Binuclear Metal Complexes. XLIV.[1] Crystal Structures and Magnetic Properties of Alkoxo-oxygen Bridged Binuclear Copper(II) Complexes with 2-[2-(Dialkylamino)ethylthio]ethanol

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Six binuclear copper(II) complexes with 2-[2-(dialkylamino)ethylthio]ethanol, $Cu_2\{R_2N(CH_2)_2S(CH_2)_2O\}_2X_2$ (abbreviated as Cu(R-nso)X, where R=CH_3, C_2H_5, n-C_3H_7, n-C_4H_9; X=Cl, Br), were characterized by magnetic susceptibility (80—300 K). The temperature dependence of the magnetic susceptibilities of Cu(C_2H_5-nso)Cl and Cu(n-C_4H_9-nso)Cl can be interpreted by the Bleaney-Bowers equation based on a binuclear structure, while the magnetic data of the other complexes do not obey the Bleaney-Bowers equation. X-Ray structure analyses have revealed that the structures of all the complexes consist of discrete alkoxo-bridged binuclear units, and the coordination geometry of each copper atom is a distorted square pyramid with two oxygen, one sulfur and one chlorine or bromine atoms in the basal plane and a nitrogen atom in the apical position. The major structural difference corresponding to the different magnetic behaviors was attributed to the conformations of the chelate ring Cu–O–C(1)–C(2)–S.

In the preceding paper, we reported the synthesis, structure, spectra and magnetic properties of binuclear copper(II) complexes with 2-[2-(dialkylamino)ethylthio]ethanol, $Cu_2\{R_2N(CH_2)_2S(CH_2)_2O\}_2X_2$ (abbreviated as Cu(R-nso)X, where R=CH_3, C_2H_5, n-C_3H_7, n-C_4H_9; X=Cl, Br).[2] The X-ray structure analysis of Cu(CH_3-nso)Br showed that the crystal consists of discrete binuclear units. However, the temperature dependence of the magnetic susceptibility of Cu(CH_3-nso)Br does not obey the Bleaney-Bowers equation[3] based on a binuclear structure. Similar behaviors were also observed for other Cu(R-nso)X complexes so far prepared except for Cu(n-C_4H_9-nso)Cl. In order to clarify the origin of their unusual magnetic property, it is desirable to compare the detailed structures for a series of this type of complexes in relation to their magnetic behaviors. Hence, in this study, we have undertaken single-crystal X-ray structure analyses for Cu(CH_3-nso)Cl, Cu(C_2H_5-nso)Cl, Cu(n-C_3H_7-nso)Cl, Cu(n-C_4H_9-nso)Cl, Cu(n-C_3H_7-nso)Br and Cu(n-C_4H_9-nso)Br.

Experimental

Crystals of Cu(R-nso)Cl (R=CH_3, C_2H_5, n-C_3H_7, n-C_4H_9) and Cu(R-nso)Br (R=n-C_3H_7, n-C_4H_9) were prepared by the method previously reported.[2] The diffraction data were measured on a Rigaku AFC-5 automated four-circle diffractometer with graphite-monocchromated Mo $K\alpha$ radiation (λ=0.71069 Å) at 20±0.5 °C. The unit-cell parameters of each crystal were determined by the least-squares refinement based on 20 high-angle reflections. The crystal data are shown in Table 1. The intensity data were collected by the 2θ-ω scan technique with a scan rate of 8° min^{-1}. For weak reflections the peak scan was repeated up to four times depending on their intensities. Three standard reflections were monitored every 100 reflections, and their intensities showed a good stability. The intensity data were corrected for the Lorentz and the polarization effects, but not for absorption.

The structures were solved by the heavy-atom method. The positions of the copper atoms were obtained from three-dimensional Patterson syntheses. Successive Fourier syntheses revealed all the nonhydrogen atoms. Refinement was

