Magnetic Properties and Crystal Structures of Binuclear Copper(II) Complexes with Heterocyclic Thione Donors of 1,3-Bis(hydroxymethyl)-2-imidazolidinethione and 1-Hydroxymethyl-3-methyl-2-imidazolidinethione

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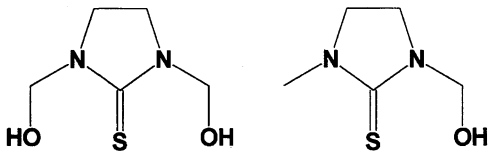
A new series of binuclear copper(II) complexes with 1,3-bis(hydroxymethyl)-2-imidazolidinethione, $[Cu(RCOO)(HL^1)]_2$ (where R=CH_3 (**1**), C_6H_5 (**2**), 2-$CH_3C_6H_4$ (**3**), 4-$CH_3C_6H_4$ (**4**), 2-ClC_6H_4 (**5**), and 2-BrC_6H_4 (**6**)), and with 1-hydroxymethyl-3-methyl-2-imidazolidinethione, $[Cu(RCOO)(L^2)]_2$ (where R=CH_3 (**7**), 2-$CH_3C_6H_4$ (**8**), and 4-$CH_3C_6H_4$ (**9**)), have been prepared. The magnetic susceptibility data of complexes **1**—**9** conform to the usual dimer equation with the $-2J$ values ranging from 227 to 992 cm^{-1}. Crystal structure analyses of **3**, **4**, **7**, and **9** revealed that two copper atoms are linked by two alkoxo-bridges with separations of 3.015(3)—3.069(3) Å in each complex. The coordination around each copper atom of the complexes is essentially a square planar configuration with one sulfur and two alkoxo-oxygen atoms of HL^1 or L^2 and one oxygen atom of carboxylates. Each alkoxo-group asymmetrically bridges with the Cu1–O1 bonds (1.90—1.92 Å), which are shorter than the Cu1′–O1 bonds (1.93—1.97 Å). The $-2J$ values for complexes **3**, **4**, **7**, and **9** are much better correlated with the Cu1′–O1 bond distances than with the alkoxo-bridging Cu1–O1–Cu1′ angles.

Recently, several reports have appeared concerning the synthesis and magnetism of binuclear copper(II) complexes with sulfur containing ligands;[1—7] however, none on those have had thione derivatives so far. This may be due to both the high reducing and poor coordinating ability of the thione sulfur atom for the copper(II) ion. As a continuing project for binuclear copper(II) complexes of sulfur-containing ligands, we have prepared a new series of di-μ-alkoxo-bridged binuclear copper(II) complexes with 1,3-bis(hydroxymethyl)-2-imidazolidinethione (H_2L^1) and 1-hydroxymethyl-3-methyl-2-imidazolidinethione (HL^2) (Chart 1). Binuclear copper(II) complexes with di-μ-hydroxo- or di-μ-alkoxo-bridges have been extensively studied. Hatfield and Hodgson have established a linear relationship between the $-2J$ value (singlet–triplet energy separation) and the Cu–O–Cu bridging angle (ϕ).[8] However, several copper(II) complexes with di-μ-alkoxo-bridges deviate remarkably from a linear relationship between $-2J$ and ϕ. This phenomenon was explained as follows: In complexes with *N*,*N*-dialkylaminoalcholato ligands, different alkyl groups cause different electronic states to exist in the bridging oxygen atoms.[9] Furthermore, the extent of the magnetic interaction are particularly sensitive to any minor changes in the geometry of the bridging oxygen atom,[10] and to the size of the dihedral angles between the planes containing the copper(II) ions.[11] The correlation between the $-2J$ values and the Cu–O–Cu angles in the present complexes was also out of the linear relationship (for example, $-2J$=992 cm^{-1} for **4** and $-2J$=438 cm^{-1} for **9**, whereas ϕ=103° is the same for each other). Based on our results, we investigated the correlation between some structural factors and the magnetic properties in the present complexes. A preliminary report on the molecular structure and magnetic properties of **3** has appeared.[12]



H_2L^1 HL^2

Chart 1.

Experimental

Materials. Anhydrous copper(II) carboxylates and the monohydrates, $Cu(RCOO)_2$ (R=C_6H_5 and 4-$CH_3C_6H_4$) and $Cu(RCOO)_2 \cdot H_2O$ (R=2-$CH_3C_6H_4$, 2-ClC_6H_4, and 2-BrC_6H_4), were prepared by using the same procedure as

described in the literature.[13,14] All other chemicals and solvents were of reagent grade.

Synthesis of Ligands. The ligand H_2L^1 was prepared according to the method of Roberts[15] by the reaction of paraformaldehyde with 2-imidazolidinethione.

The ligand HL^2 was prepared in the same way as that of H_2L^1, except for using 1-methyl-2-imidazolidinethione, which was synthesized according to a previously reported procedure.[16]

Preparation of Complexes. $[Cu(CH_3COO)(HL^1)]_2$ (1), $[Cu(2\text{-}CH_3C_6H_4COO)(HL^1)]_2$ (3), $[Cu(2\text{-}ClC_6H_4COO)(HL^1)]_2$ (5), and $[Cu(2\text{-}BrC_6H_4COO)(HL^1)]_2$ (6). A solution of copper(II) carboxylate monohydrates ($Cu(RCOO)_2H_2O$) (R=CH_3, 2-$CH_3C_6H_4$, 2-ClC_6H_4, or 2-BrC_6H_4) (2.4 mmol) in acetonitrile (30 ml) was added to a solution of the ligand H_2L^1 (2.4 mmol) in acetonitrile (30 ml). The mixture was stirred for 10 min at room temperature. The separated green crystals were collected, washed with acetonitrile, and dried in vacuo at room temperature. Anal. Found: C, 29.67; H, 4.31; N, 10.04; Cu, 22.27%. Calcd for $C_7H_{12}CuN_2O_4S$ (**1**): C, 29.62; H, 4.26; N, 9.87; Cu, 22.39%. Found: C, 43.24; H, 4.51; N, 7.81; Cu, 17.52%. Calcd for $C_{13}H_{16}CuN_2O_4S$ (**3**): C, 43.39; H, 4.48; N, 7.78; Cu, 17.66%. Found: C, 37.72; H, 3.56; N, 7.14; Cu, 16.66%. Calcd for $C_{12}H_{13}ClCuN_2O_4S$ (**5**): C, 37.90; H, 3.46; N, 7.37; Cu, 16.71%. Found: C, 33.91; H, 3.08; N, 6.58; Cu, 14.92%. Calcd for $C_{12}H_{13}BrCuN_2O_4S$ (**6**): C, 33.93; H, 3.08; N, 6.68; Cu, 14.96%.

