the same and exemplified by Cu(CH_3nso)Cl. To a solution of CH_3-nsoH (149 mg) in absolute ethanol (5 ml) was added a solution of copper(II) chloride dihydrate (85 mg) in absolute ethanol (5 ml). From the mixture, green crystals were immediately formed. They were collected by filtration and dried *in vacuo* over P_2O_5.

The nitrates and bromides, Cu(R-nso)X (X=NO_3,Br), were prepared by a method similar to that for the chlorides

Table 1. Analytical data of Cu(R-nso)X·$n$$H_2O$

Complex R	X	n	Found (Calcd) C(%)	H(%)	N(%)
CH_3	Br	0	24.70(24.71)	4.77(4.84)	4.65(4.80)
C_2H_5	Br	0	29.61(30.05)	5.43(5.67)	4.23(4.38)
n-C_3H_7	Br	0	34.70(34.53)	6.49(6.38)	4.11(4.03)
n-C_4H_9	Br	0	38.32(38.35)	7.11(6.97)	3.81(3.73)
CH_3	Cl	0	29.07(29.15)	5.73(5.71)	5.57(5.67)
C_2H_5	Cl	0	34.84(34.90)	6.66(6.59)	5.10(5.09)
n-C_3H_7	Cl	0	39.58(39.59)	7.45(7.31)	4.60(4.62)
n-C_4H_9	Cl	0	43.43(43.49)	8.06(7.91)	4.31(4.23)
CH_3	NO_3	1/2	25.67(25.48)	5.16(5.35)	10.02(9.91)
C_2H_5	NO_3	1/2	31.03(30.91)	5.98(6.16)	9.10(9.01)
n-C_3H_7	NO_3	0	36.25(36.41)	6.75(6.72)	8.11(8.49)
n-C_4H_9	NO_3	0	39.85(40.27)	7.34(7.32)	7.50(7.83)

except for using copper(II) nitrate trihydrate and copper(II) bromide, respectively, instead of copper(II) chloride dihydrate.

Carbon, hydrogen, and nitrogen analyses were carried out at the Service Center of Elemental Analysis, Kyushu University. The results of elemental analyses for these complexes 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 in the temperature range from liquid nitrogen temperature to room temperature. The apparatus was calibrated by the use of $[\mathrm{Ni(en)_3}]\mathrm{S_2O_3}$.[11] All the susceptibilities were corrected for the diamagnetism of the constituting atoms by the use of Pascal's constants.[12] Effective magnetic moments were calculated from the equation, $\mu_{\mathrm{eff}}=2.828\sqrt{(\chi_A-N\alpha)T}$, where χ_A is the atomic magnetic susceptibility and $N\alpha$ is the temperature-independent paramagnetism. For the present complexes, $N\alpha$ was assumed to be 60×10^{-6} cgs emu.[13]

X-Ray Crystal Structure Analysis of Cu(CH$_3$-nso)Br. A photographic study using Weissenberg camera indicated monoclinic symmetry. Preliminary cell constants were obtained. The systematic absences observed, l odd for $h0l$ and k odd for $0k0$, uniquely define the space group as $P2_1/c$. The unit cell parameters and intensities were measured on a Syntex $P\bar{1}$ automated four-circle diffractometer with Mo $K\alpha$ radiation monochromated by a graphite plate ($\lambda=0.71073$ Å). The crystal was ground to a sphere (radius 0.148 mm). The unit cell parameters were determined by the least-squares refinement based on the 15 reflections in the range of $21°<2\theta<31°$. The values are $a=10.133(2)$, $b=7.858(2)$, $c=14.893(3)$ Å, $\beta=118.8(1)°$ and $V=1039.3(4)$ Å^3. The density $D_m=1.85$ g/cm^3 obtained by floatation in hexane-1,2-dibromoethane solutions agrees well with the density $D_C=1.864$ g/cm^3 calculated for two dimer units per unit cell.

Intensity data were collected by the θ-2θ scan technique with a variable scan rate of 4.0 to 24.0 °/min. Three standard reflections were monitored every 50 reflections, and their intensities showed a good stability. A total of 1943 independent reflections with $2\theta\leq50°$ were collected. The intensities were corrected for the Lorentz and the polarization effects. Absorption correction was applied with the values of the absorption-correction factors, A^*, tabulated in International Tables for X-Ray Crystallography.[14] 1595 independent reflections with $|F|>3\sigma(|F|)$ were considered as "observed" and were used for the structure analysis, where $\sigma(|F|)$ is the standard deviation of the observed structure amplitude due to counting statistics. An initial scale factor and over-all temperature factor were obtained by the Wilson statistics.