TABLE 1. CRYSTAL DATA AND EXPERIMENTAL DETAILS

Complex	Cu(CH_3-nso)Cl	Cu(C_2H_5-nso)Cl	Cu(n-C_3H_7-nso)Cl	Cu(n-C_4H_9-nso)Cl	Cu(n-C_3H_7-nso)Br	Cu(n-C_4H_9-nso)Br
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/a$	$P2_1/a$	$P2_1/a$	$P2_1/a$
a/Å	7.677(1)	8.694(2)	17.829(3)	15.109(2)	17.765(2)	10.284(1)
b/Å	9.131(1)	9.879(2)	10.322(2)	9.915(1)	10.363(1)	19.806(3)
c/Å	7.564(1)	7.591(2)	7.639(1)	11.529(1)	7.831(1)	7.955(1)
α/°	99.68(1)	94.03(2)				
β/°	96.87(1)	114.59(2)	102.73(1)	109.70(1)	102.71(1)	96.76(1)
γ/°	71.79(1)	83.61(2)				
D_m/g cm^{-3}	1.65	1.55	1.46	1.35	1.63	1.55
D_c/g cm^{-3}	1.66	1.55	1.47	1.35	1.64	1.55
Z	1	1	2	2	2	2
μ (Mo $K\alpha$)/cm^{-1}	26.2	22.1	19.2	16.2	44.9	39.3
Crystal size/mm^3	0.27×0.35×0.48	0.20×0.20×0.25	0.17×0.24×0.30	0.17×0.30×0.35	0.17×0.25×0.33	0.15×0.15×0.20
$2\theta_{max}$/°	50	51	50	55	50	52
No. of unique reflections ($F_o>3\sigma(F_o)$)	1677	1957	1831	2946	1920	2330

carried out by the block-diagonal least-squares method. All the hydrogen atoms were located from the subsequent difference Fourier maps. The final R values were $R_1=\sum||F_o|-|F_c||/\sum|F_o|=0.033$, $R_2=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}=0.048$ for Cu(CH_3-nso)Cl, $R_1=0.049$, $R_2=0.065$ for Cu(C_2H_5-nso)Cl, $R_1=0.043$, $R_2=0.063$ for Cu(n-C_3H_7-nso)Cl, $R_1=0.036$, $R_2=0.054$ for Cu(n-C_4H_9-nso)Cl, $R_1=0.056$, $R_2=0.074$ for Cu(n-C_3H_7-nso)Br and $R_1=0.045$, $R_2=0.070$ for Cu(n-C_4H_9-nso)Br. In the least-squares refinement, the function minimized was $\sum w(|F_o|-k|F_c|)^2$, and the weighting schemes[4] were $w=(2.0+|F_o|+0.018\ |F_o|^2)^{-1}$ for Cu(CH_3-nso)Cl, $(4.0+|F_o|+0.016\ |F_o|^2)^{-1}$ for Cu(C_2H_5-nso)Cl, $(8.0+|F_o|+0.012\ |F_o|^2)^{-1}$ for Cu(n-C_3H_7-nso)Cl, $(6.0+|F_o|+0.010\ |F_o|^2)^{-1}$ for Cu(n-C_4H_9-nso)Cl, $(10.0+|F_o|+0.010\ |F_o|^2)^{-1}$ for Cu(n-C_3H_7-nso)Br and $(10.0+|F_o|+0.009\ |F_o|^2)^{-1}$ for Cu(n-C_4H_9-nso)Br. Final difference Fourier syntheses were featureless.

The atomic scattering factors for Br, Cu, Cl, S, O, N, and C_{val} and the anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$ for Br, Cu, Cl, and S, were taken from the International Tables for X-Ray Crystallography.[5] For the hydrogen atom, the scattering factors were adopted from the Tables of Stewart *et al.*[6] All the calculations were carried out on the FACOM

Table 2. Fractional positional parameters ($\times 10^4$) and thermal parameters of non-hydrogen atoms with their estimated standard deviations in parentheses

