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Magnetic Properties and Crystal Structure of a Novel Di-μ-Formato-Bridged Binuclear Copper(II) Complex with 1,10-Phenanthroline

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A di-μ-formato-bridged binuclear copper(II) complex with 1,10-phenanthroline, $[Cu(HCOO)(phen)(H_2O)]_2(NO_3)_2 \cdot 4H_2O$, has been prepared and characterized by magnetic susceptibilities (80-300 K) and X-ray structure analysis. The magnetic data conform to the usual dimer equation with a singlet-triplet energy separation of $-2J=125$ cm^{-1}.

A large number of binuclear copper(II) carboxylate adducts, $[Cu(RCOO)_2 \cdot L]_2$, have been isolated and their magneto-structural correlations have extensively been studied.[1-3] In most $[Cu(RCOO)_2 \cdot L]_2$ complexes, two copper(II) ions are bridged in pairs by four carboxylato groups (RCOO) and two additional unidentate ligands (L) occupy the terminal axial positions, resulting in a cage-type dimeric structure. In those studies on the copper(II) carboxylates, only a few copper(II) complexes with two bridging carboxylato groups have been reported.[4-7] Here we report the preparation and characterization of $[Cu(HCOO)(phen)(H_2O)]_2^{2+}$ complex as the first example of di-μ-formato-bridged binuclear copper(II) complexes.

The complex was obtained as follows. Formic acid (10 mmol) and 1,10-phenanthroline (10 mmol) were dissolved in 50 ml of water, and the resulting solution was adjusted to pH 5.0 with 1 mol dm^{-3} aqueous NaOH. To this solution 10 ml of 1 mol dm^{-3} aqueous $Cu(NO_3)_2$ was added under stirring, and then the pH was adjusted to 4.0. Earlier precipitates were filtered off, and the filtrate was concentrated to one third of its volume. The deep blue crystals precipitated were collected, washed with water, and air-dried at room temperature.

X-Ray structure analysis[8] revealed the structure of the complex consisting of dimeric $[Cu(HCOO)(phen)(H_2O)]_2^{2+}$ cations with five-coordinated copper ions linked by two formato ions in a syn-syn bridging arrangement (Fig. 1). The coordination around each copper atom is approximately square pyramidal with two nitrogen donors of a phenanthroline, two oxygen donors of two carboxylates occupying basal sites and an axial coordination of the water molecule. This bond