$[Cu(C_6H_5COO)(HL^1)]_2$ (2) and $[Cu(4\text{-}CH_3C_6H_4COO)(HL^1)]_2$ (4). Anhydrous copper(II) benzoate or 4-methylbenzoate, $Cu(C_6H_5COO)_2$ or $Cu(4\text{-}CH_3C_6H_4COO)_2$, (2.0 mmol) and the ligand H_2L^1 (2.4 mmol) were suspended in acetonitrile (60 ml). The mixture was stirred for 1 h at room temperature. The precipitated green crystals were collected, washed with acetonitrile (200 ml), and dried in vacuo over P_2O_5. Anal. Found: C, 41.39; H, 4.12; N, 8.06; Cu, 18.27%. Calcd for $C_{12}H_{14}CuN_2O_4S$ (**2**): C, 41.67; H, 4.08; N, 8.10; Cu, 18.37%. Found: C, 43.45; H, 4.47; N, 7.99; Cu, 17.56%. Calcd for $C_{13}H_{16}CuN_2O_4S$ (**4**): C, 43.39; H, 4.48; N, 7.78; Cu, 17.66%.

$[Cu(CH_3COO)(L^2)]_2$ (7), $[Cu(2\text{-}CH_3C_6H_4COO)(L^2)]_2$ (8), and $[Cu(4\text{-}CH_3C_6H_4COO)(L^2)]_2$ (9). A typical synthetic method is as follows. A solution of copper(II) acetate monohydrate, copper(II) 2-methylbenzoate monohydrate, or anhydrous copper(II) 4-methylbenzoate (2.4 mmol) in acetonitrile (30 ml) was added to a solution of HL^2 (2.4 mmol) in acetonitrile (30 ml). The mixture was stirred for 10 min at room temperature. A few drops of triethylamine were added to the mixture. The separated green crystals were collected, washed with acetonitrile, and dried in vacuo at room temperature. Anal. Found: C, 31.69; H, 4.41; N, 10.73; Cu, 23.65%. Calcd for $C_7H_{12}CuN_2O_3S$ (**7**): C, 31.40; H, 4.52; N, 10.46; Cu, 23.73%. Found: C, 45.52; H, 4.75; N, 8.16; Cu, 18.49%. Calcd for $C_{13}H_{16}CuN_2O_3S$ (**8**): C, 45.41; H, 4.69; N, 8.15; Cu, 18.48%. Found: C, 45.52; H, 4.73; N, 8.25; Cu, 18.46%. Calcd for $C_{13}H_{16}CuN_2O_3S$ (**9**): C, 45.41; H, 4.69; N, 8.15; Cu, 18.48%.

Physical Measurements. Carbon, hydrogen, and nitrogen analyses were carried out at the Service Center of Elemental Analysis, Kyushu University. Copper analyses were made by using a titmetric method. Infrared spectra were measured with a Hitachi 260-10 IR Spectrophotometer in the region of 4000—650 cm^{-1} on Nujol mulls. Electronic spectra were recorded on a Hitachi 323 recording Spectrophotometer by the diffuse reflectance technique. The magnetic susceptibilities in the 80—300 K temperature range were determined by the Faraday method. The susceptibilities were corrected for the diamagnetism of the constituent atoms by the use of Pascal's constants.[17] The effective magnetic moments were calculated from the equation,

$$\mu_{\text{eff}} = 2.83\sqrt{(\chi_A - N\alpha)T}, \quad (1)$$

where χ_A is the atomic magnetic susceptibility and $N\alpha$ is the temperature-independent paramagnetism.

X-Ray Crystal Structure Determination. Suitable crystals of **3**, **4**, **7**, and **9** were grown from each reaction mixture of the ligands and appropriate copper(II) carboxylates in acetonitrile. The diffraction data were measured on a Rigaku AFC5S automated four-circle diffractometer with graphite monochromated Cu $K\alpha$ (λ=1.54178 Å) or Mo $K\alpha$ (λ=0.71069 Å) radiation. The unit-cell parameters of each crystal were obtained from a least-squares refinement based on 25 high-angle reflections. The crystal data are shown in Table 1. The data were collected at a temperature of 23±1 °C using the ω–2θ scan technique to a maximum 2θ value of 120° for Cu $K\alpha$ radiation and of 50° for Mo $K\alpha$ radiation. The weak reflections ($I<10\sigma(I)$) were rescanned (maximum of 2 rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of the peak counting time to the background counting time was 2:1. The intensities of three representative reflections, which were measured after every 150 reflections, remained constant throughout data collection, indicating crystal and electronic stability (no decay correction was applied).

An empirical absorption correction, based on azimuthal scans of several reflections, was applied, which resulted in transmission factors ranging from 0.92 to 1.00 for **3**, from 0.80 to 1.00 for **4**, from 0.61 to 1.00 for **7**, and from 0.88 to 1.00 for **9**. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods.[18] The non-hydrogen atoms were refined anisotropically, except for some of the carbon atoms of **9**. Refinements were carried out by the full-matrix least-squares method.[19] Some of the hydrogen atoms were located from the subsequent difference Fourier maps and included in the refinement. The final discrepancy factors,

$$R = \sum \| F_o | - | F_c \| / \sum | F_o | \quad (2)$$

and

$$R_w = \sqrt{\left(\sum w(| F_o | - | F_c |)^2 / \sum w F_o^2\right)}, \quad (3)$$

are listed in Table 1.

The neutral-atom scattering factors were taken from Cromer and Waber.[20] Anomalous dispersion effects were included in F_{calcd}; the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[20] All calculations were performed using the TEXSAN[21] crystallographic software package of Molecular Structure Corporation. The final positional and thermal parameters along with their estimated standard deviations

Table 1. Crystal Data and Data Collection Details

	3	**4**	**7**	**9**
Formula	$C_{26}H_{32}Cu_2N_4O_8S_2$	$C_{26}H_{32}Cu_2N_4O_8S_2$	$C_{14}H_{24}Cu_2N_4O_6S_2$	$C_{26}H_{32}Cu_2N_4O_6S_2$
F. W.	719.77	719.77	535.58	687.77
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/a$	$P\bar{1}$	$P2_1/a$
a/Å	12.48(2)	14.407(10)	9.198(4)	12.373(5)
b/Å	9.228(8)	12.756(11)	9.915(4)	16.443(7)
c/Å	14.44(1)	16.437(7)	5.98(2)	14.230(3)
α/°			92.6(1)	
β/°	115.07(5)	96.92(4)	107.9(1)	95.43(3)
γ/°			106.83(4)	
V/Å^3	1507(2)	2999(3)	510(1)	2882(2)
Z	2	4	1	4
D_c/g cm^{-3}	1.590	1.594	1.74	1.585
D_m/g cm^{-3}	1.58	1.58	1.76	1.57
$F(000)$	740	1480	274	1416
μ(Cu $K\alpha$)/cm^{-1}	34.44	34.60	47.69	16.64[a]
Crystal dimensions/mm	0.15×0.2×0.6	0.1×0.3×0.3	0.3×0.4×0.7	0.15×0.1×0.2
No. of observations ($F_o>3\sigma(F_o)$)	1731	2438	1369	1534
No. of variables	190	379	127	326
Final residuals				
R	0.069	0.060	0.061	0.074
R_w	0.096	0.075	0.091	0.082
Largest peak in final Diff. fourier (e Å^{-3})	1.73	0.47	0.89	0.84

a) Mo $K\alpha$ radiation.