Atom	x	y	z	B_{eq}/Å^2
(1) Cu(CH_3-nso)Cl				
Cu	1823.2(4)	−1223.3(4)	129.3(4)	2.4
Cl	3483(1)	−2487(1)	2345(1)	3.9
S	4297(1)	−1435(1)	−1531(1)	2.8
O	519(3)	464(3)	−1206(3)	3.7
N	1324(3)	−3253(3)	−2042(4)	3.1
C(1)	1220(7)	860(7)	−2492(9)	8.2
C(2)	3122(5)	84(4)	−2892(5)	3.5
C(3)	4287(4)	−3219(4)	−3013(5)	3.3
C(4)	2388(5)	−3371(4)	−3570(4)	3.5
C(5)	1930(6)	−4724(4)	−1290(6)	4.7
C(6)	−644(5)	−2875(5)	−2640(6)	5.2
(2) Cu(C_2H_5-nso)Cl				
Cu	342(1)	1468(1)	34(1)	2.7
Cl	660(2)	2730(1)	−2094(2)	4.7
S	2140(1)	2614(1)	2794(2)	3.4
O	896(4)	−56(3)	1717(4)	3.7
N	−1916(5)	2679(4)	754(6)	3.4
C(1)	1590(8)	94(5)	3709(7)	4.7
C(2)	2726(7)	1208(5)	4440(7)	4.8
C(3)	590(6)	3691(5)	3360(7)	3.7
C(4)	−1082(6)	3087(5)	2829(7)	4.1
C(5)	−2709(7)	3893(6)	−394(9)	5.0
C(6)	−3663(9)	3609(8)	−2544(10)	6.9
C(7)	−3101(7)	1634(6)	516(9)	4.8
C(8)	−4548(8)	2082(8)	1135(13)	7.1
(3) Cu(n-C_3H_7-nso)Cl				
Cu	−154.4(3)	1419(1)	−307(1)	3.0
Cl	−260(1)	2766(1)	−2642(2)	4.5
S	−958(1)	2624(1)	1099(2)	3.6
O	−417(2)	−3(3)	1075(5)	3.9
N	883(2)	2401(4)	1987(5)	2.8
C(1)	−625(4)	212(6)	2662(8)	4.4
C(2)	−1128(3)	1369(6)	2630(8)	4.2
C(3)	−253(3)	3673(5)	2467(8)	4.0
C(4)	510(3)	3041(5)	3299(7)	3.7
C(5)	1268(3)	3390(5)	1071(7)	3.5
C(6)	1734(3)	2838(6)	−185(8)	4.1
C(7)	2008(4)	3908(7)	−1257(9)	5.3
C(8)	1418(3)	1407(5)	2894(7)	3.3
C(9)	2087(3)	1886(6)	4348(8)	4.8
C(10)	2587(4)	831(8)	5279(10)	6.0
(4) Cu(n-C_4H_9-nso)Cl				
Cu	−128.7(2)	1513.2(3)	106.2(3)	2.8
Cl	−1334(1)	2782(1)	153(1)	4.2
S	1067(1)	2905(1)	1361(1)	3.6
O	816(1)	119(2)	544(2)	3.7
N	178(2)	2682(2)	−1591(3)	3.3
C(1)	1777(2)	405(3)	1085(4)	3.8
C(2)	1902(3)	1558(3)	1981(4)	4.4
C(3)	1479(2)	3624(3)	183(3)	3.8
C(4)	689(2)	3896(3)	−1000(3)	3.6
C(5)	752(3)	1888(4)	−2157(4)	4.1
C(6)	297(3)	563(4)	−2732(4)	4.7
C(7)	982(4)	−337(5)	−3091(5)	6.7
C(8)	518(6)	−1664(5)	−3648(5)	8.6
C(9)	−742(2)	3075(4)	−2497(3)	4.0
C(10)	−726(3)	4025(4)	−3533(3)	4.7
C(11)	−1704(4)	4433(5)	−4344(4)	6.4
C(12)	−1710(5)	5486(6)	−5290(6)	9.5
(5) Cu(n-C_3H_7-nso)Br				
Br	−315(1)	2811(1)	−2763(1)	4.2
Cu	−160(1)	1408(1)	−302(1)	2.7
S	−969(1)	2594(2)	1046(2)	3.5
O	−420(3)	−26(5)	1052(6)	3.3
N	874(3)	2383(5)	1897(7)	2.8
C(1)	−617(5)	221(8)	2658(9)	3.9
C(2)	−1141(5)	1348(8)	2541(11)	3.9
C(3)	−275(5)	3650(7)	2382(10)	3.8
C(4)	500(4)	3024(7)	3186(9)	3.4
C(5)	1406(4)	1382(7)	2800(9)	3.3
C(6)	2070(5)	1805(9)	4246(11)	4.6
C(7)	2539(6)	720(11)	5176(13)	5.9
C(8)	1272(4)	3353(7)	1046(9)	3.3
C(9)	1735(5)	2784(8)	−196(11)	4.1
C(10)	1995(6)	3838(12)	−1276(13)	5.8
(6) Cu(n-C_4H_9-nso)Br				
Br	2814(1)	332.4(4)	−2180(1)	4.4
Cu	1426(1)	155.4(4)	−11(1)	2.7
S	2609(2)	859(1)	1927(2)	3.6
O	−42(4)	364(2)	1258(5)	3.2
N	2400(4)	−754(2)	1756(6)	2.8
C(1)	205(6)	518(4)	2979(7)	3.5
C(2)	1337(6)	1005(4)	3288(8)	4.0
C(3)	3689(6)	229(3)	3044(9)	4.1
C(4)	3048(6)	−439(3)	3318(8)	3.8
C(5)	3394(6)	−1094(3)	870(8)	3.6
C(6)	2838(7)	−1476(4)	−728(8)	4.3
C(7)	3867(8)	−1718(4)	−1792(9)	4.9
C(8)	4803(10)	−2212(5)	−943(12)	6.8
C(9)	1343(6)	−1210(3)	2157(8)	3.4
C(10)	1757(7)	−1836(4)	3207(10)	4.5
C(11)	593(8)	−2221(4)	3729(10)	4.8
C(12)	966(10)	−2891(4)	4552(11)	6.0