The structure was solved by the heavy atom method. The positions of the bromine and the copper atoms were obtained from a three-dimensional Patterson synthesis. The successive Fourier synthesis revealed all the nonhydrogen atoms. Refinement was carried out by the block-diagonal least-squares method. Anisotropic thermal parameters being introduced, the block-diagonal least-squares refinement yielded discrepancy factors $R_1=\sum||F_o|-|F_c||/\sum|F_o|=0.049$ and $R_2=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}=0.082$. Hydrogen atoms were inserted in their calculated positions and included in the refinement. Further refinement with anisotropic thermal parameters for nonhydrogen atoms and isotropic temperature factors for hydrogen atoms gave final values of 0.042 and 0.072 for R_1 and R_2, respectively. In the least-squares refinement the function minimized was $\sum w(|F_o|-k|F_C|)^2$, and the weighting scheme was $w=(6.76+|F_o|+0.086|F_o|^2)^{-1}$.[15] The final shift in the atomic parameters of the nonhydrogen atoms averaged 0.024σ with the maximum of 0.127σ. The final difference Fourier synthesis showed no significant features except two peaks of 0.8 e/Å^3 in the vicinity of the bromine atom. The atomic scattering factors for Br, Cu, S, O, N, and $\mathrm{C_{val}}$ and the anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$ for Br, Cu, and S, were taken from the International Tables for X-Ray Crystallography.[16] For the hydrogen atom, the scattering factors were adopted from the tables of Stewart *et al.*[17] All the calculations were carried out by the FACOM M-190 computer in the Computer Center of Kyushu University using the UNICS-II program system.[18] The drawings were made by the use of ORTEP program.[19] Lists of the observed and calculated structure factors are kept as Document No. 8032 at the Chemical Society of Japan. The final positional and thermal parameters with their estimated standard deviations are given in Table 2.

Results and Discussion

Description of the Structure of Cu(CH$_3$-nso)Br. A perspective drawing of the complex and the numbering system are illustrated in Fig. 1. Bond lengths and angles are listed in Table 3.

The crystal structure essentially consists of the alkoxo-bridged binuclear units, $\mathrm{Cu_2(CH_3\text{-}nso)_2Br_2}$. The $\mathrm{Cu_2(CH_3\text{-}nso)_2Br_2}$ unit is located at the crystallographic

TABLE 2. FRACTIONAL POSITIONAL PARAMETERS AND ANISOTROPIC TEMPERATURE FACTORS ($\times10^4$) OF NON-HYDROGEN ATOMS WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Temperature factors are of the form: $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hkB_{12}+2hlB_{13}+2klB_{23})]$.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br	2596(1)	2590(1)	4511(1)	175(1)	140(1)	104(1)	19(1)	87(1)	−13(1)
Cu	1268(1)	4898(1)	4751(1)	101(1)	103(1)	50.0(5)	6(1)	41(1)	8(1)
S	1556(2)	6772(2)	3657(1)	169(3)	156(3)	49(1)	−20(2)	58(1)	1(1)
O	−470(5)	6264(6)	4474(4)	120(7)	140(8)	69(3)	37(6)	58(4)	42(5)
N	3137(7)	6508(8)	6065(4)	130(9)	153(10)	51(3)	−14(8)	41(5)	−15(5)
C(1)	−760(15)	7823(14)	3987(11)	331(26)	240(20)	196(14)	158(19)	205(17)	139(14)
C(2)	28(10)	8212(13)	3442(7)	151(13)	253(19)	78(6)	21(13)	56(7)	56(9)
C(3)	3216(10)	7874(9)	4585(7)	148(12)	123(11)	95(6)	−7(10)	73(7)	19(7)
C(4)	3328(9)	8096(9)	5636(6)	148(12)	131(12)	76(5)	−5(10)	51(7)	−13(7)
C(5)	2621(12)	6894(15)	6803(6)	230(17)	328(23)	55(5)	−68(16)	73(8)	−61(9)
C(6)	4577(11)	5594(12)	6552(7)	153(13)	207(16)	71(6)	18(12)	9(7)	5(8)

