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Binuclear Metal Complexes. XXXII [1]. Further Studies of Binuclear Copper(II) Complexes with N-(2-alkylthioethyl)-3-aminopropanol: Synthesis, Spectral and Magnetic Properties and the Crystal Structure

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Binuclear copper(II) complexes with N-(2-alkylthioethyl)-3-aminopropanol, Cu{RS(CH$_2$)$_2$NH(CH$_2$)$_3$O}X (abbreviated as Cu(R-sno)X, where R = alkyl; X^- = BF_4^-, NO_3^-, Cl^-, Br^-), were prepared and characterized by elemental analyses, electronic spectra and magnetic susceptibilities (80–300 K). They exhibit a band around 24 × 10^3 cm^{-1} characteristic of alkoxo-bridged structure and show a very strong antiferromagnetic interaction. However, the cryomagnetic data of Cu(C_2H_5-sno)Cl·H_2O and Cu(C_2H_5-sno)Br·H_2O are unusual and do not obey the equation based on a binuclear structure. The crystal structure of Cu(C_2H_5-sno)Cl·H_2O was determined from three-dimensional X-ray diffractometer data. Crystals are triclinic, space group P$\bar{1}$, *with unit cell dimensions:* a = *8.133(1),* b = *10.459(1),* c = *6.689(1) Å, α = 94.50(1), β = 97.86(1), γ = 81.63(1)°, Z = 1. The structure was solved by the heavy atom method and refined by block-diagonal least-squares method to* R = *0.022 for 1908 independent reflections. The structure consists of alkoxo-bridged binuclear units, $Cu_2(C_2H_5\text{-}sno)_2Cl_2\cdot 2H_2O$. The geometry around the copper ion is an elongated octahedron. Although each binuclear unit is weakly connected with each other by hydrogen bonds, the distances between the binuclear clusters are too long to give rise to an intercluster magnetic interaction. Thus, it is suggested that some structural change takes place at low temperature.*

Introduction

Recently we prepared binuclear copper(II) complexes with N-(2-alkylthioethyl)-3-aminopropanol, Cu{RS(CH$_2$)$_2$NH(CH$_2$)$_3$O}ClO$_4$ (abbreviated as Cu(R-sno)ClO$_4$, where R = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, t-C_4H_9), and studied their spectral and magnetic properties [2]. By comparison of the results with those of binuclear copper(II) complexes with N,N-dialkyldiaminoalcohols, Cu{R$_2$N(CH$_2$)$_2$-NH(CH$_2$)$_3$O}X (abbreviated as Cu(R-nno)X, where R = alkyl, X = anion) [3, 4], we found that the distinct absorption band characteristic of an alkoxo-bridged structure shifts to a lower frequency and antiferromagnetic interaction becomes stronger when the sulfur donor is substituted for the nitrogen donor.

As an extension of this work, we have prepared a number of new binuclear copper(II) complexes, Cu{RS(CH$_2$)$_2$NH(CH$_2$)$_3$O}X (abbreviated as Cu(R-sno)X), changing the counterions X (X^- = BF_4^-, NO_3^-, Cl^-, Br^-), and measured the electronic spectra and temperature dependence of magnetic susceptibilities (80–300 K). Similar to Cu(R-nno)ClO$_4$ [2], they exhibit a band around 24 × 10^3 cm^{-1} characteristic of an alkoxo-bridged structure and show a very strong antiferromagnetic interaction. However, the cryomagnetic data of Cu(C_2H_5-sno)Cl·H_2O and Cu(C_2H_5-sno)Br·H_2O are unusual and do not obey the Bleaney–Bowers equation based on a binuclear structure [5]. In order to elucidate the unusual magnetic behavior of these complexes, we have undertaken a single-crystal X-ray structure analysis of Cu(C_2H_5-sno)Cl·H_2O.

Experimental

Preparation of the Complexes

N-(2-alkylthioethyl)-3-amino-propanol, R-snoH, were prepared by the method previously described [2]. The following is a typical example of the procedure for the preparation of the chlorides, Cu(R-sno)Cl.