M-200 computer in the Computer Center of Kyushu University by the use of a local version[7] of the UNICS-II[8] and the ORTEP[9] programs. The final positional and thermal parameters with their estimated standard deviations are given in Table 2. The coordinates and isotropic temperature factors of the hydrogen atoms, the anisotropic thermal parameters of the nonhydrogen atoms, and the F_o-F_c tables have been deposited as a Document No. 8213 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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 $[Ni(en)_2]S_2O_3$.[10] All the susceptibilities were corrected for the diamagnetism of the constituting atoms by the use of Pascal's constants.[11]

Description of the Structures and Discussion

The molecular structures of Cu(n-C_4H_9-nso)Cl and Cu(n-C_4H_9-nso)Br are shown in Figs 1 and 2, respectively. Selected bond lengths and bond angles are listed in Table 3.

The structures of all the complexes studied here are similar to that of Cu(CH_3-nso)Br[2] and consist of alkoxo-bridged binuclear units each of which has a center of symmetry. The coordination around each copper atom is essentially a distorted square pyramid with two alkoxo oxygen, a thioether sulfur and a chlorine or a bromine atoms in the basal plane and an amino nitrogen atom in the apical position. As can be seen in Table 3, the Cu–O and the Cu–O^i bond lengths fall in the range of 1.925—1.957 Å and 1.930—1.945 Å, respectively, and there was no definite relationship between these bond distances and the alkyl substituents, R, or the anions, X. The Cu–X distances (X=Cl or Br) are not much affected by the alkyl substituents and fall in the ranges, 2.229—2.236 Å for Cu(R-nso)Cl and 2.381—2.391 Å for Cu(R-nso)Br. These distances are comparable to the values found in chloro- or bromo[2-(dialkylamino)ethanolato]copper(II) (2.220—2.240 Å for the chloro complexes[12] and 2.333—2.395 Å for the bromo complexes[13]). The Cu–S distances fall in the ranges, 2.330—2.3446 Å for Cu(R-nso)Cl and 2.314—2.316 Å for Cu(R-nso)Br. It is to be noted that the Cu–S distances of Cu(R-nso)Cl are longer than those of Cu(R-nso)Br by 0.02 Å on the average. Since the Cu–S distance of Cu(CH_3-nso)NCS is 2.361(3) Å,[14] the Cu–S bond length decreases in the order Cu(R-nso)NCS>Cu(R-nso)Cl>Cu(R-nso)Br. The observed trend seems to accord with the