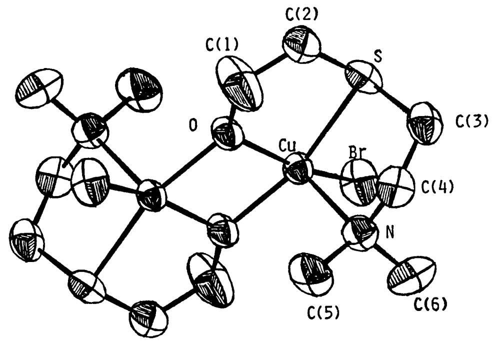


Fig. 1. Molecular structure of Cu(CH$_3$-nso)Br with thermal ellipsoids.

Table 3. Interatomic distances (l/Å) and bond angles (φ/°) with their estimated standard deviations in parentheses

Symmetry code superscript			
None	x	y	z
i	$-x$	$1-y$	$1-z$
ii	$1-x$	$1-y$	$1-z$
iii	x	$y-1$	z
iv	$-x$	$y-1/2$	$1/2-z$
(a) Copper coordination spheres			
Cu$\cdots$Cu^{i}	3.004(2)	Cu–O	1.930(5)
Cu–Br	2.385(1)	Cu–O^{i}	1.929(6)
Cu–S	2.316(2)	Cu–N	2.334(6)
Cu–O–Cu^{i}	102.2(2)	S–Cu–O	84.7(2)
Br–Cu–S	96.2(1)	S–Cu–N	85.4(2)
Br–Cu–O	156.0(1)	S–Cu–O^{i}	162.4(2)
Br–Cu–O^{i}	99.1(2)	O–Cu–O^{i}	77.8(2)
Br–Cu–N	104.5(2)	O–Cu–N	99.5(2)
O^{i}–Cu–N	99.2(2)		
(b) Ligand moiety			
O–C(1)	1.382(13)	C(3)–C(4)	1.524(15)
C(1)–C(2)	1.418(23)	N–C(4)	1.457(11)
S–C(2)	1.818(10)	N–C(5)	1.457(15)
S–C(3)	1.803(8)	N–C(6)	1.467(11)
Cu–O–C(1)	123.1(9)	C(3)–C(4)–N	113.1(6)
Cu^{i}–O–C(1)	133.6(9)	Cu–N–C(4)	108.8(4)
O–C(1)–C(2)	117.1(12)	Cu–N–C(5)	107.7(5)
C(1)–C(2)–S	115.6(7)	Cu–N–C(6)	111.2(5)
C(2)–S–Cu	97.7(4)	C(4)–N–C(5)	108.9(7)
Cu–S–C(3)	98.8(3)	C(4)–N–C(6)	109.0(7)
C(2)–S–C(3)	103.7(4)	C(5)–N–C(6)	111.2(7)
S–C(3)–C(4)	115.0(7)		
(c) Intercluster distances			
Br$\cdots$Cu^{ii}	6.097(3)	Cu$\cdots$Cu^{ii}	7.236(2)
Br$\cdots$Cu^{iv}	6.012(7)	Cu$\cdots$Cu^{iv}	7.098(4)
Cu$\cdots$S^{iv}	5.097(5)		

inversion center. The Cu–S bond length (2.316(2) Å) is almost equal to the sum of the covalent-bond radii (2.32 Å) given by Pauling.[20] This distance is rather short for the copper(II)-thioether sulfur bond length.[21–27] In the present complex the thioether donor atom is placed at the inner coordination position of the tridentate ligand, so that, upon complexation, the coordination of sulfur atom is facilitated by the chelate effect. The Cu–Br bond length (2.385(1) Å) is slightly shorter than the sum of the covalent-bond radii (2.42 Å),[20] but is comparable to those found in bromo [2-(dialkylamino)ethanolato]copper(II) (2.239—2.395 Å).[28–32]

The coordination geometry around the copper ion is intermediate between a trigonal bipyramid and a square pyramid. Viewing the structure as a square pyramid, nitrogen atom occupies the apical position, and Br, S, O, and O^{i} atoms form a basal plane. On the stand point of regarding the coordination geometry as a trigonal bipyramid, Br, O, and N define the equatorial plane of the molecule. Least-squares planes with the deviations of the atoms from the planes are given in Table 4. The degree of distortion of coordination geometry from either of the limiting structures can be estimated by the bond angle Br–Cu–O. For a regular trigonal bipyramid this angle should be 120°, whereas for a square pyramid the angle should be 180°. In this complex this angle is 156.0(1)°, showing that the coordination geometry is slightly close to the latter rather than the former. In square pyramid copper(II)

