Structure and Magnetic Properties of an Oxalic Acid Bridged Dinuclear Copper(II) Complex

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$[LCu\{\mu\text{-}(OH)_2(C_2O_2)\}CuL](ClO_4)_2$, (HL = N,N-dimethyl N-propylsalicylald-imine) was synthesised and its crystal structure was determined. $C_{26}H_{36}Cl_2Cu_2N_4O_{14}$, triclinic space group $P\bar{1}$ with $a = 9.288(9)$, $b = 10.016(11)$, $c = 10.09(2)$ Å and $\alpha = 101.05(11)$, $\beta = 108.22(10)$, $\gamma = 110.22(10)°$, V = 787(2) Å^3, Z = 2. Two copper(II) ions in a distorted square-planar coordination are bridged by an oxalic acid molecule to form dinuclear units. The copper(II) centres are separated by 5.2 Å and antiferromagnetically coupled ($J = -478$ cm^{-1}), which follows from temperature-dependent magnetic susceptibility measurements in the range 12 to 300 K.

Introduction

The most extensively studied dinuclear metal compounds by far are dinuclear copper(II) complexes, where super-exchange interactions occur between two local doublet states of copper(II) ions [1, 2]. The plasticity of the coordination sphere of copper(II) allows such a metal ion to adopt various stereochemistries and consequently different orientations of the resulting magnetic orbitals of the bridge [3].

The influence of the different substituent on the superexchange mechanism of dinuclear copper(II) oxalato complexes were studied [3, 4]. The topology regarding the planarity of the two magnetic orbitals with the bridging plane and the delocalization of the magnetic orbitals towards the bis bidentate bridges gives the two key factors influencing the exchange interaction [2]. A good number of dinuclear oxalato bridged complexes were investigated [3 - 13], but to our knowledge an oxalic acid bridged copper(II) dimer is still unknown. The present work provides the result of an X-ray structure analysis and of a temperature-dependent susceptibility measurement of copper(II) complexes with an oxalic acid bridge having a Schiff base as terminal ligand.

Experimental

Preparation

The ligand HL (N,N-dimethyl N-propylsalicylald-imine) was synthesised by refluxing 10 mmol of N,N-dimethyl 1,3-diaminopropane with 10 mmol of salicylaldehyde in 30 ml of methanol. The resulting mixture gave an orange solution containing the liquid ligand (HL) and this was used as the starting material. 10 mmol of $Cu(ClO_4)_2 \cdot 6H_2O$ was added in solid to a vigorously stirred 30 ml methanol solution of HL (10 mmol). An yellow-green coloured solid appeared after 5 min and was recrystallised from 1:1 methanol-water yielding yellow-green crystals. The elemental analysis suggests the composition $[(HL)_2Cu](ClO_4)_2$. 10 mmol of this solid was dissolved in 100 ml of water and treated with 5 mmol of an aqueous solution (5 ml) of oxalic acid. On standing at room temperature for 3 d black green crystals were obtained. The crystals were thoroughly washed with methanol and chloroform and air dried.

Analysis for $C_{26}H_{16}Cl_2Cu_2N_4O_{14}$
Calcd C 37.7 H 4.3 N 6.8 Cu 15.4 ClO_4 31.8 %,
Found C 37.9 H 4.2 N 6.5 Cu 15.6 ClO_4 31.5 %.

Susceptibility measurements

Magnetic susceptibility measurements of the powdered sample were performed on a Faraday-type magnetometer

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Table I. Crystal data and structure refinement of [LCu{μ-(OH)$_2$(C$_2$O$_2$)}CuL](ClO$_4$)$_2$.