TABLE 3. SELECTED INTERATOMIC DISTANCES (l/Å) AND BOND ANGLES (ϕ/°) OF Cu(R-nso)X

Complex	Cu(CH_3-nso)Cl	Cu(C_2H_5-nso)Cl	Cu(n-C_3H_7-nso)Cl	Cu(n-C_4H_9-nso)Cl	Cu(n-C_3H_7-nso)Br	Cu(n-C_4H_9-nso)Br
Cu···Cu	2.9955(6)	3.0181(9)	2.999(1)	3.0463(5)	2.992(1)	2.998(1)
Cu–O	1.927(2)	1.931(3)	1.925(4)	1.927(2)	1.940(5)	1.957(4)
Cu–O^{i} [a]	1.939(2)	1.937(3)	1.945(4)	1.933(2)	1.930(5)	1.933(4)
Cu–S	2.341(1)	2.334(1)	2.330(2)	2.3446(8)	2.315(2)	2.314(2)
Cu–N	2.356(3)	2.421(4)	2.468(3)	2.448(3)	2.443(5)	2.428(5)
Cu–X[b]	2.233(1)	2.229(2)	2.236(2)	2.229(1)	2.381(1)	2.391(1)
O–C(1)	1.316(8)	1.379(5)	1.362(8)	1.403(3)	1.402(10)	1.396(7)
C(1)–C(2)	1.454(6)	1.481(8)	1.490(8)	1.510(5)	1.483(11)	1.509(9)
S–C(2)	1.809(4)	1.819(6)	1.814(6)	1.810(3)	1.814(9)	1.816(7)
S–C(3)	1.817(4)	1.798(6)	1.807(5)	1.820(4)	1.801(8)	1.829(7)
C(3)–C(4)	1.511(5)	1.517(8)	1.516(7)	1.504(4)	1.526(11)	1.507(10)
N–C(4)	1.464(5)	1.482(6)	1.476(7)	1.469(4)	1.483(10)	1.477(8)
Cu–O–Cu^{i}	101.6(1)	102.6(1)	101.6(2)	104.22(9)	101.3(3)	100.9(2)
O–Cu–O^{i}	78.4(1)	77.4(1)	78.4(2)	75.78(8)	78.7(2)	79.1(2)
O–Cu–S	84.72(8)	85.00(9)	84.6(1)	84.95(6)	84.9(2)	84.6(1)
S–Cu–X	96.62(3)	95.90(6)	94.78(6)	96.82(3)	94.14(6)	94.63(5)
O^{i}–Cu–X	98.00(8)	99.2(1)	100.6(1)	98.38(7)	100.5(1)	100.0(1)
O–Cu–N	96.9(1)	99.5(2)	99.1(1)	103.1(1)	99.5(2)	98.5(2)
O^{i}–Cu–N	100.7(1)	99.8(1)	99.3(1)	107.9(1)	98.7(2)	97.5(2)
S–Cu–N	84.94(8)	84.66(9)	83.9(1)	84.32(6)	84.6(2)	85.0(1)
X–Cu–N	102.87(7)	105.8(1)	103.3(1)	97.40(7)	104.7(1)	106.6(1)
Cu–O–C(1)	123.7(2)	122.4(3)	120.7(3)	122.4(2)	119.1(4)	119.3(3)
Cu^{i}–O–C(1)	134.7(3)	132.5(3)	130.9(3)	133.0(2)	131.6(4)	131.1(4)
O–C(1)–C(2)	120.2(5)	113.2(5)	113.4(5)	109.2(3)	111.5(6)	110.3(5)
C(1)–C(2)–S	113.8(2)	114.0(3)	113.4(5)	112.3(2)	114.1(6)	113.4(5)
Cu–S–C(2)	97.4(1)	97.0(2)	97.1(2)	95.7(1)	97.2(3)	97.7(2)
Cu–S–C(3)	98.3(1)	99.8(1)	99.6(2)	99.0(1)	99.9(3)	98.9(2)
C(2)–S–C(3)	103.8(2)	104.2(3)	104.4(3)	102.4(2)	104.4(4)	104.9(3)
S–C(3)–C(4)	114.0(2)	114.9(3)	115.4(4)	112.4(3)	115.0(5)	114.7(4)
C(3)–C(4)–N	113.2(3)	113.4(5)	113.9(4)	114.0(2)	114.1(6)	114.3(5)
Cu–N–C(4)	107.6(2)	104.6(3)	106.6(3)	103.2(2)	106.6(4)	106.8(4)

a) Superscript (i) refers to the equivalent position ($-x$, $-y$, $-z$). b) X denotes Cl or Br atom.

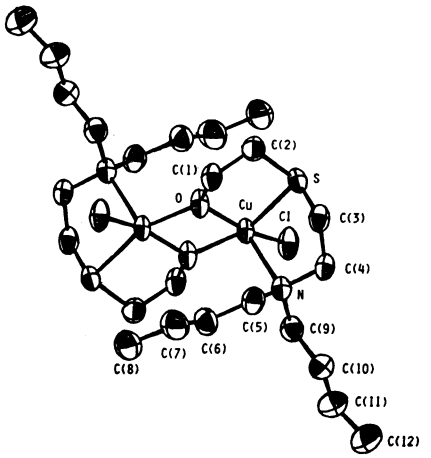

Fig. 1. Molecular Structure of Cu(n-C_4H_9-nso)Cl. Thermal ellipsoids are drawn at 50% probability level.