are given in Table 2. The coordinates and isotropic temperature factors of hydrogen atoms, the anisotropic thermal parameters of no hydrogen atoms, and the F_o-F_c tables have been deposited as Document No. 68046 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Synthesis of the Complexes. No dimeric copper(II) complexes were precipitated from the reaction mixtures of H_2L^1 or HL^2 with $CuCl_2$, $Cu(ClO_4)_2\cdot 6H_2O$, or $Cu(NO_3)_2\cdot 3H_2O$ instead of copper(II) carboxylates. Although the reason for the lack of precipitation of dimeric complexes is not clear, it may have been responsible for the large acidity of the reaction mixtures, and for the high solubility of the dimeric $[CuX(HL^1)]_2$ or $[CuX(L^2)]_2$ complexes (where X=Cl, ClO_4, and NO_3) in acetonitrile. Reduced copper(I) compounds as impurities were precipitated when the reaction mixtures of the ligands with copper(II) carboxylates were stirred for more than 1 h. The reaction of H_2L^1 with copper(II) acetate in ethanol in the presence of triethylamine led to the isolation of the polynuclear copper(II) complex, $[Cu_2(L^1)_2\cdot H_2O]_n$.[22]

Description of the Structure. X-Ray structure analyses of **3**, **4**, **7**, and **9** revealed that two copper atoms are linked by di-alkoxo-bridges with a separation of 3.015(3)—3.069(3) Å (Figs. 1, 2, 3, and 4). The crystal structures of **4** and **9** comprise two crystallographically independent binuclear molecules; they are

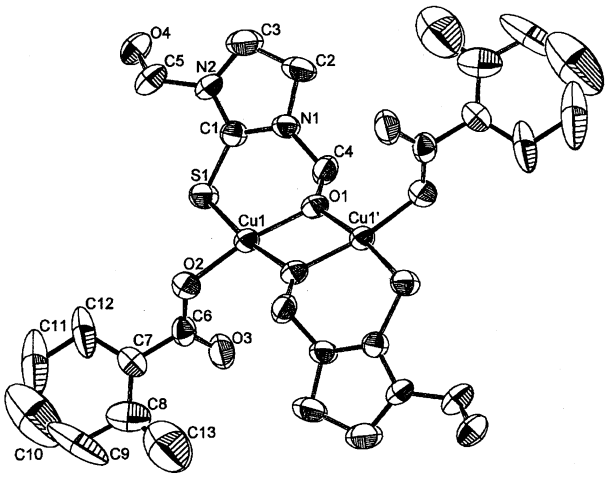


Fig. 1. A perspective view of $[Cu(2\text{-}CH_3C_6H_4COO)(HL^1)]_2$ (**3**). Hydrogen atoms are not shown for clarity.

represented as A and B. The structures of molecules A and B have almost the same arrangement, though slightly differ regarding the bond distances and angles. Selected bond distances and angles for **3**, **4**, **7**, and **9** are listed in Table 3. The coordination geometry around each copper atom is essentially square planar with one sulfur and two alkoxo-oxygen atoms of HL^1 or L^2 and one oxygen atom of the carboxylates. Each copper atom deviates slightly from the coordination plane of O_3S by 0.06, 0.11, 0.10 and 0.15 Å for **3**, **4** (both molecules A