Empirical formula	$C_{13}H_{18}ClCuN_2O_7$
Formula weight	413.28
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 9.288(9)$ Å $b = 10.016(11)$ Å $c = 10.09(2)$ Å $\alpha = 101.05(11)°$ $\beta = 108.22(10)°$ $\gamma = 110.34(8)°$
Volume	787(2) Å^3
Z	2
Density(calculated)	1.744 mg/m^3
Absorption coefficient	1.597 mm^{-1}
F(000)	424
Crystal size	0.5×0.3×0.3 mm
θ Range for data collection	2.26 to 20.03°
Index range	$-7 \leq h \leq 6, -9 \leq k \leq 9, 0 \leq l \leq 9$
Reflection collected	1168
Independent reflections	1168 [R(int) = 0.0000]
Absorption correction	Integration
Max. and min transmission	0.6784 and 0.6156
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1168/0/223
Goodness-of-fit on F^2	1.056
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0282$, $wR2 = 0.0637$
R indices (all data)	$R1 = 0.0282$, $wR2 = 0.0637$
Extinction coefficient	0.005(4)
Largest diff. peak and hole	0.481 and -0.326 e.Å^{-3}

consisting of a microbalance, equipped with an helium continuous flow cryostat. The applied magnetic field was ~ 1.2 T. The experimental susceptibility data were corrected for the underlying diamagnetism [14].

X-ray structure determination

Table II. Selected bond lengths (Å) and bond angles (°) in [LCu{μ-(OH)$_2$(C$_2$O$_2$)}CuL](ClO$_4$)$_2$.

Cu-O(1)	1.867(4) Å	Cu-N(8)	1.947(5) Å
Cu-O(2)	1.997(5) Å	Cu-O(3)	1.991(4) Å
Cu-Cu$^{\#}$	5.20 Å		
O(1)-Cu-N(8)	95.5(2)	O(1)-Cu-O(3)	170.37(14)
N(8)-Cu-O(3)	94.1(2)	O(1)-Cu-O(2)	86.9(2)
N(8)-Cu-O(2)	173.07(14)	O(3)-Cu-O(2)	83.5(2)
O(3)$^{\#}$-C-O(2)	126.1(4)	O(3)$^{\#}$-C-C$^{\#}$	117.6(6)
O(2)-C-C$^{\#}$	116.3(6)	C(1)-O(1)-Cu	128.1(3)
C-O(2)-Cu	111.4(3)	C$^{\#}$-O(3)-Cu	110.9(3)

Symmetry transformations used to generate equivalent atoms: $^{\#}$ –x, –y, –z.

A deep green crystal having 0.5×0.3×0.3 mm^3 dimension was put on a Syntex P2$_1$ diffractometer, which was then used for the determination of lattice parameters, space group and data collection [15] using graphite monochromatised MoK$_\alpha$ radiation. The lattice constants were determined by least squares refinements of the angular setting of 25 reflections near θ value 10°. The crystallographic data are listed in Table I. The stability of the crystal was checked by measuring standard reflections at fixed intervals during the data collection. However, no significant loss of intensity was noted for the crystal. The data were always corrected for Lorentz and polarisation effects. The structure was solved by direct methods using the SHELXTL PLUS [16] system and refined by a full matrix least squares calculation. Selected bond lengths and angles of the title compound are summarized in Table II.

Discussion

X-ray structure

The molecule is made up of centrosymmetric binuclear cations and uncoordinated ClO$_4$$^-$ anions. Fig. 1 gives a perspective view of the cation and Fig. 2 represents the crystal packing.

The copper(II) ions are bridged by an oxalic acid molecule. Each copper(II) ion in a distorted square planar coordination is surrounded by three oxygen and one nitrogen atoms. The Cu-O(1) and Cu-N(8) bond lengths are 1.867 and 1.947 Å respectively.