Table 4. Deviations of the atoms from least-squares planes (l/Å) and dihedral angles between them (φ/°)

(I) Plane through Cu, O, Cu^{i}, O^{i}
$0.2078X+0.5701Y+0.5965Z=6.6813$[a]
[Cu 0.000, O 0.000, Cu^{i} 0.000, O^{i} 0.000, Br -0.967, S -0.072, N 2.282, C(1) 0.204, C(2) 0.061, C(3) 1.596, C(4) 2.653, C(5) 3.002, C(6) 2.608][b]

(II) Plane through Cu, S, O
$0.2247X+0.5886Y+0.5723Z=6.6032$
[Cu 0.000, S 0.000, O 0.000, Br -0.970, N 2.290, C(1) 0.239, C(2) 0.135, C(3) 1.679, C(4) 2.703, C(5) 2.980, C(6) 2.610]

(III) Plane through Cu, S, N
$0.8041X-0.5945Y-0.3934Z=-4.0380$
[Cu 0.000, S 0.000, N 0.000, Br 2.300, O -1.892, C(1) -2.571, C(2) -1.792, C(3) 0.294, C(4) -0.335, C(5) -1.032, C(6) 1.315]

(IV) Plane through Br, O, N
$0.5130X+0.5361Y-0.8346Z=-3.1672$
[Br 0.000, O 0.000, N 0.000, Cu -0.015, S 2.283, O^{i} -1.884, C(1) 1.112, C(2) 2.362, C(3) 2.456, C(4) 1.301, C(5) -1.022, C(6) -0.242]

(V) Plane through Br, S, O, O^{i}
$0.4003X+0.4117Y+0.5246Z=5.5356$
[Br -0.120, S 0.144, O -0.204, O^{i} 0.181, Cu 0.275, N 2.581, C(1) -0.199, C(2) -0.178, C(3) 1.899, C(4) 2.837, C(5) 3.073, C(6) 3.249]

Dihedral angles between the planes (φ/°)			
(I) and (II)	1.8	(II) and (III)	100.1
(I) and (III)	100.2	(II) and (IV)	95.2
(I) and (IV)	96.9	(III) and (IV)	84.3

a) The equation of the plane is expressed as $LX+MY+NZ=D$, where X, Y, and Z are in Å units referred to the crystallographic axes. b) Deviations (l/Å) of atoms from the planes are listed in square brackets. Superscripts are defined as in Table 3.

complexes, the apical bonds are generally longer than basal ones.[33] The Cu–Br, Cu–S, Cu–O, and Cu–O^{i} bond legnths are in the range of those of the normal in-plane coordination, while the Cu–N bond length (2.334(6) Å) is significantly longer than values of a normal in-plane coordination. From these facts the geometry around the copper ion is best described as a distorted square pyramid.

Bond lengths of the ligand have normal values except for the O–C(1) and C(1)–C(2) distances. The O–C(1) (1.382(13) Å) and C(1)–C(2) (1.418(23) Å) bond lengths are shorter than the corresponding O–C and C–C distances observed in other alkoxo-bridged copper(II) complexes, respectively.[28–32,34–37] This is attributable to the large values of anisotropic thermal parameters for C(1). The thermal ellipsoid for C(1) (Fig. 1) gives strong indication of either disorder or large vibration approximately normal to the coordination plane. This is probably due to the strain of two adjacent five-membered chelate rings. The carbon atoms of the ethylene group, C(1) and C(2), are located above the plane through Cu, S, and O by 0.239 and 0.135 Å, respectively. Another five-membered chelate ring, Cu–S–C(3)–C(4)–N, assumes the usual gauche conformation, and C(3) and C(4) deviate from the plane through Cu, S, and N by 0.294 and −0.335 Å, respectively.

