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Crystal structure, magnetic properties and orbital interactions of the binuclear fumarato-bridged bis[(*N*-(2-diethylamino)ethyl)-salicylidenaminato)copper(II)] complex

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Abstract

The title compound of formula $[Cu_2(SalNEt_2)_2(C_4H_2O_4)]$, where $SalNEt_2$ = *N*-(2-(diethylamino)ethyl)-salicylidenaminate, has been synthesized and its structure solved at room temperature. It crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 10.463(2)$, $b = 16.048(2)$, $c = 9.434(1)$ Å, $\beta = 106.91(1)°$ and $Z = 2$. In the molecular structure of this centrosymmetric compound the two equivalent copper(II) ions are bridged by the fumarato ligand coordinated in an amphimonodentate mode. The local geometry around both copper(II) ions is approximately square planar. Magnetic susceptibility data for the complex as a function of temperature show weak exchange interactions. The fitting of these data to the HDVV ($\hat{H} = -2J\hat{S}_1\hat{S}_2$), $S_1 = S_2 = 1/2$ spin exchange model, yields a $2J$ value of -1.8 cm^{-1} An orbital interpretation of the observed weak antiferromagnetic interactions is presented based on the results of extended Huckel calculations on a model compound.

Introduction

Dicarboxylates have been used extensively as bridging ligands in Cu(II) binuclear complexes providing thus the means to design molecular systems with expected magnetic properties [1–4]. In the frame of our work on the interaction between transition-metal ions through extended bridging ligands [5–7], we focus here on the efficiency of fumarate dianion to couple two paramagnetic copper(II) ions. Obviously, such oxygen ligand-bridged metal–metal systems are expected to present very small antiferromagnetic coupling, if any at all, and consequently they may present a reversal of the sign of the superexchange parameter *J*, serving thus as possible candidates to observe the phenomenon of accidental orthogonality of magnetic orbitals [8]. In this paper, we report the synthesis and magnetic properties of a new binuclear Cu(II) μ-fumarato complex of the formula $[Cu_2(SalNEt_2)_2(C_4H_2O_4)]$, where $SalNEt_2$ stands for the anion of the *N*-(2-diethylamino)-ethyl)salicylidenaminato ligand. We also describe the crystal structure of this compound. As far as we know, it is the first time that the crystal structure of a copper(II)–fumarato complex with full magnetic characterization is reported. The crystal structure of (μ-fumarato)bis{[*N*,*N*-bis(diethylaminoethyl)ethylamine]-copper(II)} has previously been published [9], and the magnetic behaviour of the (μ-fumarato)-bis(dicyclopentadienyltitanium(III)) [10], has been studied. In addition, the magnitude of exchange coupling is discussed in the light of extended Huckel molecular orbital calculations.

Experimental

Physical measurements

IR spectra were recorded on a Perkin-Elmer 1463 spectrophotometer (4000–250 cm^{-1}) using KBr pellets. UV–Vis spectra of methanol solutions and Nujol films were measured on a Perkin-Elmer Hitachi 200 spectrophotometer. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 elemental analyzer. Magnetic susceptibility of polycrystalline samples were measured over the temperature range 4.2–300 K, using a Princeton Applied Research 155 vibrating sample magnetometer. The applied magnetic field was 10 kOe. Mercury(tetrakisthiocyanato)cobaltate(II) was used as a susceptibility standard [11]. Diamagnetic corrections of the constituent atoms were calculated from Pascal's constants. The value 60×10^{-6} cm^3 mol^{-1} was used for

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the temperature-independent paramagnetism of the copper(II) ion. Magnetism of the sample was found to be field independent.

Materials

Fumaric acid, salicylaldehyde (Sal) and *N*,*N*-diethylethylenediamine were obtained commercially. Cu(SalNEt$_2$)(Sal), where SalNEt$_2$ is the Schiff base derived from salicylaldehyde and *N*,*N*-diethylethylenediamine, was isolated as previously described [12].

Synthesis

The complex was prepared by the addition of a 1×10^{-3} mol sample of fumaric acid in 5 ml of methanol to a 2×10^{-3} mol sample of Cu(SalNEt$_2$)(Sal) in 20 ml of methanol, under continuous stirring at room temperature, and the mixture was refluxed for 1 h. The green microcrystalline precipitate formed was filtered off, washed with cold methanol and dried *in vacuo*. The yield of the reaction was about 75%. Single crystals suitable for the structure and magnetic determinations were obtained by slow evaporation of a methanol solution.

Anal. Calc. for $C_{30}H_{40}N_4O_6Cu_2$: C, 53.71; H, 5.93; N, 8.24. Found: C, 53.67; H, 5.89; N, 8.20%.