Table 2. Fractional Positional Parameters and Thermal Parameters of Non-Hydrogen Atoms with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}/Å^2
Complex **3**[a]				
Cu1	0.05327(9)	0.1505(1)	1.00219(7)	3.37(4)
S1	−0.0244(2)	0.3638(2)	0.9167(1)	4.20(8)
O1	−0.0901(4)	0.0411(5)	0.9376(3)	3.7(2)
O2	0.2009(5)	0.2387(6)	1.0865(4)	4.3(2)
O3	0.1437(5)	0.2633(7)	1.2121(4)	5.4(3)
O4	−0.1267(5)	0.5751(6)	0.6376(4)	4.9(2)
N1	−0.1820(6)	0.1764(7)	0.7862(4)	4.3(3)
N2	−0.1286(6)	0.3480(7)	0.7107(5)	4.3(3)
C1	−0.1142(7)	0.2936(7)	0.8003(5)	3.5(3)
C2	−0.253(1)	0.150(1)	0.6780(6)	6.4(4)
C3	−0.206(1)	0.261(1)	0.6275(6)	6.4(5)
C4	−0.1969(7)	0.1004(9)	0.8688(6)	4.2(3)
C5	−0.0562(8)	0.462(1)	0.6965(6)	5.0(4)
C6	0.2130(7)	0.2875(8)	1.1728(6)	3.8(3)
C7	0.3227(7)	0.3753(9)	1.2306(6)	4.3(3)
C8	0.392(1)	0.363(1)	1.3335(8)	6.8(5)
C9	0.494(1)	0.452(2)	1.384(1)	12(1)
C10	0.517(2)	0.553(4)	1.331(2)	17(2)
C11	0.451(2)	0.575(2)	1.233(2)	13(1)
C12	0.352(1)	0.483(1)	1.174(1)	8.2(6)
C13	0.382(2)	0.264(2)	1.391(1)	13(1)
Complex **4**: Molecule A[b]				
Cu1	0.5554(1)	0.0788(1)	0.45743(8)	4.07(7)
S1	0.6601(2)	0.2032(2)	0.5108(2)	4.8(1)
O1	0.5656(5)	−0.0105(6)	0.5522(4)	5.2(4)
O2	0.5423(5)	0.1388(5)	0.3483(4)	4.8(4)
O3	0.6111(6)	−0.0126(6)	0.3323(4)	5.9(4)
O4	0.7269(6)	0.4287(6)	0.7092(5)	7.3(5)
N1	0.6427(6)	0.0974(7)	0.6527(5)	4.9(5)
N2	0.6702(7)	0.2670(7)	0.6682(6)	5.2(5)
C1	0.6572(7)	0.1884(9)	0.6137(6)	4.2(5)
C2	0.6420(8)	0.114(1)	0.7399(6)	5.9(6)
C3	0.6583(8)	0.233(1)	0.7506(6)	5.9(6)
C4	0.6377(8)	−0.004(1)	0.6097(7)	5.7(6)
C5	0.6693(9)	0.377(1)	0.6487(8)	6.3(7)
C6	0.5786(7)	0.0732(9)	0.3032(6)	3.7(4)
C7	0.5823(7)	0.1006(8)	0.2161(6)	3.6(5)
C8	0.5697(7)	0.2025(9)	0.1909(7)	4.6(5)
C9	0.5720(8)	0.231(1)	0.1085(7)	5.1(6)
C10	0.5817(8)	0.151(1)	0.0507(7)	5.4(6)
C11	0.5971(9)	0.052(1)	0.0783(6)	5.6(6)
C12	0.5959(8)	0.0240(8)	0.1587(6)	5.2(6)
C13	0.580(1)	0.180(1)	−0.0400(7)	7.6(8)
Complex **4**: Molecule B[c]				
Cu2	0.5615(1)	−0.4241(1)	0.05285(8)	4.42(7)
S2	0.6661(2)	−0.3004(2)	0.0224(2)	5.2(4)
O5	0.5511(5)	−0.4931(5)	−0.0510(4)	5.1(4)
O6	0.5624(6)	−0.3724(6)	0.1626(4)	5.7(4)
O7	0.6278(6)	−0.5242(7)	0.2019(5)	7.5(5)
O8	0.770(1)	−0.0876(8)	−0.0820(6)	12.4(8)
N3	0.6416(6)	−0.3892(7)	−0.1274(5)	4.5(4)
N4	0.6767(6)	−0.2241(7)	−0.1278(5)	4.8(5)
C14	0.6610(7)	−0.3054(8)	−0.0824(6)	3.9(5)
C15	0.6401(8)	−0.363(1)	−0.2161(6)	5.3(6)
C16	0.6678(8)	−0.251(1)	−0.2176(6)	5.1(6)
C17	0.6261(8)	−0.4958(9)	−0.0975(6)	4.9(6)
C18	0.680(1)	−0.114(1)	−0.103(1)	10(1)
C19	0.5962(8)	−0.439(1)	0.2176(6)	4.7(6)
C20	0.5942(6)	−0.4061(8)	0.3044(6)	3.7(5)
C21	0.5848(6)	−0.3009(8)	0.3252(6)	3.6(5)
C22	0.5879(7)	−0.2754(8)	0.4085(5)	3.8(5)
C23	0.5936(7)	−0.350(1)	0.4675(6)	4.6(6)
C24	0.5981(8)	−0.4561(8)	0.4456(6)	4.4(5)
C25	0.5994(7)	−0.4821(8)	0.3649(6)	4.0(5)
C26	0.5975(8)	−0.322(1)	0.5588(6)	6.3(7)
Complex **7**[d]				
Cu1	0.98641(9)	0.42169(8)	0.2126(1)	2.14(4)
S1	1.0808(2)	0.2445(2)	0.3496(3)	2.86(6)
O1	1.0980(5)	0.4499(5)	−0.0320(7)	2.9(2)
O2	0.8541(4)	0.4006(4)	0.4362(7)	2.4(1)
O3	0.6826(5)	0.2452(5)	0.1684(9)	3.8(2)
N1	1.2265(5)	0.2726(5)	−0.010(1)	2.5(2)
N2	1.2156(6)	0.0779(5)	0.153(1)	3.0(2)
C1	1.1774(6)	0.1985(6)	0.155(1)	2.3(2)
C2	1.3284(7)	0.2124(7)	−0.116(1)	3.0(2)
C3	1.2999(8)	0.0684(7)	−0.028(1)	3.7(3)
C4	1.2379(7)	0.4232(6)	−0.023(1)	2.6(2)
C5	1.1663(9)	−0.0375(7)	0.288(1)	4.0(3)
C6	0.7210(6)	0.3104(6)	0.362(1)	2.4(2)
C7	0.6101(8)	0.2893(8)	0.521(1)	4.2(3)
Complex **9**: molecule A[e]				
Cu1	0.0732(2)	0.0503(2)	0.9430(2)	3.1(2)
S1	0.1864(5)	0.0080(4)	0.8345(5)	3.9(3)
O1	−0.021(1)	−0.042(1)	0.931(1)	3.4(7)
O2	0.141(1)	0.1574(9)	0.956(1)	3.6(8)
O3	−0.030(1)	0.182(1)	0.903(1)	5(1)
N1	0.084(1)	−0.134(1)	0.853(1)	3(1)
N2	0.254(2)	−0.145(1)	0.820(1)	4(1)
C1	0.173(2)	−0.094(1)	0.838(2)	2.9(5)[g]
C2	0.097(2)	−0.225(1)	0.846(2)	5(1)
C3	0.218(2)	−0.229(1)	0.832(2)	5(2)
C4	−0.021(2)	−0.097(2)	0.857(2)	4(1)
C5	0.364(2)	−0.126(2)	0.807(2)	7(2)
C6	0.061(2)	0.205(1)	0.925(2)	3(1)
C7	0.090(2)	0.293(1)	0.922(1)	2.4(4)[g]
C8	0.198(2)	0.321(1)	0.925(1)	1.8(4)[g]
C9	0.223(2)	0.405(1)	0.920(2)	3(1)
C10	0.137(2)	0.459(1)	0.912(1)	2(1)
C11	0.036(2)	0.434(1)	0.908(1)	3(1)
C12	0.007(2)	0.350(1)	0.910(2)	3.2(5)[g]
C13	0.167(2)	0.549(1)	0.906(2)	4(1)
Complex **9**: molecule B[f]				
Cu2	0.4152(2)	0.0497(2)	0.4420(2)	3.6(2)
S2	0.2774(5)	0.0100(4)	0.3338(5)	4.6(4)
O4	0.504(1)	−0.044(1)	0.433(1)	4.2(8)
O5	0.353(1)	0.1577(9)	0.457(1)	4.1(8)
O6	0.499(1)	0.1804(9)	0.386(1)	5(1)
N3	0.388(2)	−0.135(1)	0.348(1)	4(1)
N4	0.212(2)	−0.144(1)	0.323(1)	4(1)
C14	0.291(2)	−0.093(2)	0.330(2)	4(1)
C15	0.365(2)	−0.222(2)	0.342(2)	5(1)
C16	0.248(3)	−0.229(2)	0.323(2)	8(2)
C17	0.489(2)	−0.093(2)	0.355(2)	4(1)
C18	0.097(2)	−0.124(2)	0.313(2)	6(2)
C19	0.419(2)	0.203(1)	0.417(2)	3(1)
C20	0.391(2)	0.296(1)	0.418(1)	3(1)
C21	0.468(2)	0.351(1)	0.404(1)	3(1)
C22	0.443(2)	0.435(1)	0.404(2)	4(1)
C23	0.337(2)	0.458(1)	0.418(1)	2.4(4)[g]
C24	0.261(2)	0.401(1)	0.424(2)	3.2(5)[g]
C25	0.286(2)	0.319(1)	0.428(2)	2.9(5)[g]
C26	0.314(2)	0.549(2)	0.415(2)	7(2)

Symmetry code a) $-x, -y, 2-z$: b) molecule A: $1-x, -y, 1-z$: c) molecule B: $1-x, -1-y, -z$: d) $2-x, 1-y, -z$: e) molecule A: $-x, -y, 2-z$: f) molecule B: $1-x, -y, 1-z$. g) Refined isotropically.

Table 3. Selected Interatomic Distances (Å) and Bond Angles (°) with Their Estimated Standard Deviations in Parentheses