Cu(C_2H_5-sno)Cl·H_2O

A solution (5 ml) of C_2H_5-snoH (163 mg) in absolute ethanol was mixed with a solution (5 ml) of copper(II) chloride dihydrate (86 mg) in absolute ethanol. The resulting dark green solution was allowed to stand for several days. Dark green crystals separated were collected and dried *in vacuo* over P_2O_5.

The tetrafluoroborates, nitrates and bromides were prepared by a method similar to that for the chlorides except for using copper(II) tetrafluoroborate hexahydrate, copper(II) nitrate trihydrate and copper(II) bromide, respectively, instead of copper(II) chloride dihydrate.

TABLE I. Analytical Data.

Complex	C (%)	H (%)	N (%)
	found (calcd)	found (calcd)	found (calcd)
$Cu(C_2H_5\text{-sno})BF_4$	26.64 (26.89)	5.43 (5.16)	4.23 (4.48)
$Cu(n\text{-}C_3H_7\text{-sno})BF_4 \cdot 1/2H_2O$	28.34 (28.63)	5.76 (5.71)	4.00 (4.17)
$Cu(i\text{-}C_3H_7\text{-sno})BF_4 \cdot 1/2C_2H_5OH$	30.77 (30.91)	6.09 (6.05)	4.01 (4.01)
$Cu(n\text{-}C_4H_9\text{-sno})BF_4 \cdot H_2O$	30.38 (30.14)	6.10 (6.18)	3.80 (3.90)
$Cu(n\text{-}C_3H_7\text{-sno})NO_3 \cdot C_2H_5OH$	34.02 (34.52)	6.84 (6.95)	8.14 (8.05)
$Cu(i\text{-}C_3H_7\text{-sno})NO_3 \cdot H_2O$	30.23 (30.04)	6.34 (6.30)	8.67 (8.76)
$Cu(t\text{-}C_4H_9\text{-sno})NO_3$	33.90 (34.22)	6.39 (6.38)	8.75 (8.87)
$Cu(C_2H_5\text{-sno})Cl \cdot H_2O$	30.11 (30.10)	6.47 (6.50)	4.96 (5.02)
$Cu(i\text{-}C_3H_7\text{-sno})Cl$	34.88 (34.90)	6.66 (6.59)	5.04 (5.09)
$Cu(t\text{-}C_4H_9\text{-sno})Cl$	37.45 (37.36)	7.05 (6.97)	4.69 (4.84)
$Cu(C_2H_5\text{-sno})Br \cdot H_2O$	26.26 (25.97)	5.60 (5.60)	4.28 (4.33)
$Cu(t\text{-}C_4H_9\text{-sno})Br$	31.97 (32.39)	6.04 (6.04)	4.08 (4.20)

Carbon, hydrogen and nitrogen analyses were carried out at the Service Center of Elemental Analysis, Kyushu University. The result of elemental analyses for the new complexes are listed in Table I.

Physical Measurements

Infrared spectra were measured with a Hitachi Grating Infrared Spectrophotometer Model 215 on a KBr disk. Electronic spectra were measured with a Shimazu 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 [6].

Structure Determination of $Cu(C_2H_5\text{-sno})Cl \cdot H_2O$

Preliminary Weissenberg photographs revealed no systematic absences and showed triclinic symmetry. The unit cell parameters and intensities were measured on a Syntex $P\bar{1}$ automated four-circle diffractometer with Mo-K_α radiation monochromated by a graphite plate (λ = 0.71073 Å). The crystal was ground to a sphere by Bond's method [7] (radius 0.129 mm). The unit cell parameters were determined by the least-squares refinement based on the 15 reflections in the range of $23 < 2\theta < 32°$. The values are a = 8.133(1), b = 10.459(1), c = 6.689(1) Å, α = 94.50(1), β = 97.86(1), γ = 81.63(1)° and V = 556.6(1) Å^3. The density D_m = 1.65 g/cm^3 obtained by flotation in hexane–1,2-dibromoethane solutions agrees well with the density D_c = 1.666 g/cm^3 calculated for one dimer unit per unit cell. Of the two possible triclinic space groups, the centrosymmetric space group $P\bar{1}$ was assumed on the basis of its more frequent occurrence. Successful solution and refinement in this space group support this choice.