X-ray data collection and refinement

The crystal system and the space group were determined from preliminary oscillation and Weissenberg photographs. Unit cell dimensions were derived from at least-squares refinement of the setting angles of 15 automatically centred reflections in the range $21<2\theta<23°$ on a Syntex P2$_1$ diffractometer upgraded by Crystal Logic using a Nb filtered Mo Kα radiation. The intensities of three standard reflections monitored after every 67 reflections showed an intensity fluctuation less than 3%. Lorentz–polarization and a numerical absorption correction were applied. Cell parameters and other relevant details are quoted in Table 1.

A Patterson map showed the position of the Cu atom and all the non-hydrogen atoms were located from subsequent difference Fourier maps. Refinement was carried out by blocked full-matrix least-squares in which $\Sigma w\Delta^2$ was minimized with SHELX76 [13]. All hydrogen positions were located from a difference Fourier map and were refined isotropically. The final positional and equivalent thermal parameters of the non-hydrogen atoms are given in Table 2.

TABLE 1 Crystallographic data for the complex

Formula	$C_{30}H_{40}N_4O_6Cu_2$
Space group	$P2_1/c$
a (Å)	10.463(2)
b (Å)	16.048(2)
c (Å)	9.434(1)
β (°)	106.91(1)
V (Å^3)	1515.6(1)
Z	2
λ (Mo Kα) (Å)	0.71069
D_m (g cm^{-3})	1.50
D_c (g cm^{-3})	1.489
μ (cm^{-1})	14.68
Formula weight	679.75
F_o	$>3.0\sigma(F_o)$
R_{int}	0.0097
N_r^{a}	270
Data used	2435
Data unique	2685
$\Delta\rho_{max}$ (e Å^{-3})	0.328
$\Delta\rho_{min}$ (e Å^{-3})	−0.272
R^{b}	0.0290
R_w^{c}	0.0300

$^a N_r$ = number of refined parameters $^b R=\Sigma|\Delta F|/\Sigma|F_o|$. $^c R_w=[\Sigma w(\Delta F)^2/\Sigma w|F_o|^2]^{1/2}$.

TABLE 2. Positional and equivalent thermal parameters of the non-hydrogen atoms^a

Atom	x/a	y/b	z/c	U_{eq}^{b}
Cu	0.17461(3)	0.10688(2)	0.15281(3)	0.0333
N(1)	0.0058(2)	0.1333(2)	0.0106(2)	0.0371
N(2)	0.2536(2)	0.1280(1)	−0.0225(2)	0.0325
O(1)	0.3468(2)	0.0821(1)	0.2912(2)	0.0424
O(3)	0.0974(2)	0.1027(2)	0.3123(2)	0.0513
C(2)	0.3521(3)	0.0038(2)	0.3189(3)	0.0395
C(1)	0.4596(3)	−0.0244(2)	0.4527(3)	0.0370
O(2)	0.2748(2)	−0.0475(2)	0.2434(2)	0.0536
C(3)	−0.0233(3)	0.1227(2)	0.3104(3)	0.0388
C(4)	−0.0610(3)	0.1158(2)	0.4426(3)	0.0489
C(5)	−0.1845(3)	0.1385(2)	0.4499(4)	0.0562
C(6)	−0.2796(3)	0.1703(2)	0.3258(4)	0.0580
C(7)	−0.2487(3)	0.1755(2)	0.1956(4)	0.0497
C(8)	−0.1235(3)	0.1513(2)	0.1830(3)	0.0366
C(9)	−0.1027(3)	0.1527(2)	0.0389(3)	0.0377
C(10)	0.0122(3)	0.1363(3)	−0.1430(3)	0.0466
C(11)	0.1474(3)	0.1715(2)	−0.1385(3)	0.0442
C(12)	0.2840(4)	0.0445(2)	−0.0751(4)	0.0541
C(13)	0.3445(6)	0.0445(3)	−0.2035(5)	0.0821
C(14)	0.3784(3)	0.1784(2)	0.0232(3)	0.0434
C(15)	0.3661(5)	0.2559(3)	0.1052(5)	0.0609

^{a}e.s.d.s in the last significant digits are given in parentheses $^b U_{eq}=(U_{11}+U_{22}+U_{33})/3$ Symmetry code $1-x$, $-y$, $1-z$.

Results and discussion

Description of the structure

A perspective view of the complex along with the atom labelling scheme is presented in Fig. 1. Selected bond lengths and angles are given in Table 3.