	3	4		7	9	
		Molecule A	Molecule B		Molecule A	Molecule B
Cu1–Cu1′	3.069(3)	3.015(3)	3.027(3)	3.051(7)	3.035(6)	3.024(6)
Cu1–O1	1.918(5)	1.921(7)	1.910(6)	1.919(5)	1.92(1)	1.90(1)
O1–Cu1′	1.938(5)	1.939(7)	1.932(7)	1.946(5)	1.97(1)	1.95(1)
Cu1–O2	1.908(5)	1.938(6)	1.919(7)	1.943(5)	1.95(1)	1.96(1)
Cu1–S1	2.308(3)	2.289(3)	2.280(3)	2.295(2)	2.288(7)	2.282(7)
C1–S1	1.705(7)	1.71(1)	1.72(1)	1.705(6)	1.69(2)	1.70(3)
C1–N1	1.33(1)	1.36(1)	1.31(1)	1.326(8)	1.32(1)	1.39(3)
C1–N2	1.328(9)	1.34(1)	1.31(1)	1.341(8)	1.34(3)	1.28(3)
C2–N1	1.45(1)	1.45(1)	1.49(1)	1.461(7)	1.50(3)	1.47(3)
C3–N2	1.43(1)	1.45(1)	1.51(1)	1.451(9)	1.47(3)	1.48(3)
C4–N1	1.46(1)	1.47(1)	1.47(1)	1.473(7)	1.45(2)	1.43(3)
C5–N2	1.45(1)	1.44(1)	1.46(2)	1.443(9)	1.43(3)	1.45(3)
C2–C3	1.52(1)	1.55(2)	1.48(1)	1.51(1)	1.54(3)	1.45(3)
C4–O1	1.392(9)	1.32(1)	1.40(1)	1.380(6)	1.38(2)	1.38(3)
C5–O4	1.40(1)	1.38(1)	1.35(2)			
C6–O2	1.272(9)	1.27(1)	1.29(1)	1.276(7)	1.30(3)	1.28(2)
C6–O3	1.239(9)	1.26(1)	1.22(1)	1.240(8)	1.21(2)	1.19(2)
Cu1–O1–Cu1′	105.5(2)	102.7(3)	103.9(3)	104.2(3)	102.7(7)	103.4(7)
C4–O1–Cu1	123.6(5)	121.2(7)	121.2(6)	123.4(4)	123(1)	120(1)
C4–O1–Cu1′	130.7(5)	135.2(7)	132.9(6)	128.8(4)	132(1)	136(2)
O1–Cu1–S1	95.4(2)	96.8(2)	96.1(2)	95.2(2)	96.0(4)	97.3(5)
O1–Cu1–O1′	74.5(2)	77.3(3)	76.1(3)	75.8(2)	77.3(7)	76.6(7)
O2–Cu1–O1′	97.0(2)	96.7(3)	96.5(3)	97.6(2)	98.6(6)	97.0(7)
O2–Cu1–S1	92.9(2)	93.9(3)	92.2(2)	91.0(2)	93.1(5)	93.0(5)
O1–Cu1–O2	170.1(2)	166.8(3)	171.6(3)	172.9(2)	167.8(6)	167.9(7)
S1–Cu1–O1′	169.9(2)	152.5(2)	161.9(3)	167.5(2)	150.3(5)	151.9(5)
C1–S1–Cu1	98.9(3)	102.1(4)	104.2(4)	107.3(2)	102.5(8)	104(1)
N1–C1–S1	124.6(5)	125.9(8)	125.3(8)	126.9(5)	126(2)	125(2)
N2–C1–S1	125.3(6)	124.1(8)	123.5(8)	122.9(5)	122(2)	125(2)
N1–C1–N2	110.1(6)	110(1)	111(1)	110.1(5)	112(2)	109(2)
C1–N1–C2	111.2(7)	111(1)	110.1(9)	111.2(5)	113(2)	109(2)
C1–N1–C4	123.7(6)	121.8(9)	126.5(8)	124.3(5)	124(2)	121(2)
C2–N1–C4	124.3(7)	127(1)	123.4(8)	119.6(5)	122(2)	130(2)
C1–N2–C3	111.8(6)	112(1)	112.1(9)	110.8(5)	109(2)	113(2)
C1–N2–C5	121.7(7)	126(1)	127(1)	126.4(5)	129(2)	126(2)
C3–N2–C5	121.7(7)	120(1)	119(1)	122.4(5)	121(2)	120(2)
N1–C4–O1	110.9(6)	113(1)	108.6(9)	113.2(5)	112(2)	113(2)

and B), **7**, and **9** (both molecules A and B), respectively. The salient structural feature of the complexes is that the Cu1′–O1 bond (1.932(7)—1.97(1) Å) trans to sulfur is significantly longer than the cis Cu1–O1 bond (1.90(1)—1.921(7) Å) in each complex. Elder and co-workers first detailed this sulfur-induced structural trans effect (STE) in $[Co(en)_2(SCH_2COO)]^+$,[23] $[Co(en)_2(SCH_2CH_2NH_2)]^{2+}$,[23] $[(NH_3)_5CoSO_3]^+$,[24,25] and $[(NH_3)_5CoS(O)_2C_6H_4CH_3]^{2+}$ [25] in which each trans (to sulfur) Co–N distance is 0.04—0.08 Å longer than the average cis Co–N bond. The differences between the Cu1′–O1 and Cu1–O1 bond distances (0.018(7)—0.05(1) Å) are somewhat less than the STE of sulfur found for the Co–N bond. However, it is possible to say unequivocally that a lengthening of the trans Cu–O bond takes place. This STE of sulfur has also been observed in di-alkoxo-bridged binuclear copper(II) complexes with 2-[2-(dialkylamino)ethylthio]ethanol, $Cu_2\{R_2N(CH_2)_2S(CH_2)_2O\}_2X_2$[6] (where R=$CH_3$, n-C_3H_7; X=Cl and R=CH_3; X=NCS), in which each bridging Cu–O bond trans to sulfur is considerably longer by 0.012(2)—0.040(6) Å than the corresponding cis bridging Cu–O bond.

The Cu1···$O3_{carboxylato}$ distances of **9** (2.55(1) for molecules A and B) and **4** (2.576(7) Å for molecule A) are almost comparable to those in monomeric copper(II) carboxylate complexes (2.49—2.71 Å)[26] for which the carboxylate coordination was identified as being intermediate between strictly unidentate and strictly bidentate-chelate.[27] In **3**, **4** (molecule B), and **7**, however, the Cu1···$O3_{carboxylato}$ distances (2.940(6), 2.825(9), and 2.793(5) Å, respectively) are considerably longer than those in **4** (molecule A) and **9**, indicating that the carboxylate coordination mode in **3**, **4** (molecule

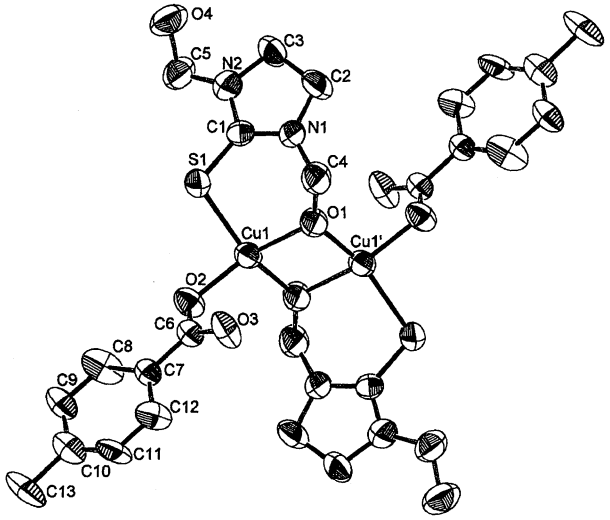


Fig. 2. A perspective view of $[Cu(4\text{-}CH_3C_6H_4COO)(HL^1)]_2$ (**4**: molecule A).