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 good stability. A total of 2207 independent reflections with $2\theta < 52°$ were collected. The intensities were corrected for the Lorentz and the polarization effects. Absorption corrections were not applied on account of μr = 0.30 [8]. 1908 independent reflections with $I > 3\sigma(I)$ were considered as 'observed' and were used for the structure analysis, where $\sigma(I)$ was calculated for each reflection on the basis of counting statistics.

The structure was solved by the heavy atom method. The position of the copper atom was 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 $R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0| = 0.039$ and $R_2 = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2} = 0.064$. At this stage, a difference Fourier map revealed all the hydrogen atoms. Further refinement including the hydrogen atoms yielded final values of 0.022 and 0.033 for R_1 and R_2, respectively. In the least-squares refinement the function minimized was $\Sigma w(|F_0| - k|F_c|)^2$, and the weighting scheme was $w = (4.0 + |F_0| + 0.0187|F_0|^2)^{-1}$ [9]. The final shift in the atomic parameters of the nonhydrogen atoms averaged 0.023σ with the maximum of 0.138σ. The final difference Fourier synthesis showed no significant features except one trough of −0.4 e/Å^3 in the vicinity of the copper atom. The atomic scattering factors for Cu, Cl, S, O, N and C_{val} and the anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$ for Cu and S, were taken from the International Tables for X-ray Crystallography [10]. For the hydrogen atom, the scattering factors were adopted from the tables of Stewart *et al.* [11]. All the calculations were carried out on the FACOM M-190 computer in the Computer

TABLE II. Fractional Positional Parameters and Anisotropic Temperature Factors (× 10^4) 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}
Cu	−364.3(3)	1384.9(2)	615.1(4)	63.1(4)	39.0(2)	172(1)	−10.0(2)	−1.9(4)	−19.3(3)
Cl	735(1)	2396(1)	−2607(1)	163(1)	88(1)	111(1)	−13(1)	22(1)	8(1)
S	−2831(1)	2945(1)	860(1)	83(1)	51.6(5)	151(1)	−5.6(5)	20(1)	1(1)
O	1413(2)	−73(1)	1042(2)	57(2)	44(1)	239(4)	−12(1)	2(2)	−24(2)
O(W)	−1757(2)	759(2)	3941(3)	150(3)	96(2)	214(5)	−10(2)	−9(3)	26(2)
N	888(2)	2555(2)	2549(2)	88(3)	46(1)	93(3)	−14(2)	6(2)	−1(2)
C(1)	3112(3)	117(2)	1089(4)	60(3)	58(2)	217(6)	−13(2)	7(3)	−18(3)
C(2)	3607(3)	1108(2)	2746(3)	70(3)	67(2)	162(5)	−24(2)	−12(3)	3(3)
C(3)	2704(3)	2459(2)	2407(3)	86(3)	54(2)	147(5)	−34(2)	1(3)	−11(2)
C(4)	76(3)	3906(2)	2447(3)	125(4)	42(2)	140(5)	−19(2)	1(3)	−19(2)
C(5)	−1737(3)	3984(2)	2723(3)	134(4)	59(2)	151(5)	0(2)	11(4)	−28(3)
C(6)	−3175(3)	3922(2)	−1322(4)	125(4)	69(2)	182(6)	−6(2)	11(4)	27(3)
C(7)	−4272(4)	3316(3)	−3020(4)	143(5)	124(3)	200(6)	−21(3)	−18(4)	26(4)

Center of Kyushu University by the use of the UNICS-II program system [12]. The drawings were made by the use of ORTEP program [13]. A list of observed and calculated structure factors is available from the Editor. The final positional and thermal parameters with their estimated standard deviations are given in Tables II and III.

Results and Discussion

Crystal and Molecular Structure of Cu(C_2H_5-sno)Cl·H_2O

The crystal structure essentially consists of alkoxo-bridged centrosymmetric binuclear units. An ORTEP plot of the structure is shown in Fig. 1 with the numbering system. The coordination geometry around the copper ion is elongated octahedron. The distorted square plane around the copper atom is formed by thioether sulfur atom, amino nitrogen atom and two alkoxo oxygen atoms. The elongated octahedral coordination is achieved by the weak coordinations of chlorine atom and water at the apical positions.

