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Magnetic Properties and Crystal Structure of Binuclear Copper(II) Complexes with 1,3-Bis(hydroxymethyl)-2-imidazolidinethione

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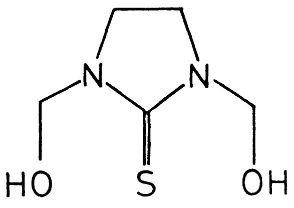
Reaction of copper(II) carboxylates with 1,3-bis(hydroxymethyl)-2-imidazolidinethione (H_2L) gives a new series of binuclear copper(II) complexes, $[Cu(RCOO)(HL)]_2$ (where R=methyl and substituted phenyl). The magnetic data for the complexes conform to the usual dimer equation with values of -2J ranging from 227 - 1023 cm^{-1}.

Recently, several reports have appeared on the synthesis and magnetism of binuclear copper(II) complexes with sulfur donor ligands,$^{1-6)}$ though few on those with thione derivatives so far. This may be due to both the high reducing and poor coordinating ability of thione sulfur atom.


H_2L

As a part of a continuing project on binuclear copper(II) complexes of sulfur-containing ligands, we have prepared a new series of binuclear copper(II) complexes with 1,3-bis(hydroxymethyl)-2-imidazolidinethione, $[Cu(RCOO)(HL)]_2$ (where R=CH_3, C_6H_5, 2-$CH_3C_6H_4$, 4-$CH_3C_6H_4$, 2-ClC_6H_4, and 2-BrC_6H_4). Here we report the preparation and characterization of novel binuclear copper(II) complexes with heterocyclic thione donor ligands.

The complexes were obtained as follows. A solution of copper(II) carboxylate monohydrate or acetone adduct (2.4 mmol) in acetonitrile (30 cm^3) was added to a solution of H_2L (2.4 mmol) in acetonitrile (30 cm^3). The mixture was stirred for 0.5 h at room temperature. The separated dark green crystals were collected, washed with acetonitrile, and dried in vacuo at room temperature. No binuclear copper(II) complexes free from reduced impurities were obtained when methanol or ethanol was used as a solvent instead of acetonitrile.

X-Ray structure analysis$^{7)}$ of $[Cu(2\text{-}CH_3C_6H_4COO)(HL)]_2$ revealed that two copper atoms are linked by two alkoxo-bridges with a separation of 3.069(3) Å (Fig. 1). The coordination around each copper atom is square planar with one