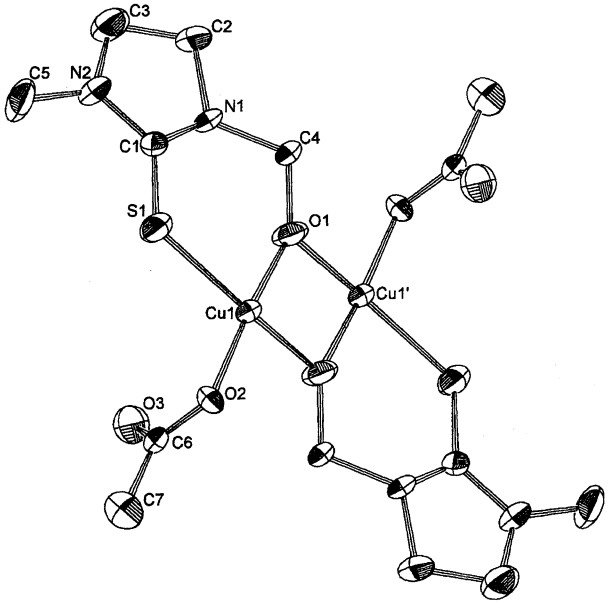


Fig. 3. A perspective view of $[Cu(CH_3COO)(L^2)]_2$ (**7**).

B), and **7** is an unidentate type. In **3** and **7**, weak interdimer bonds were observed between the adjacent molecules. The Cu1···O4″$_{alcoholic}$ distance for **3** and the Cu1···O2″$_{carboxylato}$ distance for **7** are 2.639(6) and 2.591(7) Å, respectively. The Cu1–O–Cu1′ bridging angles are 103—105°, corresponding to the maximum value of those found in other di-alkoxo-bridged copper(II) dimers, which range from 98—105°.[5,6] The Cu1–S bond distances (2.28—2.31 Å) are slightly shorter than those found for copper(II) complexes with thioether ligands (2.30—2.36 Å),[5] and fall in the range of those for copper(I) complexes with heterocyclic thione donors (2.20—2.39 Å).[28] The bond distances of C1–N1 and C1–N2 (1.28—1.39 Å) are considerably shorter than those of the other C–N bonds (Ave. 1.45 Å). The C1–S1 bond distances (1.69—1.72 Å) are slightly longer than

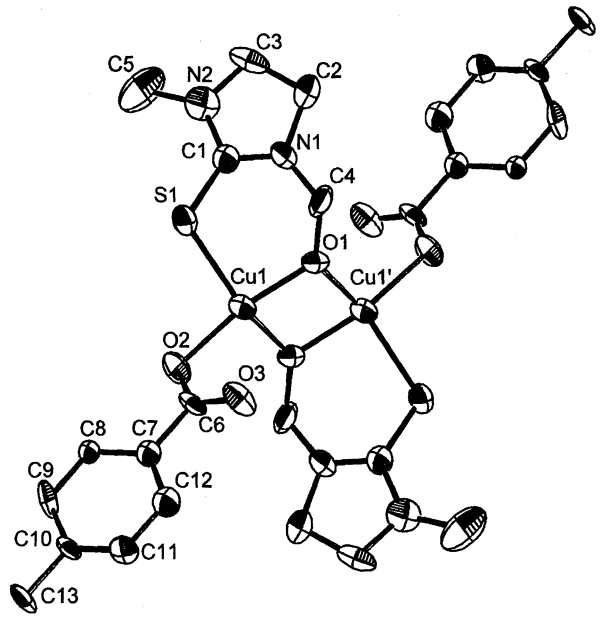


Fig. 4. A perspective view of $[Cu(4\text{-}CH_3C_6H_4COO)(L^2)]_2$ (**9**: molecule A). The C1, C7, C8, and C12 atoms are refined isotropically.

those found for typical heterocyclic thiones (1.64—1.71).[28] These shortening in the C–N bond and the lengthening in the C–S bonds indicate a strong tendency for delocalization of the π-electron density within the heterocyclic thioamide of the ligands upon coordination.

The dihedral angles between the least-squares plane of the imidazolidinethione moiety involving C4 and the O_3S coordination plane are in 22.1—47.5°. The six-membered chelate ring, Cu1–S1–C1–N1–C4–O1, is bent at the S1···C4 axis to almost the same degree as the dihedral angles. This bending at the S1···C4 axis is also reflected in a simultaneous closing of the C1–S1–Cu1 and N1–C4–O1 angles, having average values of 103.1° and 111.7°, respectively. These average bond angles of C1–S1–Cu1 and N1–C4–O1 are smaller by 25° and 9.7° than the corresponding C–O–Cu and C–C–O angles found in binuclear copper(II) complexes of 1,3,5-triketonates[29] having almost planar six-membered chelate rings with only oxygen donor atoms. Therefore, such a large bending of the chelate ring can be ascribable to the small bond angle and the large radius of the sulfur atom compared with the oxygen atom.

Infrared Spectra. IR data are listed in Table 4. The IR spectra of the free ligand H_2L^1 showed two OH stretching bands at 3401 and 3258 cm^{-1}, which are attributed to the inter- and intra-molecular hydrogen bond, respectively. The present complexes with the H_2L^1 ligand possess only one band at around 3200 cm^{-1}. This indicates that one of the OH groups in the free H_2L^1 ligand loses the alcoholic proton upon complexation. Organic compounds containing a thioamide group give rise to four characteristic IR

Table 4. IR Data for Complexes **1**—**9** and the Ligands

Compound	OH		Thioamide II	Thioamide IV	ν_{COO} as	ν_{COO} s
H_2L^1	3401	3258	1240	725		
1		3370	1247	721	1581	1387
2		3140	1250	721	1610	1376
3		3180	1249	718	1601	1377
4		3167	1245	721	1590	1376
5		3230	1252	717	1586	1376
6		3270	1256	721	1603	1385
HL^2		3290	1253	721		
7			1288	708	1593	1377
8			1282	716	1615	1374
9			1282	717	1593	1364

bands, which are known as thioamide bands.[30,31] Of the four thioamide bands, those showing the most significant changes upon complexation are Band II and Band IV. Band II makes major contributions from $\nu_{C-N}+\nu_{C=S}$,[31,32] and shows a blue shift on the order of 5—35 cm^{-1}. Band IV is mainly due to $\nu_{C=S}$,[31,32] and a slight red shift of about 3—8 cm^{-1} was observed. These shifts in Band II and Band IV are explained on the basis of a considerable shortening in the thioamide C–N bond and a slight lengthening in the C–S bond upon complexation, respectively.

The antisymmetric (ν_{asCOO}, 1581—1615 cm^{-1}) and symmetric (ν_{sCOO}, 1364—1387 cm^{-1}) carboxylate stretching vibrations in the present complexes were shifted to higher and lower frequencies than those in the corresponding ionic carboxylates (ν_{asCOO}, 1578—1580 cm^{-1}; ν_{sCOO}, 1414—1420 cm^{-1}),[33] respectively. These IR spectral data show that the carboxylate coordination in the present complexes is closer to an unidentate type.[34]

Electronic Spectra. The electronic spectra of the present complexes were recorded by the diffuse reflectance technique. The spectra of all the complexes resemble each other in shape. Some of the electronic spectra of the complexes are shown in Fig. 5, and the wavenumbers of the band maxima ($\tilde{\nu}_{max}$) are listed in Table 5. The spectral similarity suggests that complexes **1**, **2**, **5**, **6**, and **8** also have the same configuration around each copper(II) ion as those in **3**, **4**, **7**, and **9**. The spectra show three bands having maxima at 30—35×10^3 cm^{-1}, ca. 25×10^3, and ca. 15×10^3 cm^{-1} with a shoulder at ca. 11×10^3 cm^{-1}. The bands at around 15×10^3 cm^{-1} are assigned to d–d transitions. The bands at around 25×10^3 cm^{-1} are attributable to the complex formation between the ligands, because no bands were observed for the ligands near to this wavenumber. A similar band was found at around 24—29×10^3 cm^{-1} for alkoxo-bridged binuclear copper(II) complexes. This band was assigned to the charge-transfer band from the nonbonding π-orbital on the bridging oxygen to a vacant 3d-orbital of the copper(II) ions.[35] It seems that the band at around 25×10^3 cm^{-1} found for the present complexes has the same origin as the band for alkoxo-bridged binuclear copper(II) complexes. The band at around 30—35×10^3 cm^{-1} should be assigned to the σ(S)→d(Cu) charge transfer band,[4,36] because the free ligand shows no absorption below 40×10^3 cm^{-1}.