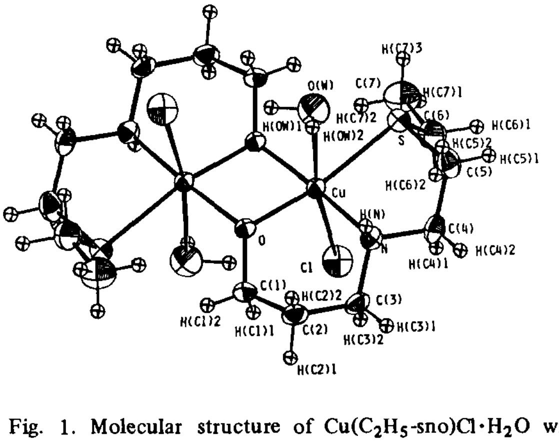

Fig. 1. Molecular structure of Cu(C_2H_5-sno)Cl·H_2O with thermal ellipsoids.

TABLE III. Fractional Positional Parameters (× 10^3) and Isotropic Temperature Factors of Hydrogen Atoms. The average of estimated standard deviations of the isotropic temperature factors is 0.6 Å^2.

Atom	x	y	z	B (Å^2)
H(C1)1	331(3)	48(2)	−18(4)	3.2
H(C1)2	384(3)	−69(2)	134(4)	3.1
H(C2)1	478(4)	115(3)	271(4)	3.8
H(C2)2	348(3)	86(3)	410(4)	3.6
H(C3)1	321(3)	308(2)	332(4)	2.7
H(C3)2	283(3)	271(3)	109(4)	3.1
H(N)	89(3)	226(3)	387(4)	3.1
H(C4)1	28(3)	413(2)	112(4)	3.1
H(C4)2	59(4)	445(3)	335(4)	3.6
H(C5)1	−231(4)	484(3)	271(4)	3.7
H(C5)2	−187(3)	367(3)	395(4)	3.6
H(C6)1	−367(4)	482(3)	−78(4)	4.3
H(C6)2	−220(3)	415(2)	−164(4)	3.0
H(C7)1	−453(4)	380(3)	−408(4)	3.9
H(C7)2	−379(4)	250(3)	−350(4)	4.0
H(C7)3	−523(4)	318(3)	−276(4)	4.8
H(OW)1	−152(4)	−14(3)	357(4)	4.0
H(OW)2	−110(4)	70(3)	480(4)	4.5

The interatomic distances and bond angles with their estimated standard deviations are listed in Table IV. The Cu–S bond length (2.4101(6) Å) is longer than the sum of the covalent-bond radii (2.32 Å) given by Pauling [14]. This Cu–S bond length is long in comparison with those (2.17–2.37 Å) determined for complexes with sulfur-donor ligands other than thioether [15–24]. This fact implies that thioether has relatively low affinity toward copper(II)

TABLE IV. Interatomic Distances (l/Å) and Bond Angles (φ/°) with Their Estimated Standard Deviations in Parentheses.

Symmetry code

Superscript			
None	x	y	z
i	$-x$	$-y$	$-z$
ii	x	y	$1+z$
iii	$-x$	$-y$	$1-z$

(a) Copper coordination spheres

Cu---Cu^{i}	2.9461(5)	Cu–O^{i}	1.919(1)
Cu–Cl	2.7792(8)	Cu–O(W)	2.792(2)
Cu–S	2.4101(6)	Cu–N	1.991(2)
Cu–O	1.952(1)	O---O^{i}	2.511(2)
Cu–O–Cu^{i}	99.11(6)	S–Cu–O(W)	74.04(4)
Cl–Cu–S	97.44(2)	S–Cu–N	87.61(5)
Cl–Cu–O	98.50(5)	O–Cu–O^{i}	80.89(6)
Cl–Cu–O^{i}	94.21(5)	O–Cu–O(W)	90.05(6)
Cl–Cu–N	90.27(6)	O–Cu–N	92.38(6)
Cl–Cu–O(W)	170.88(4)	O(W)–Cu–O^{i}	90.25(7)
S–Cu–O^{i}	97.89(4)	O(W)–Cu–N	86.20(7)