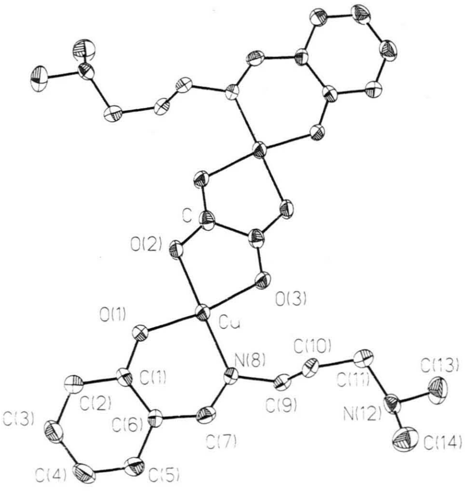

Fig. 1. Perspective view of the cation of [LCu{μ-(OH)$_2$(C$_2$O$_2$)}CuL](ClO$_4$)$_2$.

Table III. Some magnetic and structrual data for similar compounds.

Complexes	h_M [Å]	α [°]	γ [°]	J [cm^{-1}]	Ref.
$(tmen)_2Cu_2(ox)$	0.18	4.8	8.4	–385	[3, 17]
$(bipy)_2Cu_2(ox)$	0.10	4.4	3.2	–385	[13, 17]
$(bzpm)_2Cu_2(ox)$	0.19	0	8.8	–349	[11, 17]
$(mpz)_2Cu_2(ox)$	0.24	5.3	13.9	–402	[8, 17]
$(L)_2Cu_2(oxH_2)$	0.06	4.7	3.9	–478	This work

tmen = trtramethylethylene diamine, bipy = 2,2'-bipyridine, bzpm = bromozepam, mpz = mepirizole, ox = oxalato anion, oxH_2 = oxalic acid.

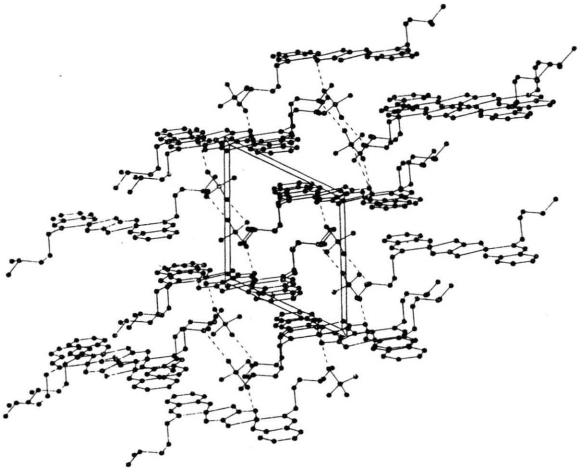

Fig. 2. Crystal packing of $[LCu\{\mu\text{-}(OH)_2(C_2O_2)\}CuL](ClO_4)_2$.

The bond lengths of the copper atom to the oxygen atoms of the oxalic acid molecule are close to 1.99 Å. The C-O bond lengths of the oxalic acid bridge range from 1.250(6) to 1.252(6) Å and do not differ significantly. The length of the C- C bond in $C_2O_2(OH)_2$ is of a typical single bond 1.522 Å. The distance between the two copper centres is 5.2 Å which is within the range of other reported similar dinuclear copper(II) complexes [5 - 8].

Three distortion parameters (i) displacement of the metal atoms out of the equatorial plane (h_M), (ii) the twist angle (α), (iii) the angle between the oxalato plane and the equatorial plane (γ) are important for discussing the magnetic properties [17]. For the complex $[LCu\{\mu\text{-}(OH)_2(C_2O_2)\}CuL](ClO_4)_2$, h_M is only ± 0.06 Å, $\alpha = 4.7(5)°$ and $\gamma = 3.9(3)°$. These values are in good agreement with other reported values of similar dinuclear oxalato bridged complexes (Table III).

