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The First μ_3-Oxalato-Bridged Copper Complex with Tridentate Schiff Base Ligand *N*-Ethyl-*N′*-Salicylidene-1,2-diaminoethane: Synthesis, Structure, and Magnetic Properties

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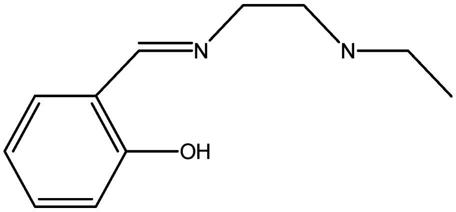
The first μ_3-oxalato-bridged copper(II) complex, $\{[Cu_3(L)_3(\mu_3\text{-}C_2O_4)][Cu(L)(H_2O)](ClO_4)_2\}\cdot 0.5(H_2O)\cdot 0.5(CH_3OH)$, where HL = *N*-ethyl-*N′*-salicylidene-1,2-diaminoethane, has been synthesized and characterized by variable-temperature magnetic susceptibility measurement. The complex exhibits ferromagnetic coupling between the oxalato-bridged copper atoms and antiferromagnetic coupling between the oxygen-bridged copper atoms.

The study of the magnetic interactions in di- and polynuclear metal complexes is playing a key role in the development of magnetochemistry. Oxalate dianion, a typical bis-bidentate ligand, can bind with one or two metal centers, which allows successful synthesis of homo- and/or heteronuclear metal complexes with interesting stereochemistry.[1] Hoffmann[2] has thoroughly discussed the magnetic interactions of dinuclear oxalato-bridged complexes on the basis of molecular orbital theory. Kahn and colleagues[3] described a theory to predict the magnetic interactions in oxalate bridge copper(II) binuclear complexes. In the present work, we report the structural and magnetic characterization of a μ_3-oxalato-bridged copper(II) complex $\{[Cu_3(L)_3(\mu_3\text{-}C_2O_4)][Cu(L)(H_2O)](ClO_4)_2\}\cdot 0.5(H_2O)\cdot 0.5(CH_3OH)$, where HL = *N*-ethyl-*N′*-salicylidene-1,2-diaminoethane. As far as we know, this is the first report of a copper(II) complex with $\mu_3\text{-}C_2O_4^{2-}$.

A tridentate ligand (Chart 1) was prepared by refluxing a solution of 1 mmol of salicylaldehyde and 1 mmol of *N*-ethylethylenediamine in 10 mL of ethanol for 1 h. The complex $\{[Cu_3(L)_3(\mu_3\text{-}C_2O_4)][Cu(L)(H_2O)](ClO_4)_2\}\cdot 0.5(H_2O)\cdot 0.5(CH_3OH)$ was synthesized by adding 1 mmol of $Cu(ClO_4)_2\cdot 6H_2O$ in 10 mL of methanol to the ligand solution prepared above. Then 0.5 mmol of $K_2[Cu(C_2O_4)_2]\cdot 2H_2O$ in 5 mL of water was added. X-ray quality single crystals were obtained by slow evaporation of the resulting solution.

Chart 1



The structure[4] of the tetranulear complex contains $[Cu_3(L)_3(\mu_3\text{-}C_2O_4)]^+$ and $[Cu(L)(H_2O)]^+$ cations and ClO_4^- anions. A perspective drawing of the cations is shown in Figure 1, and selected bond lengths and angles are listed in Table 1. In the $[Cu_3(L)_3(\mu_3\text{-}C_2O_4)]^+$ cation, Cu1, Cu2, and Cu3 are bridged by $C_2O_4^{2-}$ to form an asymmetric unit. Cu1 has a distorted square planar geometry in $[CuN_2O_2]$ with average Cu−O and Cu−N bond lengths of 1.923(12) and 1.978(16) Å, respectively. Cu2 and Cu3 are in a $[CuN_2O_3]$ square pyramidal environment. The basal plane of each copper contains two N and one O donor atoms from the tridentate Schiff base ligand and one O donor atom from