(b) Ligand moiety

O–C(1)	1.420(3)	C(3)–H(C3)1	0.95(2)
C(1)–C(2)	1.511(3)	C(3)–H(C3)2	0.96(3)
C(2)–C(3)	1.514(3)	N–H(N)	0.96(3)
N–C(3)	1.482(3)	C(4)–H(C4)1	0.98(3)
N–C(4)	1.472(3)	C(4)–H(C4)2	0.90(3)
C(4)–C(5)	1.500(4)	C(5)–H(C5)1	0.94(3)
S–C(5)	1.814(2)	C(5)–H(C5)2	0.93(3)
S–C(6)	1.814(3)	C(6)–H(C6)1	1.03(3)
C(6)–C(7)	1.504(4)	C(6)–H(C6)2	0.91(3)
C(1)–H(C1)1	1.00(3)	C(7)–H(C7)1	0.89(3)
C(1)–H(C1)2	0.97(2)	C(7)–H(C7)2	0.94(3)
C(2)–H(C2)1	0.97(3)	C(7)–H(C7)3	0.85(3)
C(2)–H(C2)2	0.98(3)		

Cu–S–C(5)	93.06(8)
Cu–S–C(6)	108.72(8)
Cu–O–C(1)	119.8(1)
Cu^{i}–O–C(1)	124.7(1)
Cu–N–C(3)	115.7(1)
Cu–N–C(4)	111.0(1)
O–C(1)–C(2)	111.5(2)
C(1)–C(2)–C(3)	113.4(2)
N–C(3)–C(2)	112.1(2)
C(3)–N–C(4)	111.0(2)
N–C(4)–C(5)	109.8(2)
S–C(5)–C(4)	111.8(2)
C(5)–S–C(6)	100.8(1)
S–C(6)–C(7)	110.4(2)
O–C(1)–H(C1)1	111.8(15)
O(C1)–H(C1)2	109.9(17)
C(2)–C(1)–H(C1)1	104.6(15)
C(2)–C(1)–H(C1)2	107.8(15)
H(C1)1–C(1)–H(C1)2	111.0(21)
C(1)–C(2)–H(C2)1	106.3(16)
C(1)–C(2)–H(C2)2	112.9(17)
C(3)–C(2)–H(C2)1	106.0(17)

TABLE IV. *(Continued)*

C(3)–C(2)–H(C2)2	109.7(15)
H(C2)1–C(2)–H(C2)2	108.0(23)
C(2)–C(3)–H(C3)1	110.7(14)
C(2)–C(3)–H(C3)2	110.5(15)
N–C(3)–H(C3)1	111.1(16)
N–C(3)–H(C3)2	107.9(15)
H(C3)1–C(3)–H(C3)2	104.2(23)
Cu–N–H(N)	106.3(16)
C(3)–N–H(N)	101.9(16)
C(4)–N–H(N)	110.5(15)
N–C(4)–H(C4)1	102.7(14)
N–C(4)–H(C4)2	112.5(17)
C(5)–C(4)–H(C4)1	115.2(15)
C(5)–C(4)–H(C4)2	110.6(18)
H(C4)1–C(4)–H(C4)2	105.8(25)
C(4)–C(5)–H(C5)1	113.1(19)
C(4)–C(5)–H(C5)2	111.7(16)
S–C(5)–H(C5)1	110.0(16)
S–C(5)–H(C5)2	103.3(17)
H(C5)1–C(5)–H(C5)2	106.3(24)
S–C(6)–H(C6)1	104.0(17)
S–C(6)–H(C6)2	112.5(15)
C(7)–C(6)–H(C6)1	114.8(16)
C(7)–C(6)–H(C6)2	116.6(15)
H(C6)1–C(6)–H(C6)2	97.3(24)
C(6)–C(7)–H(C7)1	112.5(19)
C(6)–C(7)–H(C7)2	113.3(17)
C(6)–C(7)–H(C7)3	116.6(20)
H(C7)1–C(7)–H(C7)2	106.8(25)
H(C7)1–C(7)–H(C7)3	102.8(28)
H(C7)2–C(7)–H(C7)3	103.8(28)