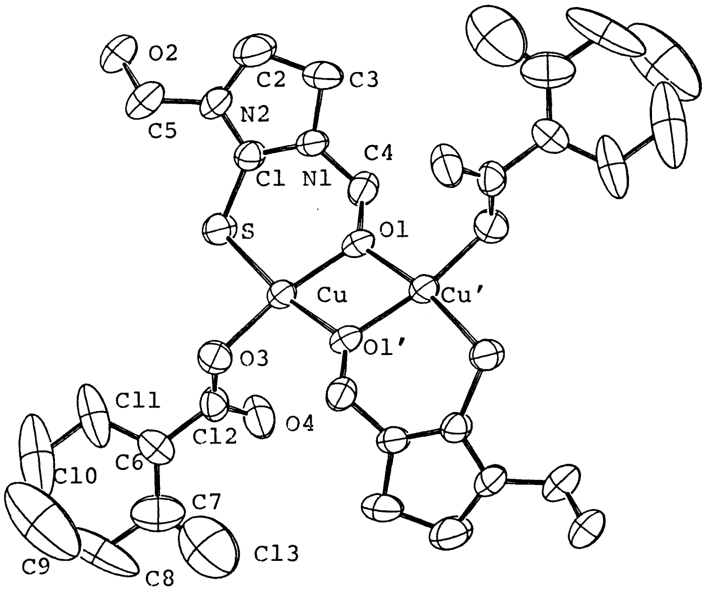


Fig. 1. Perspective view of $[Cu(2\text{-}CH_3C_6H_4COO)(HL)]_2$. The crystal structure consists of alkoxo-bridged binuclear unit which has a center of symmetry. Selected bond lengths (l/Å) and angles (φ/°): Cu...Cu' 3.069(3), Cu-O1 1.918(5), Cu-O1' 1.938(5), Cu-O3 1.908(5), Cu-S 2.308(3), S-C1 1.705(7), O1-C4 1.392(9); Cu-O1-Cu' 105.5(2), O1-Cu-O1' 74.5(2), O1-Cu-S 95.4(2), O3-Cu-S 92.9(2), O3-Cu-O1' 97.0(2), O1-Cu-O3 170.1(2), O1'-Cu-S 169.9(2), C4-O1-Cu 123.6(5), C4-O1-Cu' 130.7(5), C1-S-Cu 98.9(3).

sulfur donor, two alkoxo-oxygens of H_2L, and one oxygen donor of 2-toluate. The copper atom deviates slightly from the basal plane by 0.084 Å. Each alkoxo group is symmetrically bound with the Cu-O1 bond shorter than the Cu-O1' bond. The Cu...O4 distance (2.940(6) Å) is considerably longer than those in copper(II) carboxylate complexes (2.49 - 2.71 Å)[8] for which the carboxylate coordination was identified as intermediate between strictly unidentate and strictly bidetate-chelate.[9] Thus, the carboxylate coordination is a unidentate type. The Cu-O-Cu' bridging angle is 105.5(2)° corresponding to the maximum value of those found in other di-alkoxo-bridged copper(II) dimers which range from 98 - 105°.[5,10] The Cu-S bond length (2.308(3) Å) falls in the range of those found for copper(II) complexes with thioether ligands (2.30 - 2.36 Å)[5] and copper(I) complexes with heterocyclic thione donors (2.20 - 2.39 Å).[11]

The magnetic susceptibilities of the complexes were determined over the temperature range of 80-300 K. Some of the magnetic susceptibility data are shown in Fig. 2. The magnetic properties for the complexes are well represented by the usual expression for the molar susceptibility of an isolated pair of interacting ions of spin 1/2,[12] indicating the existence of an antiferromagnetic interaction. The best-fit parameters of $-2J$, g, and $N\alpha$ were obtained by a nonlinear least-squares fitting procedure. These values are summarized in Table 2. The close agreement between the observed and calculated magnetic

Table 1. Magnetic data of $[Cu(RCOO)(HL)]_2$ complexes

R	$-2J/cm^{-1}$	g	$N\alpha \times 10^6/emu^{a)}$
CH_3	576	2.20	60
C_6H_5	755	2.20	100
$2\text{-}CH_3C_6H_4$	847	2.20	50
$4\text{-}CH_3C_6H_4$	1023	2.20	50
$2\text{-}ClC_6H_4$	227	2.08	60
$2\text{-}BrC_6H_4$	231	2.06	60

a) Nα is temperature independent paramagnetism per gram-ion of copper(II). 1 emu=$4\pi \times 10^{-6}m^3$.

susceptibilities of the present complexes is powerful evidence for a binuclear structure. It has been found that the magnetic interaction in di-alkoxo-bridged binuclear copper(II) complexes is dependent on both the Cu-O-Cu bridging angle and planarity of the Cu_2O_2 plane.[10)] The -2J value(847 cm^{-1}) for $[Cu(2\text{-}CH_3C_6H_4COO)(HL)]_2$ is very large as expected from its large Cu-O-Cu angle (105.5°) and the planarity of the Cu_2O_2 plane.