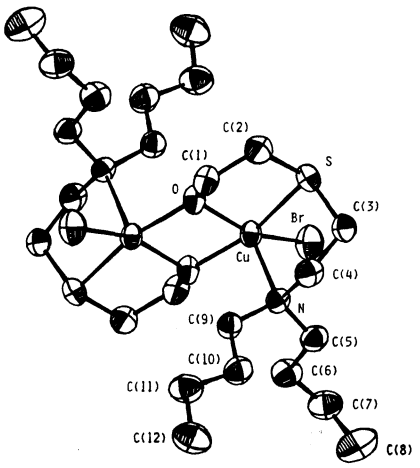

Fig. 2. Molecular Structure of Cu(n-C_4H_9-nso)Br. Thermal ellipsoids are drawn at 50% probability level.

softness of the anion X. It is known that Cu(I)–S bond length is shorter than Cu(II)–S bond length when S is a thioether sulfur.[15] Therefore, our results may be interpreted in the following way: when a donor atom is replaced with softer one, the softness of the copper ion would increase and, consequently, the Cu–S bond would become to be more covalent and shortened. The axial Cu–N bond distances increases in the order Cu(CH_3-nso)X < Cu(C_2H_5-nso)X < Cu(n-C_4H_9-nso)X < Cu(n-C_3H_7-nso)X.

The five-membered chelate ring, Cu–O–C(1)–C(2)–S, assumes two types of conformation. One is the gauche conformation as is usually observed for saturated five-membered chelate rings, *i.e.*, C(1) and C(2) are located below and above the plane defined by Cu, S, and O, respectively. The other is the envelope conformation *i.e.*, both carbon atoms, C(1) and C(2) are placed in the same side of the Cu–S–O plane (Table 4).[16] The chelate ring of Cu(n-C_4H_9-nso)Cl assumes the former conformation and the latter is observed for Cu(CH_3-nso)Cl, Cu(n-C_3H_7-nso)Cl, Cu(CH_3-nso)Br, Cu(n-C_3H_7-nso)Br and Cu(n-C_4H_9-nso)Br. As for Cu(C_2H_5-nso)Cl, the chelate ring is intermediate between the envelope and the gauche conformations. The other chelate ring,

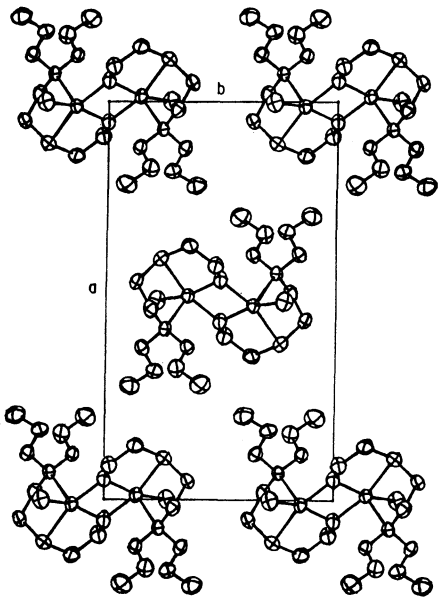

Fig. 3. Projection of the unit cell of Cu(n-C_3H_7-nso)Cl on the ab plane.

Cu–S–C(3)–C(4)–N, is of the gauche conformation for all the Cu(R-nso)X complexes.

The packing diagram is exemplified by the projection of the unit cell of Cu(n-C_3H_7-nso)Cl in Fig. 3. As is evident from the shortest separations between the nonhydrogen atoms of the binuclear units (S···S ($1-x$, $-y$, $-z$ of 3.538(1) Å in Cu(CH_3-nso)Cl, Cl···C(4) (x, y, $z-1$) of 3.534(5) Å in Cu(C_2H_5-nso)Cl, Cl···C(4) (x, y, $z-1$) of 3.669(6) Å in Cu(n-C_3H_7-nso)Cl, Cl···C(4) ($-x$, $1-y$, $-z$) of 3.480(3) Å in Cu(n-C_4H_9-nso)Cl, Br···C(4) (x, y, $z-1$) of 3.772(8) Å in Cu(n-C_3H_7-nso)Br and C(2)···C(12) ($1/2-x$, $1/2+y$, $1-z$) of 3.78(1) Å in Cu(n-C_4H_9-nso)Br), all the crystals consist of discrete binuclear units. Therefore, their magnetic properties were expected to be interpreted by the Bleaney-Bowers equation based on the Heisenberg model on the assumption of a binuclear structure,[3]