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(4) Crystal data for the complex: $C_{46.50}H_{65}Cl_2Cu_4N_8O_{18}$, $M_w = 1349.13$, monoclinic, space group $P2(1)/c$, $a = 17.766(5)$ Å, $b = 14.662(4)$ Å, $c = 23.412(7)$ Å, $\beta = 106.469(6)°$, $V = 5848(3)$ Å^3, $Z = 4$, $D_c = 1.532$ g cm^{-3}, $F(000) = 2776$, $\mu = 1.600$, $T = 293(2)$ K, crystal size 0.30 × 0.25 × 0.20 mm, total reflections 23675, independent reflections 10323 ($R_{int} = 0.1443$), with $[I > 2\sigma(I)]$ 3623 observed data and 689 parameters. Bruker Smart 1000 diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), data collection in the range $1.20° < \theta < 25.03°(-18 \leq h \leq 21, -17 \leq k \leq 17, -26 \leq l \leq 27)$, and absorption effects (max, min transmission = 0.4703 and 0.6454). The structure was solved by direct methods due to Sheldrick and refined by full-matrix least squares on F^2 using SHELXL-97 (Sheldrick, G. M., University of Göttingen). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located from a difference Fourier map. Refinement converged with wR2 = 0.1872 for all data and R1 = 0.0688 for $2\sigma(I)$ data. CCDC: 200261.

10.1021/ic034003z CCC: $25.00

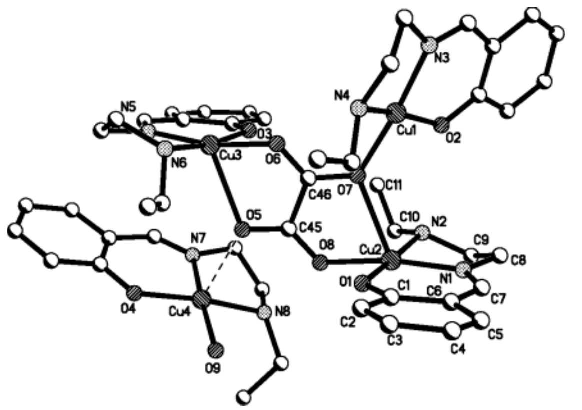

Figure 1. Perspective view of unit of the complex.

Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for the Complex

Bond Lengths			
Cu(1)−O(2)	1.887(6)	Cu(1)−N(3)	1.915(8)
Cu(1)−O(7)	1.958(6)	Cu(1)−N(4)	2.041(8)
Cu(2)−N(1)	1.920(9)	Cu(2)−O(1)	1.930(7)
Cu(2)−O(8)	2.002(6)	Cu(2)−N(2)	2.019(8)
Cu(2)−O(7)	2.366(6)	Cu(3)−O(3)	1.895(7)
Cu(3)−N(5)	1.909(9)	Cu(3)−O(6)	2.020(6)
Cu(3)−N(6)	2.022(9)	Cu(3)−O(5)	2.376(6)
Cu(4)−O(4)	1.910(7)	Cu(4)−N(7)	1.928(10)
Cu(4)−N(8)	1.999(9)	Cu(4)−O(9)	2.006(7)
Bond Angles			
O(2)−Cu(1)−N(3)	99.4(3)	O(2)−Cu(1)−O(7)	86.5(3)
N(3)−Cu(1)−O(7)	173.9(3)	O(2)−Cu(1)−N(4)	165.1(3)
N(3)−Cu(1)−N(4)	84.5(3)	O(7)−Cu(1)−N(4)	96.2(3)
N(1)−Cu(2)−O(1)	93.7(3)	N(1)−Cu(2)−O(8)	169.9(3)
O(1)−Cu(2)−O(8)	87.9(3)	N(1)−Cu(2)−N(2)	83.6(4)
O(1)−Cu(2)−N(2)	174.7(3)	O(8)−Cu(2)−N(2)	95.6(3)
N(1)−Cu(2)−O(7)	113.9(3)	O(1)−Cu(2)−O(7)	88.2(2)
O(8)−Cu(2)−O(7)	76.1(2)	N(2)−Cu(2)−O(7)	88.7(3)
O(3)−Cu(3)−N(5)	93.9(4)	O(3)−Cu(3)−O(6)	87.5(3)
N(5)−Cu(3)−O(6)	167.6(3)	O(3)−Cu(3)−N(6)	170.7(4)
N(5)−Cu(3)−N(6)	85.2(4)	O(6)−Cu(3)−N(6)	91.5(3)
O(3)−Cu(3)−O(5)	86.3(3)	N(5)−Cu(3)−O(5)	116.6(3)
O(6)−Cu(3)−O(5)	75.8(3)	N(6)−Cu(3)−O(5)	102.4(3)
O(4)−Cu(4)−N(7)	93.6(4)	O(4)−Cu(4)−N(8)	169.8(3)
N(7)−Cu(4)−N(8)	83.6(4)	O(4)−Cu(4)−O(9)	89.8(3)
N(7)−Cu(4)−O(9)	176.5(4)	N(8)−Cu(4)−O(9)	92.9(4)