The bond angles around the nitrogen atom (Cu-N-C(4) 108.8(4), Cu-N-C(5) 107.7(5), Cu-N-C(6) 111.2(5), C(4)-N-C(5) 108.9(7), C(4)-N-C(6) 109.0(7), C(5)-N-C(6) 111.2(7)°) are close to that for a regular tetrahedron, whereas the bond angles around the sulfur atom (Cu-S-C(2) 97.7(4), Cu-S-C(3) 98.8(3), C(2)–S–C(3) 103.7(4)°) are considerably less than those around the nitrogen atom.

The molecular packing in the unit cell is shown in Fig. 2. As is evident from the packing diagram and the distances between the binuclear clusters (Table 3), the complex consists of discrete dimeric units.

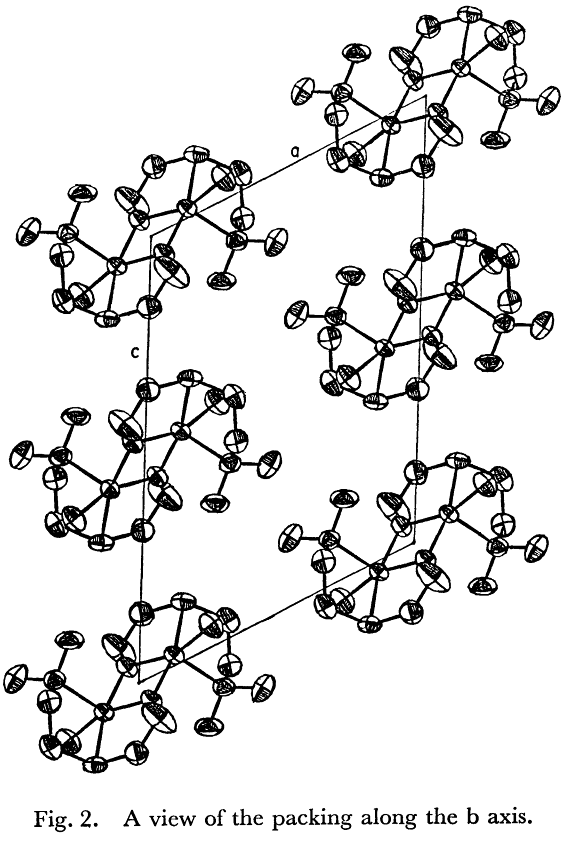


Fig. 2. A view of the packing along the b axis.

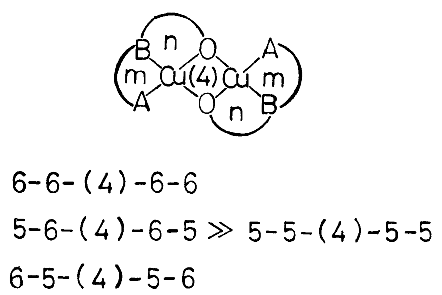


Fig. 3. The fused chelate ring system of alkoxo-bridged copper(II) complexes.

As shown in Fig. 3, the fused chelate ring system of a binuclear copper(II) complex with amino alcohol is expressed with m–n–(4)–n–m. It is known that for the formation of the binuclear copper(II) complexes the favorable chelate ring system is 6–6–(4)–6–6 and 5–6–(4)–6–5 fused chelate ring systems.[38] The binuclear cluster consisting of 6–5–(4)–5–6 fused chelate ring system may be stable in some cases,[37,39] but it often forms a stable tetranuclear cubane structure.[34,40–44] On the other hand, it has been believed that the 5–5–(4)–5–5 fused chelate ring system is unfavorable in forming a binuclear structure, since no stable binuclear copper(II) complex containing such a fused chelate ring system has been isolated so far.[38,45–49] However, the present X-ray crystal structure analysis showed that the binuclear units containing a 5–5–(4)–5–5 fused chelate ring system exist in the crystal. This complex is the first example of such a binuclear copper(II) complex. The moderate stability of the binuclear structure can be ascribed to the "small bond angle" and the "large radius" of the sulfur atom.