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

where χ_A is susceptibility per copper atom and N, g, J, β, and $N\alpha$ have the usual meanings. However, the temperature dependence of the magnetic susceptibilities of the majority of the Cu(R-nso)X complexes can not be explained by the above equation. This result might be due to the fact that there are polymorphism and by chance the crystal structures of the samples used for magnetic measurements and X-ray analyses are different. In order to check this possibility, magnetic susceptibilities have been measured over the temperature range 80—300 K for crystals taken from the same crop as those used in the X-ray work. Similarly to the previous result, the data for Cu(n-C_4H_9-nso)Cl obey the Bleaney-Bowers equation using $g=2.10$, $-2J=745$ cm^{-1} and $N\alpha=34\times10^{-6}$ cgs emu with very slight deviations from the previous ones ($g=2.10$, $-2J=735$ cm^{-1}, $N\alpha=60\times10^{-6}$ cgs emu)[2] and the experimental χ_A-T curves for the other complexes except for Cu(C_2H_5-nso)Cl

Table 4. Coefficients of equations of mean planes[a] and deviations of atoms from the planes

(1) Plane through Cu, O, S

Complex	l	m	n	d	Distances from the plane (l/Å)
Cu(CH_3-nso)Cl	0.4426	0.6604	0.5681	−0.0626	C(1) −0.075, C(2) −0.068
Cu(C_2H_5-nso)Cl	0.9256	−0.1988	−0.5834	−0.0285	C(1) −0.353, C(2) 0.018
Cu(n-C_3H_7-nso)Cl	0.6313	0.2206	0.5861	0.0118	C(1) 0.525, C(2) 0.208
Cu(n-C_4H_9-nso)Cl	−0.5641	−0.2410	0.9337	−0.1376	C(1) −0.305, C(2) 0.277
Cu(n-C_3H_7-nso)Br	0.6265	0.2260	0.5898	0.0121	C(1) 0.580, C(2) 0.208
Cu(n-C_4H_9-nso)Br	0.1695	−0.7834	0.5739	0.0023	C(1) 0.590, C(2) 0.173

(2) Plane through Cu, S, N

Complex	l	m	n	d	Distortions from the plane (l/Å)
Cu(CH_3-nso)Cl	0.3418	−0.6122	0.6110	1.2219	C(3) 0.310, C(4) −0.361
Cu(C_2H_5-nso)Cl	−0.3030	−0.7975	0.6569	−1.2298	C(3) −0.158, C(4) 0.493
Cu(n-C_3H_7-nso)Cl	−0.1861	−0.7671	0.6399	−1.2225	C(3) −0.396, C(4) 0.258
Cu(n-C_4H_9-nso)Cl	−0.7212	0.6928	0.2396	1.2089	C(3) −0.280, C(4) 0.441
Cu(n-C_3H_7-nso)Br	−0.1819	−0.7649	0.6429	−1.2166	C(3) −0.389, C(4) 0.262
Cu(n-C_4H_9-nso)Br	0.8403	−0.0295	−0.6365	1.2286	C(3) 0.405, C(4) −0.249

(3) Plane through O, O^i, S, X[b]

Complex	l	m	n	d	Distances from the plane (l/Å)
Cu(CH_3-nso)Cl	0.4311	0.7968	0.4159	−0.0056	O 0.135, O^i −0.124, S −0.097, Cl 0.086, Cu −0.240, N −2.565
Cu(C_2H_5-nso)Cl	0.8795	−0.3733	−0.3909	−0.0093	O 0.206, O^i −0.187, S −0.147, Cl 0.129, Cu −0.281, N −2.668
Cu(n-C_3H_7-nso)Cl	0.7125	0.3748	0.4216	0.0102	O −0.194, O^i 0.174, S 0.142, Cl −0.122, Cu 0.244, N 2.681
Cu(n-C_4H_9-nso)Cl	−0.3830	−0.3224	0.9441	−0.0034	O 0.086, O^i −0.079, S −0.060, Cl 0.053, Cu −0.290, N −2.688
Cu(n-C_3H_7-nso)Br	0.7132	0.3974	0.4063	0.0132	O −0.222, O^i 0.195, S 0.160, Br −0.134, Cu 0.268, N 2.679
Cu(n-C_4H_9-nso)Br	0.3718	−0.8225	0.3838	0.0141	O −0.239, O^i 0.211, S 0.173, Br −0.145, Cu 0.274, N 2.668

a) The equation of the plane is expressed as $lX+mY+nZ=d$, where X, Y, Z are in Å units referred to the crystallographic axes. b) Superscript (i) refers to the equivalent position $(-X, -Y, -Z)$.