the bridging oxalate ligand. These Cu−O and Cu−N bonds vary from 1.895(7) to 2.020(6) Å and from 1.909(9) to 2.022(9) Å, respectively. The remaining oxalate-oxygen atom occupies the apical position of the coordination sphere with bond lengths of 2.366(6) Å (Cu2−O7) and 2.376(6) Å (Cu3−O5). The copper atoms Cu2 and Cu3 are displaced by 0.048(2) and 0.183(1) Å from their basal planes toward the apical atoms O7 and O5, respectively. The distances of Cu···Cu are 3.871(1) Å (Cu1···Cu2), 5.597(2) Å (Cu2···Cu3), and 5.079(1) Å (Cu1···Cu3). The Cu2···Cu3 distance is slightly longer than those of 5.1−5.4 Å found in dimeric copper(II) complexes.[5] The coordination geometry of the other cation, $[Cu(L)(H_2O)]^+$, is a four-coordinated square with average Cu−O and Cu−N bond lengths of 1.958(14) and 1.964(19) Å, respectively. The distance between Cu4 and O5 of the bridging oxalate is 2.544(2) Å, showing a weakly coordinated interaction.[6]

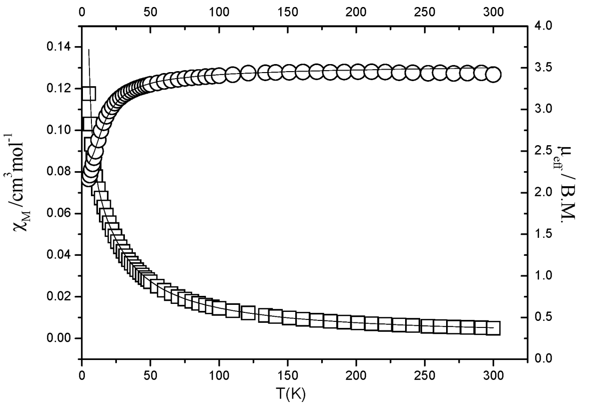

Figure 2. Temperature dependence of χ_M and μ_{eff} for the complex: ○, μ_{eff}; □, χ_M. The solid lines are theoretical fits based on eq 1.

In the oxalate dianion, the C−O bond lengths range from 1.239(11) to 1.280(10) Å and the C−C bond length is 1.547(13) Å. These lengths are typical for oxalato-bridged binuclear complexes.[1b,7] The oxalate dianion is planar (maximum deviation, 0.0338 Å). Cu1, Cu2, and Cu3 deviate by 0.144(2), −0.478(2), and 0.589(2) Å from the plane, respectively. The dihedral angles between the mean copper basal planes of Cu1, Cu2, and Cu3 and the oxalate plane are 53.0(3)°, 97.6(2)°, and 104.4(3)°, respectively. The bite angles formed by the Cu atoms and the two O atoms of ligand are 76.1(2)° (O7−Cu2−O8) and 75.8(3)° (O5−Cu3−O6). The values are close to those reported for oxalato-bridged copper(II) complexes containing the asymmetrical bis-chelating oxalate.[7b,8]

The perchlorate anions are very disordered, with the oxygen atoms occupying seven sites. In addition, a number of hydrogen bonds exist in the crystal. The H atoms of C7, C43, N4, N8, and the water molecules are all involved in hydrogen bonds with the oxygen atoms of the oxalate dianion. An extensive 3-D network of hydrogen bonds stabilizes the crystal structure.

The X-band ESR spectrum of the complex at room temperature consists of a symmetric feature centered at $g = 2.09$ in the solid state. No splitting has been observed at 110 K.