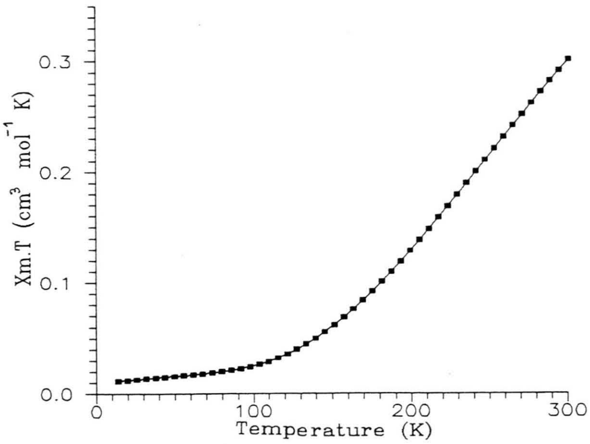

Fig. 3. Experimental (■) and calculated (—) temperature dependence of $\chi_M T$ for $[LCu\{\mu\text{-}(OH)_2(C_2O_2)\}CuL](ClO_4)_2$.

Magnetic properties

Magnetic susceptibility measurement for a powdered sample of the complex was performed by the Faraday method in the temperature range 12-300 K. Experimental data were corrected for the underlying diamagnetism. The data were fitted to the Bleaney-Bowers expression

$$\chi_M = \frac{Ng^2\beta^2}{kT}\frac{2e^x}{1+3e^x}(1-\rho) + \frac{Ng^2\beta^2}{2kT}\rho + N_\alpha,$$

where x = J/kT, using the isotropic exchange Hamiltonian ($H = -JS_1S_2$) for two interacting $S = {}^1/_2$ centres. J is the singlet-triplet energy gap arising from the intramolecular interaction and ρ is the molar fraction of monomeric impurity. N_α($60\cdot10^{-6}$cm^3/mol for each copper atom) is the temperature-independent paramagnetism. The least-squares fit of the data displayed in Fig. 3 leads to $J = -478$ cm^{-1}, $g = 2.11$ and $\rho = 1.20\%$.

All the oxalato-bridged dinuclear copper(II) complexes with copper atoms in a tetragonal environment (*i. e.*, square planar, square pyramidal or pseudo octahedral) with a centrosymmetric structure, so far have been found to be antiferromagnetic [3, 5, 17]. It is a remarkable feature of their magnetic behaviour that the magnitude of the coupling constant appears to be only slightly sensitive to the structural differences, with values of J between –330 and –402 cm^{-1} [17]. Related di- and trinuclear oxamato and oxamidato-bridged complexes have also been synthesised and appear to behave similarly [17 - 18]. The present complex $[LCu\{\mu\text{-}(OH)_2(C_2O_2)\}CuL](ClO_4)_2$ shows a quite larger value of J = –478 cm^{-1} though it has the same range of distortions found in other related compounds (Table III).

Besides the structural factors, the magnitude of the superexchange interaction depends to a great extent on the electronic structure of the bridging ligand [2 - 4]. When paired copper atoms are separated from each other by three diamagnetic atoms (for example Cu-O-C-O-Cu links), two paths are conceivable for the migration of a positive hole, one via π-electronic clouds and the other via σ-bonding electron orbitals of the O-C-O bonds [19]. The π-path can give rise to a strong antiferromagnetic coupling whereas the σ-path leads to ferromagnetic interaction [19]. In the clusters of oxalato bridged copper(II) dimers the positive holes can migrate through the π-bond system of the Cu-O-C-O-Cu links, giving rise to antiferromagnetism in agreement with the sign of the exchange integrals. The oxalato group coordinated to copper(II) ions by oxygen atoms have a formal negative charge and this hinders the migration of positive holes through the π-bond system and weakens antiferromagnetic interaction between copper atoms [20]. This formal negative charge has been removed in this complex $[LCu\{\mu\text{-}(OH)_2(C_2O_2)\}CuL](ClO_4)_2$, where two copper(II) ions are neutrally bridged by an oxalic acid molecule. Owing to this effect, the magnetic interaction is presumed to operate more strongly in $[LCu\{\mu\text{-}(OH)_2(C_2O_2)\}CuL](ClO_4)_2$, than in oxalato-bridged complexes.

Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre. Copies of the data CCDC no. 102092, can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code +(1223) 336-033, e-mail: heale@ccdc.cam.ac.uk).

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