largely deviate from the Bleaney-Bowers equation. However, in the case of Cu(C_2H_5-nso)Cl, contrary to the previous result, the present data can almost be fitted to the curve calculated by the Bleaney-Bowers equation with $g=2.10$, $-2J=425\ cm^{-1}$ and $N\alpha=60\times10^{-6}$ cgs emu although the fitness between the calculated and observed curves is slightly poor in the range near room temperature. Thus, we have found that the major structural difference corresponding to these magnetic behaviors lies in the conformation of the five-membered chelate ring. Among the complexes presently studied Cu(n-C_4H_9-nso)Cl and Cu(C_2H_5-nso)-Cl are the only complexes which obey the Bleaney-Bowers equation and are also the only complexes whose chelate ring Cu–O–C(1)–C(2)–S assumes a gauche or an intermediate conformation. As for the other complexes the magnetic behaviors can not be interpreted by any theoretical equations and the Cu–O–C(1)–C(2)–S rings all assume envelope conformations. In the envelope conformation, the strain of the chelate ring may be larger than that for the gauche conformation, although the energy difference between them seems to be little. Therefore, it is likely that an interconversion between the two conformations takes place with change of temperature. Assuming that the envelope conformation changes to a stable gauche conformation with lowering of temperature, this change may cause a slight structural change of the coordination sphere and the geometry

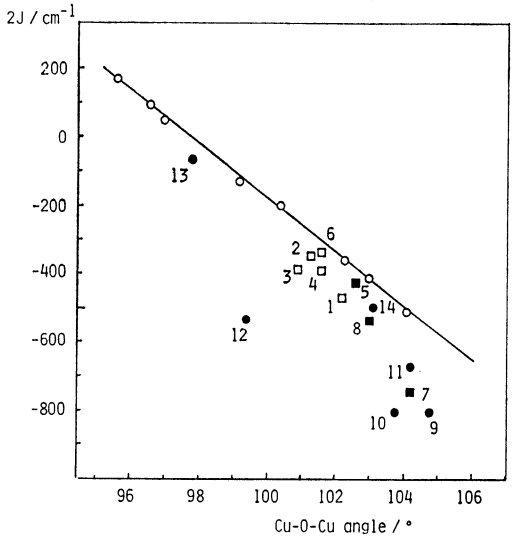

Fig. 4. Plot of the Cu–O–Cu angle *vs.* the $2J$ value.
1; Cu(CH_3-nso)Br, 2; Cu(n-C_3H_7-nso)Br, 3; Cu(n-C_4H_9-nso)Br, 4; Cu(CH_3-nso)Cl, 5; Cu(C_2H_5-nso)Cl, 6; Cu(n-C_3H_7-nso)Cl, 7; Cu(n-C_4H_9-nso)Cl, 8; Cu(CH_3-nso)NCS,[14] 9; α-Cu(C_2H_5-2)Br,[20] 10; α-Cu(n-C_4H_9-2)Br,[20] 11; Cu(n-C_3H_7-2)NCO,[21] 12; Cu(C_2H_5-2-3)$ClO_4\cdot H_2O$,[20] 13; Cu(H-3-2)$I\cdot H_2O$,[22] 14; Cu(bdhe)ClO_4.[23]
The straight line represents the linear relationship observed for the hydroxo-bridged copper(II) complexes.[18]

around the bridging oxygen atom. This may lead to a temperature dependence of the J value, since it is known that a slight change in bond angle may bring about a considerable change in J value.[17,18] In the case of Cu(C_2H_5-nso)Cl, the small deviation from the binuclear model in the magnetic susceptibilities may arise from the intermediate conformation of the chelate ring at room temperature.

In Fig. 4, the exchange parameters, $2J$, for Cu(R-nso)X are plotted against the Cu–O–Cu angles together with the data available in the literature for hydroxo- and alkoxo-bridged binuclear copper(II) complexes. For the complexes which show the unusual magnetic behavior, the values are estimated from Eq. 2[19] by the use of the magnetic moments, μ_{eff}, at room temperature. Hatfield and co-workers found a linear relationship between the spin singlet-triplet separation, $2J$, and the Cu–O–Cu angle for hydroxo-bridged binuclear copper(II) complexes.[18] As shown in Fig. 4, no such clear relationship is found for alkoxo-bridged complexes including Cu(R-nso)X. This may be due to the variation of planarity of the equatorial coordination plane and the effects of axial coordination.

$$-2J = 0.695\ T\ln[3[4.41/\mu_{eff}^2 - 1)] \quad (2)$$

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