Magnetic susceptibility measurements of a crystalline sample were carried out in the temperature range 5−300 K on a Maglab system2000 magnetometer at a field strength of 10000 G. The μ_{eff} decreases from 3.41 μ_B at room

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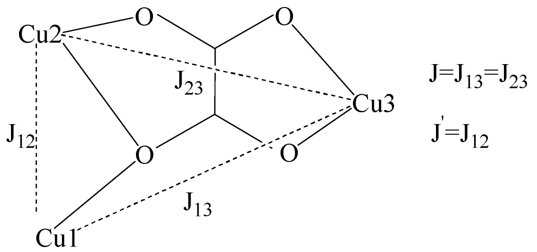
Chart 2



temperature to 2.17 μ_B at 5 K (Figure 2). This curve is typical of an overall antiferromagnetic coupling between copper(II) ions within the trinuclear Cu(II) unit.

Since the complex contains $[Cu_3(L)_3(\mu_3\text{-}C_2O_4)]^+$ and $[Cu(L)(H_2O)]^+$ cations, the χ_M can be divided into two parts, χ_{tri} and χ_{Cu}. In the $[Cu_3(L)_3(\mu_3\text{-}C_2O_4)]^+$ cation, there are three different coupling constants. In a simplified view, we considered that the exchange integrals between the copper ions bridged by oxalate are identical ($J = J_{13} = J_{23}$). J' is the exchange integral between the copper ions bridged by oxygen (Chart 2). The expression for the susceptibility then becomes

$$\chi_M = \chi_{tri} + \chi_{Cu} \tag{1}$$

where

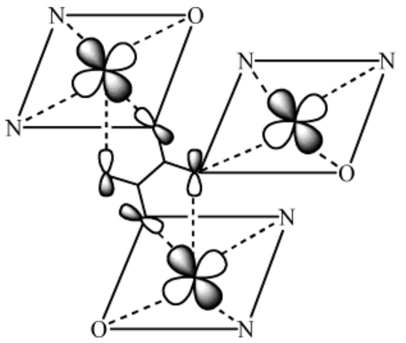
$$\chi_{tri} = \frac{Ng^2\beta^2}{4\kappa T} \times \left[\frac{10\exp(J/\kappa T) + \exp(-2J/\kappa T) + \exp(-2J'/\kappa T)}{2\exp(J/\kappa T) + \exp(-2J/\kappa T) + \exp(-2J'/\kappa T)}\right] + N\alpha$$

and

$$\chi_{Cu} = \frac{Ng^2\beta^2}{3\kappa T}\left(\frac{3}{4}\right) = \frac{Ng^2\beta^2}{4\kappa T}$$

in which $N\alpha$, β, κ, and g have their usual meanings. The temperature-independent paramagnetism, $N\alpha$ for the three Cu(II) centers, was taken as 180×10^{-6} cm^3 mol^{-1}. A least-squares fit of the susceptibility data led to the values of $J = 1.48$ cm^{-1}, $J' = -12.82$ cm^{-1}, $g = 2.01$, and $R = 9.47 \times 10^{-3}$. These values confirm the ferromagnetic character of the magnetic interaction between the copper(II) ions via oxalate and the antiferromagnetic interaction between the copper(II) ions via the oxygen atom. Since J' is much larger than J in this system, the copper atoms within the trinuclear unit shows an overall antiferromagnetic coupling.

Chart 3



The oxygen-bridged copper atoms in the complex have a bridge angle (Cu1−O7−Cu2) of 126.8(3)°, which shows antiferromagnetic coupling. This is usually found in oxygen-bridged Cu(II) dimers with bridging angle larger than 97.5°.[9] The weak ferromagnetic interactions of the copper atoms with the oxalate bridge are rare but can be understood using the orbital exchange pathway shown in Chart 3. The values of the tetragonality parameter[10] ($\tau = 0.08$ for Cu2 and 0.05 for Cu3) in the complex are consistent with square pyramidal geometry. The distances between the copper atoms and the coordination atoms in the apical positions (2.366(6) Å for Cu2, 2.376(6) Å for Cu3) are longer than those in the basal planes (1.920(9)−2.019(8) Å for Cu2 and 1.895(7)−2.022(9) Å for Cu3). In this situation the unpaired electron resides in a $d_{x^2-y^2}$ type orbital. According to Kahn's model,[11] the exchange integral (J) can be decomposed in two terms, one ferromagnetic (J_F) and the other antiferromagnetic contributions (J_{AF}). In this model, the value of J_{AF} is proportional to the square of the integral overlap (S^2). In our case (see Chart 3), the value of S is very small and is close to zero (accidental orthogonality), which leads to ferromagnetic coupling. This situation is in agreement with the ferromagnetic interaction observed between copper atoms in other oxalato-bridged copper(II) complexes.[7b,12]

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