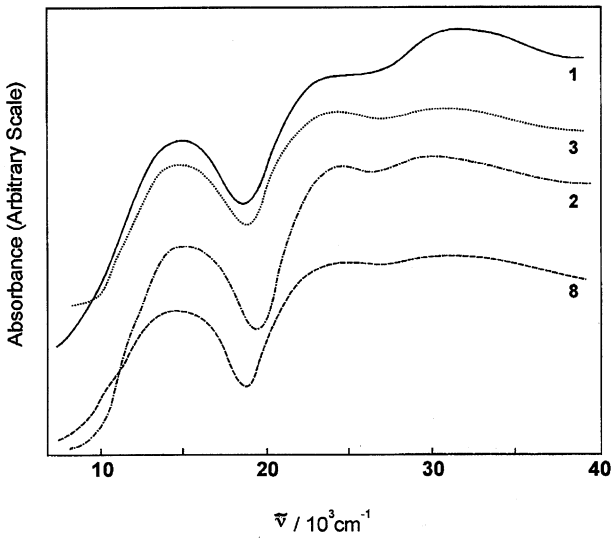


Fig. 5. Reflectance spectra of **1**, **2**, **3**, and **8**.

Table 5. Electronic Spectral Data for Complexes **1**—**9**

Complex	$\tilde{\nu}/10^3$ cm^{-1}			
1	31.7	24.2	14.9	11.1
2	30.1	24.3	14.9	11.1
3	31.0	24.6	14.9	11.3
4	34.4	24.2	16.4	11.5
5	31.2	24.8	14.7	11.1
6	32.2	24.8	14.5	11.1
7	35.2	26.3	14.9	11.1
8	32.8	27.0	14.7	11.1
9	31.2	24.8	14.7	11.1

Magnetic Susceptibility. The magnetic susceptibilities of the complexes were determined over the temperature range of 80—300 K. The data are shown in Figs. 6 and 7 as plots of the molar magnetic susceptibility (χ_A) vs. the temperature. The magnetic data for the present complexes are well represented by the Bleaney–Bowers equation,[37]

$$\chi_A = \frac{Ng^2\beta^2}{kT}\left(\frac{1}{3+\exp(-2J/kT)}\right)+N\alpha, \qquad (4)$$

where χ_A is the susceptibility per copper atom, $-2J$ is equal to the energy separation between the spin–singlet and spin–triplet states, and the other symbols have their usual meanings. The best-fit parameters of $-2J$, g, and $N\alpha$ were obtained by a nonlinear least-squares fitting procedure. The quantity of the fit was estimated by means of a discrepancy index,

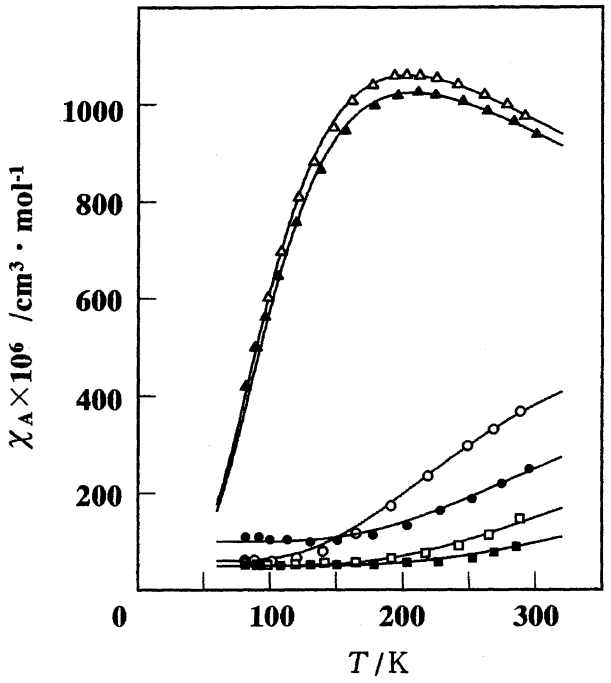


Fig. 6. Temperature dependence of magnetic susceptibilities for **1** (○), **2** (●), **3** (□), **4** (■), **5** (△), and **6** (▲). The solid curves were obtained as described in the text.

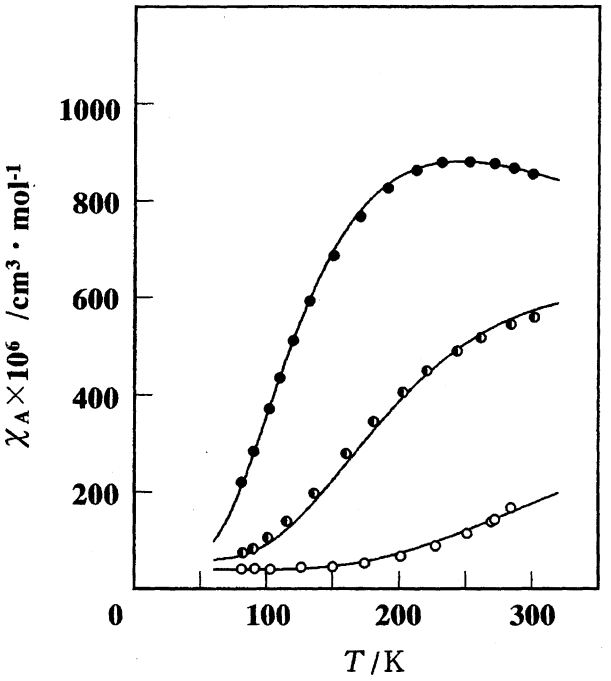


Fig. 7. Temperature dependence of magnetic susceptibilities for **7** (○), **8** (●), and **9** (◐).

$$\sigma_{dis} = \sqrt{\frac{\sum(\chi_{obsd} - \chi_{calcd})^2}{\sum \chi^2_{obsd}}}. \quad (5)$$

The values of $-2J$, g, $N\alpha$, μ_{eff} and σ_{dis} are summarized in Table 6. The close agreement between the observed and calculated temperature dependence of the magnetic susceptibility is powerful evidence for a binuclear structure of all the complexes presented here.