Infrared Spectra. The OH stretching vibration band at $\approx$3350 cm^{-1} observed for the free ligands is absent in the spectra of the copper(II) complexes. This indicates that the alcoholic proton is lost upon complexation. In the case of the nitrates, Cu(R-nso)NO$_3$, strong bands appear at 1280—1295, 1375—1410, and 1455—1480 cm^{-1} and a sharp band at 810 cm^{-1}, which are indicative of monodentate nitrate coordination.[50]

Electronic Spectra. The band maxima of the diffuse reflectance spectra and the electronic absorption spectra in 1,2-dichloroethane solutions are given in Table 5. The band around 12.5×10^{3} cm^{-1} is undoubtedly assigned to a d-d transition. Judging from the band shape and position, five-coordinate copper environment is assumed.[51] The infrared spectra of Cu(R-nso)NO$_3$ are consistent with this view. Moreover, the X-ray crystal structure analysis of Cu(CH$_3$-nso)Br confirms the five-coordinate copper(II) dimer. The position of the d-d band does not vary significantly with changing the anion X. The band at 22.3—26.2×

Table 5. Band maxima ($\tilde{\nu}_{max}$) of electronic spectra of Cu(R-nso)X·nH$_2$O

Complex R	X	n	Reflectance spectra $\tilde{\nu}_{max}/10^3$ cm^{-1}			Absorption spectra (in 1,2-dichloroethane) $\tilde{\nu}_{max}/10^3$ cm^{-1} (ε)				
CH_3	Br	0		12.1	22.4	12.2(160)	22.9(1730)	29.6sh(3090)	33.9(4480)	
C_2H_5	Br	0		12.4	22.5	12.8(153)	22.7(1850)	29.6sh(2910)	34.0(4460)	
n-C_3H_7	Br	0		12.2	22.4	13.2(159)	22.6(2090)	29.6sh(2750)	34.0(4260)	
n-C_4H_9	Br	0		12.1	22.3	13.2(142)	22.6(1940)	29.4sh(2600)	34.0(4160)	
CH_3	Cl	0		12.6	23.5	12.4(108)	24.1(1610)	31.4(3410)		37.9(3830)
C_2H_5	Cl	0		12.2	23.8	13.2(102)	23.9(1420)	31.8(2430)		37.7(2950)
n-C_3H_7	Cl	0		12.6	23.5	13.6(137)	23.9(1230)	31.7(2440)		37.7(2900)
n-C_4H_9	Cl	0		12.5	23.8	13.6(96)	23.8(1580)	31.8(3320)		37.6(4070)
CH_3	NO_3	1/2	8.9sh	12.9	26.1sh	13.4(96)	26.2(1020)		32.9(3230)	
C_2H_5	NO_3	1/2	8.7sh	13.0	26.2sh					
n-C_3H_7	NO_3	0	9.1sh	12.8	26.0sh					
n-C_4H_9	NO_3	0	8.7sh	12.8	25.6sh					

a) sh=shoulder.

10^3 cm^{-1} should correspond to the band observed at 24—25×10^3 cm^{-1} for Cu(R-sno)X,[1,7)] and is assigned to the pπ(O)→d(Cu) charge transfer transition. This charge transfer band of Cu(R-nso)X shifts to a lower frequency with the change of X in the order NO$_3$>Cl>Br. Assuming that the nonbonding pπ electron on alkoxide oxygen varies little in energy, the charge transfer band reflects the optical electronegativity of the copper ion. Since optical electronegativity of a metal increases when a donor atom is replaced with a more softer one, the optical electronegativity of the copper ion for Cu(R-nso)X should increase in the order of X=NO$_3$<Cl<Br. The pπ(O)→d(Cu) transition observed for Cu(R-nso)X is compatible with this expectation. The absorption around 30×10^3 cm^{-1} may be assigned to the σ(S)→d(Cu) charge transfer transition.[52—54)] The ultraviolet absorptions (≈34×10^3 cm^{-1}) of Cu(R-nso)Br fall in the range for either the Br→d(Cu) or the σ(N)→d(Cu) transition. The absorption at 38×10^3 cm^{-1} of Cu(R-nso)Cl may be assigned to a superposition of the Cl→d(Cu) and the σ(N)→d(Cu) transitions.[52—56)]

Magnetic Susceptibilities. The magnetic susceptibilities were measured over the temperature range 80—300 K. The magnetic moments per copper atom are subnormal at room temperature and decrease with lowering of temperature, indicating the existence of an antiferromagnetic spin-exchange interaction (Table 6). The temperature dependence of magnetic susceptibility for Cu(n-C$_4$H$_9$-nso)Cl is shown in Fig. 4. The small increase in the magnetic susceptibility at low temperature is most likely due to a small amount of mononuclear paramagnetic impurity. Accordingly, the impurity term was added to the Bleaney-Bowers equation[57)] giving,