(c) Water molecule

O(W)–H(OW)1	0.95(3)	O(W)–H(OW)2	0.73(3)
H(OW)1–O(W)–H(OW)2	91(3)		

(d) Intercluster distances

Cu---Cl^{ii}	4.5705(9)	O(W)---Cu^{ii}	4.474(2)
Cu---O(W)^{iii}	4.438(2)		

ion [25–33]. The Cu–O bond lengths (1.919(1) and 1.952(1) Å) and the Cu–N bond length (1.991(2) Å) fall in the range of those of the alkoxo-bridged binuclear copper(II) complexes [34–40]. The two apical bond lengths, Cu–O(W) and Cu–Cl are 2.792(2) and 2.7792(8) Å, respectively. The central four-membered Cu_2O_2 ring is exactly planar, because the copper and oxygen atoms are related by an inversion center. The Cu–Cu^{i} distance (2.9461(5) Å) is the shortest among those of alkoxo-bridged binuclear copper(II) complexes so far reported [34–40]. The Cu–O–Cu^{i} angle (99.11(6)°) is almost equal to that for the binuclear complex with the diamino-alcohol, $Cu(C_2H_5\text{-nno})ClO_4 \cdot 1/2H_2O$ (99.4°) [39].

Bond lengths of the ligand have normal values [41]. It is interesting to compare the geometries around the sulfur and the nitrogen atoms. The nitrogen atom is tetrahedrally bonded (Cu–N–C(3) 115.7(1), Cu–N–C(4) 111.0(1), C(3)–N–C(4) 111.0 (2)°), indicating that the bonds are formed by the sp^3 hybridized orbitals. On the other hand, the sulfur atom assumes a trigonal pyramidal arrangement with Cu, C(5) and C(6) (Cu–S–C(5) 93.06(8), Cu–S–C (6) 108.72(8), C(5)–S–C(6) 100.8(1)°).

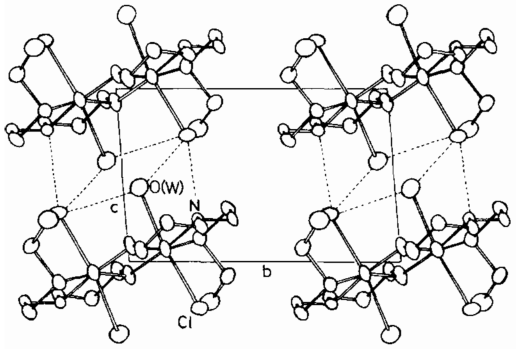

Fig. 2. Projection of the unit cell on the bc plane. The hydrogen bonds are represented by broken lines.

The molecular packing in the unit cell is shown in Fig. 2. As shown in Fig. 2, there are hydrogen bonds between the chlorine atoms and the water molecules or the amino groups. Hydrogen bonds are listed in Table V. Thus, each binuclear unit, $Cu_2(C_2H_5\text{-sno})_2Cl_2(H_2O)_2$, is weakly connected with two of its neighbors by hydrogen bonds, so that a one-dimensional infinite chain is formed (Cu---Cl^{ii} 4.5705(9), Cu---$O(W)^{iii}$ 4.438(2), O(W)---Cu^{ii} 4.474(2) Å).

TABLE V. Hydrogen-bond Distances (l/Å) and Angles (φ/°) with Their Estimated Standard Deviations in Parentheses.