Table 6. Magnetic Data for Complexes **1**—**9**

Complex	$-2J$ / cm^{-1}	g	$N\alpha \times 10^6$ / cm^3 mol^{-1}	μ_{eff} B.M. (T/K)	$\sigma_{dis} \times 10^2$
1	576	2.20	60	0.84 (288.7)	3.53
2	755	2.20	100	0.59 (294.9)	4.30
3	847	2.20	50	0.47 (287.9)	5.59
4	992	2.13	50	0.30 (285.5)	5.94
5	227	2.08	60	1.46 (291.6)	0.71
6	231	2.06	60	1.45 (300.3)	1.82
7	777	2.20	40	0.54 (284.3)	4.96
8	274	2.07	60	1.38 (300.4)	0.75
9	438	2.14	60	1.10 (301.6)	3.63

The magnetic properties for the complexes indicated the existence of an antiferromagnetic interaction. It has been found that the magnitude of the magnetic interaction in di-alkoxo-bridged binuclear copper(II) complexes depends on the Cu–Cu distance, the Cu–O–Cu bridging angle, the planarity around each Cu atom, and the geometry of the bridging alkoxo oxygen atom.[9—11] The $-2J$ values and the structural data for complexes **3**, **4**, **7**, and **9** are summarized in Table 7. An inspection of the data in Table 7 reveals that the $-2J$ values for these complexes are closely connected with the bond distances of Cu1′–O1 (longer bridge), whereas the values are unrelated to the bond distances of Cu1–O1 (shorter bridge). The $-2J$ values for the complexes are represented as a function of the Cu1′–O1 bond distance in Fig. 8. The best least-squares line through their available values has a slope of -21096 cm^{-1} Å^{-1} and an intercept of 41794 cm^{-1} with an R^2 coefficient of 0.958. The elongation of the Cu–O bridging bond distance reduces the overlap of the magnetic orbitals, leading to a reduction in the magnitude of the exchange interaction.[38] This is a very novel example of binuclear copper(II) complexes in which a linear correlation between the $-2J$ value and the bridging bond distance (longer bridge) has been observed unequivocally. The $-2J$ values for the complexes are also correlative with the average of the Cu–O bridging bond distances. However, the quality of the best least-squares fitting with an R^2 coefficient of 0.853 is not better than that for $-2J$ vs. Cu1′–O1. From the data given in Table 7 and other structural data for complexes **3**, **4**, **7**, and **9**, it should be noted that there are no systematic relations between the $-2J$ value and each of the other structural factors, except for the Cu1′–O1 distance. For example, the Cu1$\cdots$O3$_{carboxylato}$ distances of the complexes (the average values for **4** and **9**) have less connection with the $-2J$ values (the order of increase in the Cu1$\cdots$O3$_{carboxylato}$ distances is **3**>**7**>**4**>**9** whereas the order in the $-2J$ values is **4**>**3**>**7**>**9**), though the shorter Cu1$\cdots$O3$_{carboxylato}$ distances leads to a larger deviation of the Cu atom from the basal plane. This does not mean that these structural factors are unim-

Table 7. Structural Data[a] and $-2J$ Values for Complexes **3**, **4**, **7**, and **9**

Complex	Cu1–O1–Cu1′ / °	Solid angle around O1/°	Cu1–Cu1′ / Å	Cu1-basal[b] / Å	Cu1–O1 (shorter)/Å	Cu1′–O1 (longer)/Å	$-2J$ / cm^{-1}
3	105.5(2)	359.8	3.069(3)	0.06	1.918(5)	1.938(5)	847
4	103.3(3)	358.6	3.021(3)	0.11	1.916(7)	1.936(7)	992
7	104.2(3)	356.4	3.051(7)	0.10	1.919(5)	1.946(5)	777
9	103.1(7)	358.6	3.029(6)	0.15	1.91(1)	1.96(1)	438

a) Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. Estimated standard deviations in parentheses are average esd's for an individual distance or angle. b) Deviation of Cu atom from the O_3S coordination plane.

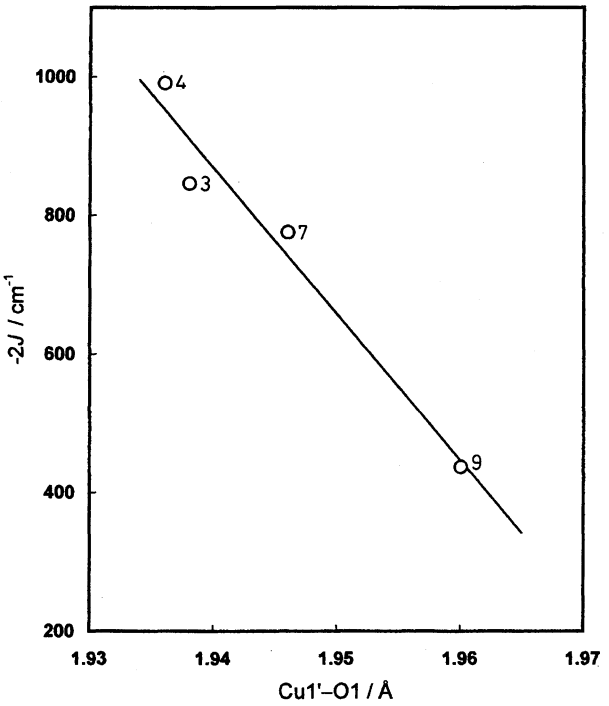


Fig. 8. A plot of the Cu1′–O1 bond distances between the $-2J$ values for **3**, **4**, **7**, and **9**.

portant, but only that they do not vary enough to play a significant role.

The relation between the magnetism of μ-tetrakis-(carboxylato)-bridged binuclear copper(II) complexes, $[Cu(RCOO)_2 \cdot L]_2$ (where L=terminal monodentate ligands such as pyridine), and the physicochemical nature of R is still a greatly disputed subject.[14,39] Regarding the influence of the R group on the magnetism in the present complexes, however, no significant relation was observed; the order of increase in the pK_a of the parent acid RCOOH is **1**>**4**>**2**>**3**>**5**>**6**, whereas the order in the $-2J$ values in **4**>**3**>**2**>**1**>**6**>**5** for the $[Cu(RCOO)(HL^1)]_2$ complexes. Furthermore, no immediate connection exists between the Cu1–O2 distance and the pK_a of the parent acid RCOOH: The average distances are 1.928(7) for **4** and 1.96(1) Å for **9**, whereas both complexes have the same carboxylate.

Although the crystal structures for **1**, **2**, **5**, **6**, and **8** have not yet been determined, the strength of the antiferromagnetic interaction observed for these complexes seems to be dependent on the Cu–O bridging distance, since the IR and electronic spectra for these complexes are very similar to those for the other complexes. We have just prepared and determined the structure of the alkoxo-bridged binuclear copper(II) complex with the O_3S coordination plane, $[Cu(4\text{-}CH_3C_6H_4COO)(L^3)]$ (where L^3=anion of 1,3-diethyl-1-hydroxymethylthiourea), similar to the present complexes.[40] A set of the $-2J$ value (700 cm^{-1}) and the longer bridging bond distance trans to the sulfur (1.947(7) Å) for this complex appears to be in fairly good agreement with the best least-squares line: The $-2J$ value is smaller by 20 cm^{-1} than the estimated value from the bridging bond distance. This fact indicates that the STE of sulfur is effective in alkoxo-bridged binuclear copper(II) complexes with thione containing ligands, and that the strength of the antiferromagnetic interaction is closely connected with the longer bridging bond distance.

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Function minimized: $\sum w(|F_o|-|F_c|)^2$,
where $w=4F_o^2/\sigma^2(F_o^2)$.
Standard deviation of an observation of unit weight:
$[\sum w(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$
where N_o=number of observations,
N_v=number of variables.

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