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

where χ_A is susceptibility per copper atom, p is the

Table 6. Magnetic data of Cu(R-nso)X·nH$_2$O

Complex R	X	n	μ_{eff}/B.M. (T/K)	
CH_3	Br	0	1.01(294)	0.26(85)
C_2H_5	Br	0	0.84(299)	0.22(83)
n-C_3H_7	Br	0	1.25(294)	0.38(86)
n-C_4H_9	Br	0	1.17(294)	0.19(83)
CH_3	Cl	0	1.16(293)	0.25(82)
C_2H_5	Cl	0	1.07(295)	0.17(83)
n-C_3H_7	Cl	0	1.27(295)	0.66(83)
n-C_4H_9	Cl	0	0.63(297)	0.24(85)
CH_3	NO_3	1/2	1.19(296)	0.45(83)
C_2H_5	NO_3	1/2	1.00(291)	0.35(83)
n-C_3H_7	NO_3	0	1.35(294)	0.52(84)
n-C_4H_9	NO_3	0	1.50(297)	1.06(84)

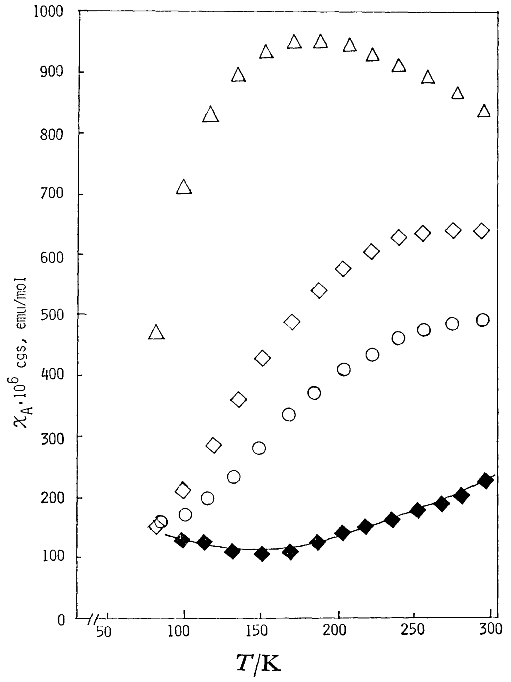


Fig. 4. Temperature dependence of magnetic susceptibilities of Cu(CH$_3$-nso)Br (○), Cu(CH$_3$-nso)Cl (◇), Cu(n-C$_3$H$_7$-nso)NO$_3$ (△), Cu(n-C$_4$H$_9$-nso)Cl (◆). The solid curve was calculated from Eq. 1.

ratio of mononuclear copper(II) ions to total copper(II) ions, and N, g, J, β, and $N\alpha$ have the usual meanings.[58] The $-2J$, g, $N\alpha$, and p values obtained by the best fit of the susceptibility data to Eq. 1 are 735 cm^{-1}, 2.10, 60×10^{-6} cgs emu/mol, and 0.015, respectively. The $-2J$ value, the energy separation between the spin-singlet ground state and the lowest spin-triplet state, is comparable to those of Cu(R-sno)X,[1,7] indicating that a strong antiferromagnetic interaction is operating between the copper(II) ions. However, the temperature dependence of magnetic susceptibilities of Cu(R-nso)X (R=CH_3, C_2H_5, n-C_3H_7, n-C_4H_9; X=Br, Cl, NO_3) except for Cu(n-C_4H_3-nso)Cl can not be interpreted by the equation based on a binuclear structure, in spite of the present X-ray result that Cu(CH_3-nso)Br consists of discrete binuclear clusters. Some of the examples are shown in Fig. 4. Therefore, it seems to be difficult to explain the magnetic behavior only in terms of the crystal structure obtained here. For the reasonable explanation, one should notice the crystal structure is not always independent of temperature. A remarkable variation in the coordination sphere around the copper atom may take place at low temperature, and this may cause the deviation of the χ_A-T curve from the theoretical one.

The authors wish to express sincere thanks to Prof's. Ikuhiko Ueda and Shigeaki Kawano of Kyushu University for their helpful advices and discussions. The present work was partially supported by a Grant-in-Aid for Scientific Research No. 454199 from the Ministry of Education, Science and Culture.

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