Symmetry Code

Superscript			
None	x	y	z
i	$-x$	$-y$	$-z$
ii	x	y	$1+z$
iii	$-x$	$-y$	$1-z$

D–H---A	D---A	H---A	∠D–H---A
O(W)–H(OW)1---Cl^{i}	3.364(2)	2.42(3)	176.6(26)
O(W)–H(OW)2---Cl^{ii}	3.389(2)	2.82(3)	136.6(27)
N–H(N)---Cl^{ii}	3.277(2)	2.37(3)	157.6(21)
O(W)–H(OW)2---$O(W)^{iii}$	3.258(3)	2.66(3)	141.0(27)
N–H(N)---O(W)	3.320(3)	2.85(3)	111.5(18)

Electronic Spectra

The band maxima of the diffuse reflectance and absorption spectra of the present complexes are listed in Table VI. In both spectra, a distinct absorption band is observed in the near-ultraviolet region (24–25 × 10^3 cm^{-1}). The frequency of the band for the present complexes is a little lower than that for Cu(R-nno)X [3, 4]. The similar trend was observed for $Cu(R\text{-sno})ClO_4$ [2]. These facts indicate that the copper atoms of Cu(R-sno)X are higher in "optical electronegativity" than those of Cu(R-nno)X [2]. In the ultraviolet region, a peak at 30–33 × 10^3 cm^{-1} and a shoulder at 37 × 10^3 cm^{-1} were observed, which can be assigned to the $\sigma(S) \rightarrow d_{x^2-y^2}(Cu)$ transition and the $\sigma(N) \rightarrow d_{x^2-y^2}(Cu)$ transition, respectively [2].

Magnetic Susceptibilities

The magnetic moments of the complexes except for $Cu(C_2H_5\text{-sno})Cl \cdot H_2O$ and $Cu(C_2H_5\text{-sno})Br \cdot H_2O$ are very low at room temperature, indicating the existence of a very strong antiferromagnetic interaction in these complexes. Their cryomagnetic data may be accounted for by the Bleaney–Bowers equation for an isotropic exchange interaction in a copper(II) dimer [5]

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

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 VII were evaluated from the best fit of their cryomagnetic data to the Bleaney–Bowers equation. The $-2J$ values, the energy separations between the spin-singlet ground states and the spin-triplet excited state, for these complexes are generally larger than those determined for the series of binuclear complexes, Cu(R-nno)X. Therefore, antiferromagnetic interaction seems to become stronger upon substitution of the sulfur donor for the nitrogen donor [2].

In the case of $Cu(C_2H_5\text{-sno})Cl \cdot H_2O$ and $Cu(C_2H_5\text{-sno})Br \cdot H_2O$, the magnetic moments are subnormal at room temperature. However, the cryomagnetic data cannot be interpreted by the Bleaney–Bowers equation (Fig. 3). The present X-ray crystal structure analysis of $Cu(C_2H_5\text{-sno})Cl \cdot H_2O$ showed that binuclear clusters are weakly connected with each other by hydrogen bonds. Although antiferromagnetic interaction through hydrogen bonding has been found in a few copper(II) complexes [42–44], in the present complexes the distances between the binuclear clusters seem to be too long to give rise to such an intercluster magnetic interaction. Thus, it seems to be difficult to explain the magnetic behavior only in terms of the interaction via hydrogen bonding. As a reasonable explanation, some change of the crystal structure may take place at low temperature, so that temperature dependence of magnetic susceptibilities deviates from the binuclear model.