The reflectance spectra of the present complexes are very similar in shape. The spectra show three bands having maxima at 30 - 34×10^3, ca. 25×10^3, and ca. 15×10^3 cm^{-1}. The band around 25×10^3 cm^{-1} is attributable to the complex formation between the ligand and copper(II) ion, because no bands were observed for the ligand in the near UV region. This band is assigned to the charge-transfer band from the non-bonding pπ-orbital on the bridging oxygen to a vacant 3d-orbital of the copper(II) ions.[13)] The band around 30 - 34×10^3 cm^{-1} may be assigned to the $\sigma(S) \longrightarrow d(Cu)$ charge transfer band.[4,14)]

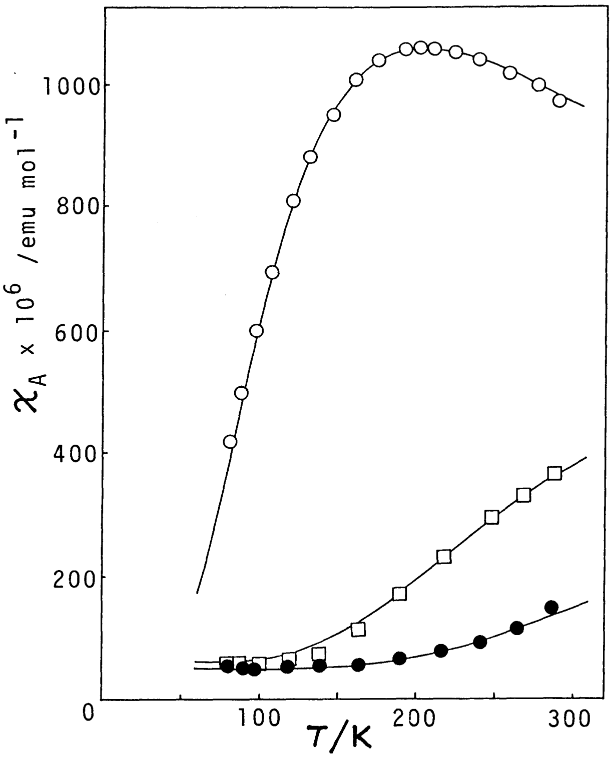


Fig. 2. Temperature dependence of magnetic susceptibilities of $[Cu(RCOO)(HL)]_2$ complexes: (□) R=CH_3, (●) R=$2\text{-}CH_3C_6H_4$, and (○) R=$2\text{-}ClC_6H_4$ The solid curves were obtained as described in text.

The IR spectra of the free ligand shows two OH stretching bands at 3401 and 3258 cm^{-1}, which are attributed to the intermolecular hydrogen bond and intramolecular hydrogen bond respectively. The present complexes possess only one band around 3200 cm^{-1}. This indicates that one of OH groups in the free ligand lose the alcoholic proton upon complexation. The antisymmetric(ν_{as}COO, 1588 - 1610 cm^{-1}) and symmetric(ν_{s}COO, 1376 - 1387 cm^{-1}) carboxylate stretching vibration in the present complexes were shifted to higher and lower frequencies than those in the corresponding ionic carboxylates (ν_{as}COO, 1578 - 1580 cm^{-1}; ν_{s}COO, 1414 - 1420 cm^{-1})[15] respectively. This indicates that the carboxylate coordination in the present complexes is a unidentate type[15a,16] which is novel in copper(II) complexes.

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7) The crystal data are as follows: $Cu_2C_{26}H_{32}N_4O_8S_2$, MW=719.77, monoclinic, $P2_1/c$, a=12.48(2), b=9.228(8), c=14.44(1) Å, β=115.07(5)°, V=1507(2) $Å^3$, Z=2, D_m=1.58(1), D_x=1.59 g cm^{-3}. Intensity measurements were carried out for 2θ<120° on a Rigaku AFC-5S four-circle diffractometer with Cu Kα radiation. The structure was solved using TEXRAY software package programs(TEXSAN). The positional parameters of the copper and sulfur atoms were determined by the direct method. The remaining non-hydrogen atoms were located by the Fourier maps of the difference direct method. Refinements were carried out by the full matrix least-square method. The final residual value was R=0.069 for 1731 reflections with $|F_o|>3\sigma(|F_o|)$.
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