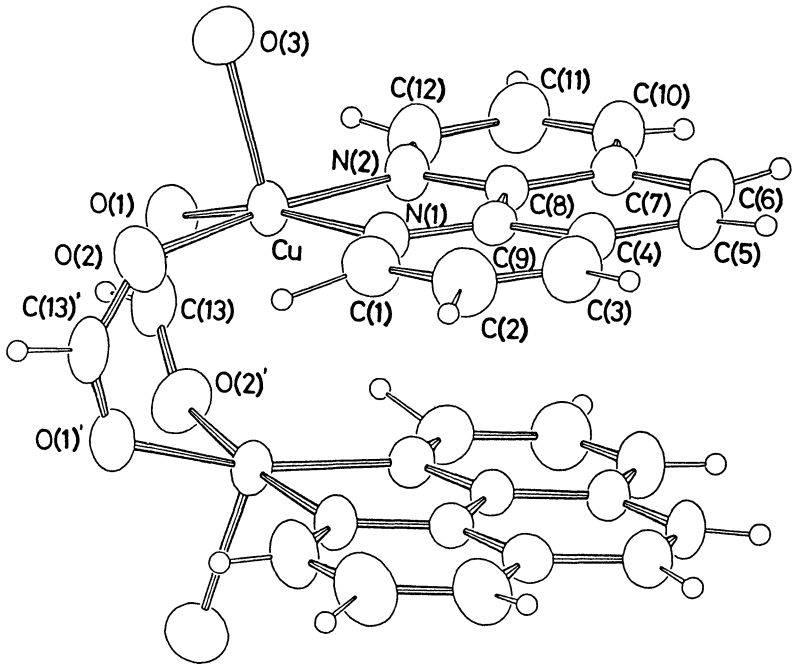

Fig. 1. Perspective view of $[Cu(HCOO)(phen)(H_2O)]_2^{2+}$. The complex cation has a twofold axis of rotation through the center of the two formate carbon atoms. Selected bond lengths (1/Å) and angles (φ/°): Cu...Cu' 3.103(2), Cu-O(1) 1.962(4), Cu-O(2) 1.959(4), Cu-O(3) 2.161(5), Cu-N(1) 2.010(4), Cu-N(2) 2.007(4), O(1)-C(13) 1.245(7); O(1)-Cu-N(1) 164.0(2), O(2)-Cu-N(2) 173.5(2), Cu-O(1)-C(13) 125.2(4), Cu-O(2)-C(13)' 132.1(4), O(1)-C(13)-O(2)' 127.7(5).

distance Cu-O(H_2O) is significantly longer than those of Cu-O(formate) bonds in the basal plane. The molecular structure is very similar to that in $[Cu(phC_2H_4CO_2)(phen)(H_2O)]_2(NO_3)_2 \cdot 4H_2O$.[7]

A noteworthy feature of this structure is the Cu...Cu distance of 3.103(2) Å, longer by 0.3-0.5 Å than the corresponding ones in usual copper(II) carboxylate dimers of $[Cu(RCOO)_2 \cdot L]_2$.[2,3,9] This elongation of the Cu...Cu distance in the present complex is reflected in a significant increase in the mean Cu-O-C bond angle (128.6°): the typical value of ca. 123° is found in the structures of $[Cu(RCOO)_2 \cdot L]_2$ complexes.[2] However, in spite of the longer Cu...Cu distance the Cu-O-C-O-Cu' distance (6.406 Å) through the carboxylate bridges and the O-C-O opening angle(127.7°) fall within the range of values given for $[Cu(RCOO)_2 \cdot L]_2$ by Doedens.[2] Although the dihedral angle between the basal coordination planes around each Cu atom is 22.4°, the angle between the phenanthroline planes is only 5.7°.

The magnetic property of the present complex is clearly of interest because of its status as the first documented example of di-μ-formato bridged dimeric copper(II) complex. The magnetic data are represented graphically in Fig. 2. The best fit of the magnetic data to the usual expression for the molar susceptibility of an isolated pair of interacting ions of spin 1/2[10] was obtained for g=2.18, $-2J=125$ cm^{-1}, and $N\alpha=60\times10^{-6}$ emu mol^{-1}. The -2J value of

125 cm^{-1} for the present complex is considerably smaller than those found in tetra-μ-formato-bridged complexes $[(CH_3)_4N]_2[Cu(HCOO)_2(NCS)]_2$ ($-2J = 485 cm^{-1}$)[11] and $[Cu(HCOO)_2(urea)]_2$ ($-2J \simeq 500 cm^{-1}$)[12]. Although the Cu...Cu distance (3.103(2) Å) in this case is much longer than those in these copper(II) formates[11,13,14], recent works have clearly demonstrated that the Cu...Cu separation is not the major factor in determining the -2J value in these systems.[3,14] Therefore, such a decrease in antiferromagnetic interaction can be explained in terms of a decrease in the number of the bridging formato ions, through which superexchange interaction is operative: from four to two in the present complex. An analogous dimeric structure bridged by two carboxylate groups in the syn-syn bridging type exists in crystals of the *p*-toluidine adduct of copper(II) propionate, $[Cu_2(C_2H_5COO)_4(p\text{-toluidine})_2]_n$,[4] and di-μ-propionato-*O*,*O*'-bis[*N*-*p*-tolylsalicylideneaminatocopper(II)], $[Cu(C_2H_5COO)(salN\text{-}p\text{-tolyl})]_2$.[6] The structures of these complexes are very similar to each other and basically composed of di-μ-propionato-bridged dimers which are linked into one-dimensional polymeric chains by relatively long monatomic oxygen-bridges. The -2J values (105 cm^{-1} and 101 cm^{-1}) of these complexes are about one third of that of anhydrous copper(II) propionate ($-2J = 300 cm^{-1}$).[15] The magnitude of antiferromagnetic interaction observed in the present complex is much stronger than those in these propionate complexes. As a continuation of this study, we have recently prepared an analogous dimeric copper(II) acetate complex, $[Cu(CH_3COO)(phen)(H_2O)]_2(NO_3)_2 \cdot 4H_2O$, for which the estimated -2J value was 86 cm^{-1}.[16] These facts indicate that binuclear copper(II) formates show a stronger antiferromagnetic interaction than copper(II) acetates or propionates not only in the complexes with the cage-type structure but also in those with di-μ-carboxylato bridges.