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

Complex	Reflectance Spectra $\tilde{\nu}_{max}/10^3$ cm^{-1}		Absorption Spectra (in methanol) $\tilde{\nu}_{max}/10^3$ cm^{-1} (ϵ)				
Cu(C_2H_5-sno)BF_4	16.8	25.1	16.7(152)	24.9(2310)		33.2(4030)	37.3sh(2530)
Cu(n-C_3H_7-sno)$BF_4 \cdot 1/2H_2O$	16.9	24.8	16.7(153)	24.8(2460)		33.1(4280)	37.5sh(2630)
Cu(i-C_3H_7-sno)$BF_4 \cdot 1/2C_2H_5OH$	17.3	25.1	16.7(179)	24.7(2400)	30.1sh(3120)	33.2(4090)	37.5sh(2650)
Cu(n-C_4H_9-sno)$BF_4 \cdot H_2O$	16.8	24.8	16.9(171)	24.8(2600)		33.0(4560)	37.3sh(2830)
Cu(n-C_3H_7-sno)$NO_3 \cdot C_2H_5OH$	16.2	24.5	16.8(165)	24.8(2560)		33.1(4630)	37.2sh(2900)
Cu(i-C_3H_7-sno)$NO_3 \cdot H_2O$	16.8	24.8	16.8(180)	24.7(2460)	29.8sh(3040)	33.2(4290)	37.0sh(2880)
Cu(t-C_4H_9-sno)NO_3	14.7	23.9	16.7(203)	24.1(1290)	29.7(4460)	33.9(3770)	36.5sh(2980)
Cu(C_2H_5-sno)Cl$\cdot H_2O$	15.3	24.0	16.3(175)	24.8(2320)		33.1(4440)	37.3sh(2830)
Cu(i-C_3H_7-sno)Cl	13.2	25.2	16.3(193)	24.7(2230)	30.3(3650)	33.3(4230)	36.5sh(3050)
Cu(t-C_4H_9-sno)Cl	12.7	26.3	15.9(199)	23.8(975)	29.7(4570)	33.8(3630)	
Cu(C_2H_5-sno)Br$\cdot H_2O$	15.7	23.9	16.2(169)	24.5(2270)		33.2(4270)	
Cu(t-C_4H_9-sno)Br	13.3	24.6	15.9(202)	23.7(1030)	29.6(4240)	33.7(3550)	

TABLE VII. Magnetic Data.[a]

Complex	μ_{eff}/B.M. (T/K)	$-2J$/cm^{-1}	$N\alpha/10^{-6}$ cgs, emu
Cu(C_2H_5-sno)BF_4	0.35(296)	970	56
Cu(n-C_3H_7-sno)$BF_4 \cdot 1/2H_2O$	0.41(294)	895	50
Cu(i-C_3H_7-sno)$BF_4 \cdot 1/2C_2H_5OH$	0.23(293)	1120	50
Cu(n-C_4H_9-sno)$BF_4 \cdot H_2O$	0.40(296)	990	46
Cu(n-C_3H_7-sno)$NO_3 \cdot C_2H_5OH$	0.52(296)	880	66
Cu(i-C_3H_7-sno)$NO_3 \cdot H_2O$	0.50(296)	835	46
Cu(t-C_4H_9-sno)NO_3	0.68(297)	680	60
Cu(C_2H_5-sno)Cl$\cdot H_2O$	1.14(295)	–	–
Cu(i-C_3H_7-sno)Cl	0.53(297)	780	38
Cu(t-C_4H_9-sno)Cl	0.54(294)	770	50
Cu(C_2H_5-sno)Br$\cdot H_2O$	0.92(293)	–	–
Cu(t-C_4H_9-sno)Br	0.35(295)	1020	51

[a] For all the complexes $g = 2.10$ was assumed except for Cu(t-C_4H_9-2·3-sno)Cl ($g = 2.15$).

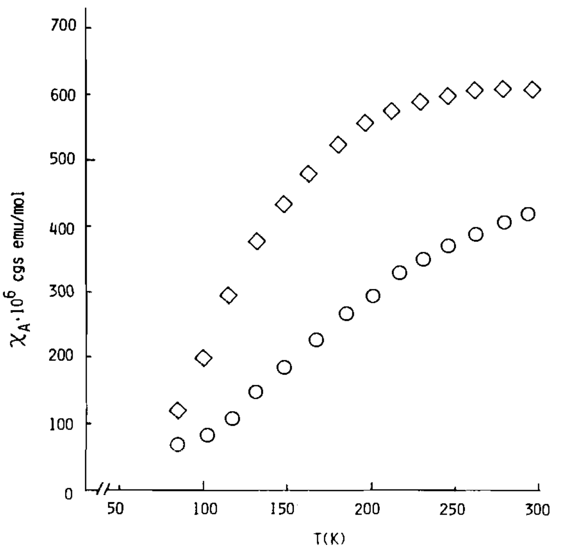

Fig. 3. Temperature dependence of magnetic susceptibilities of Cu(C_2H_5-sno)Cl$\cdot H_2O$ (◇) and Cu(C_2H_5-sno)Br$\cdot H_2O$ (○).

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