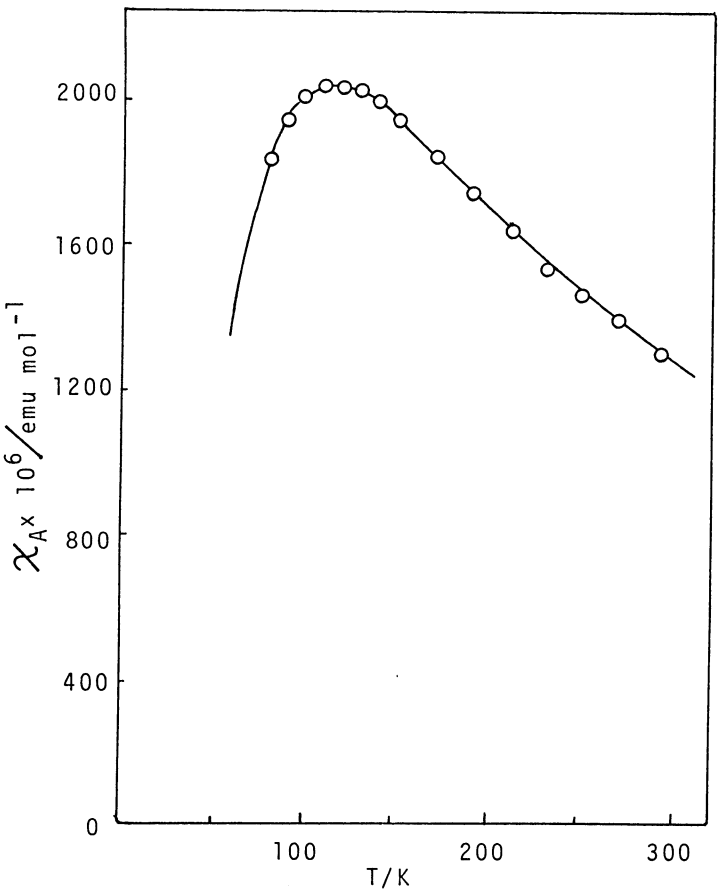

Fig. 2. Temperature dependence of magnetic susceptibilities of $[Cu(HCOO)(phen)(H_2O)]_2(NO_3)_2 \cdot 4H_2O$

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8) The crystal data are as follows: $Cu_2C_{26}N_4H_{22}O_6 \cdot 2NO_3 \cdot 4H_2O$, MW 809.6, monoclinic, I2/a, a=18.850(2), b=9.775(2), c=17.752(2)A, β=99.03(1), V=3230.4(8) $Å^3$, Z=4, Dm=1.68(2), Dx=1.66 g cm^{-3}. Intensity measurements were carried out for $2\theta \leqq 55°$ on a Rigaku AFC-5 four-circle diffractometer with Mo Kα radiation. The structure was solved by heavy atom method and refined to R=0.055 for 2511 unique reflections. Full details of X-ray structure determination will be published in Bull. Chem. Soc. Jpn.
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