The structure consists of centrosymmetrical binuclear units in which the two Cu(II) ions are bridged by an amphimonodentate fumarate dianion through its O(1) and O′(1) atoms. The local geometry around each Cu(II) ion is approximately square planar involving the two nitrogen atoms (N(1), N(2)) and the oxygen atom

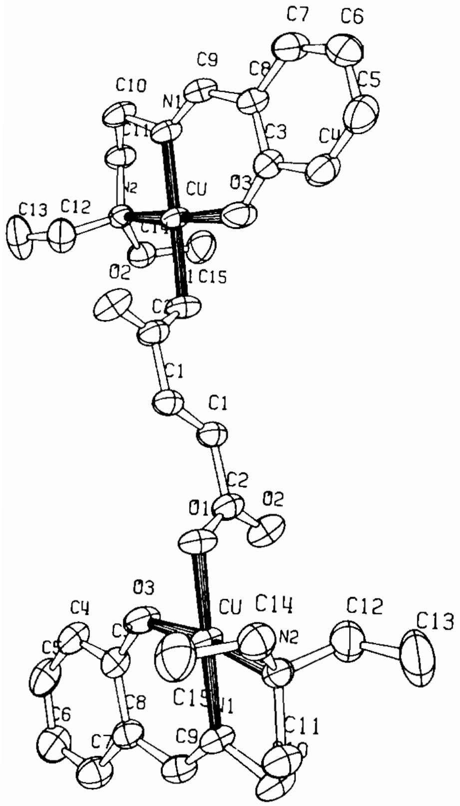

Fig. 1. A perspective view of [$Cu_2(SalNEt_2)_2(C_4H_2O_4)$] along with the atom labelling scheme.

TABLE 3. Bond lengths (Å) and angles (°)^a

Copper chromophore			
Cu–N(1)	1.929(2)	N(2)–Cu–N(1)	84 6(1)
Cu–N(2)	2.081(2)	O(3)–Cu–O(1)	89.2(1)
Cu–O(1)	1.934(2)	O(3)–Cu–N(1)	92 5(1)
Cu–O(3)	1.905(2)	O(1)–Cu–N(2)	93.6(1)
Fumarato bridge			
C(2)–O(1)	1.280(3)	O(2)–C(2)–O(1)	123.9(2)
C(2)–O(2)	1.227(3)	O(2)–C(2)–C(1)	119.6(3)
C(1)–C(2)	1.496(3)	C(1)–C(2)–O(1)	116.5(2)
C(1)–C′(1)	1.298(6)	C(2)–O(1)–Cu	108.4(2)

^{a}e.s.d.s in the last significant digits are given in parentheses.

O(3) of the $SalNEt_2$ ligand as well as an oxygen atom O(1) from the fumarato ligand. The largest deviation from their mean plane is 0.065 Å for the O(1) atom. The Cu–O(1), Cu–O(3), Cu–N(1) and Cu–N(2) bond lengths of 1.934(2), 1.905(2), 1.929(2) and 2.081(2) Å, respectively, are in agreement with analogous literature distances [7]. In line with the amphimonodentate coordination mode of the carboxylate groups is the marked difference of 0.053 Å between the two C–O distances implying a partial double bond character of the C(2)–O(2) bond. A larger double bond character is also observed for the C(1)–C′(1) bond (1.299(6) Å) as compared to the C(1)–C(2) bond length of 1.496(3) Å. These values are in accordance with similar observations in fumarato complexes [9, 14]. Another interesting feature of this structure is the value of 5.4° for the dihedral angle between the plane of the carboxylate group and that of the double bond, C(2)–C(1)–C′(1), whereas the dihedral between the former and the mean plane of the chromophore is 99.5°. The intramolecular Cu · · · Cu′ distance is 8.8242(5) Å, whereas the shorter intermolecular Cu · · · Cu′ one is 8.8660(6) Å. Finally, the geometry of the Schiff base is quite normal [15, 16, 7] and will therefore not be discussed in detail here.

Spectroscopic characterization

The most interesting features of the IR spectrum of this compound are the positions [17] of the $\nu_{as}(COO)$ and $\nu_s(COO)$ bands at 1586 and 1373 cm^{-1}, respectively. Their difference, $\Delta = 213$ cm^{-1}, is characteristic of the monodentate coordination mode of fumaric acid [18].

The ligand field spectrum of a Nujol mull sample of the complex shows a shoulder at *c.* 17.81 kK which is found as a broad band at 16.18 kK (log $\epsilon = 2.56$) in methanol solution. The position of this band is characteristic of planar four-coordinated Cu(II) chromophores [19–22], in accordance with our crystallographic results. Accordingly, the same square planar local geometry should remain in solution, since the shape of this band remains unchanged. At higher energies a CT band at 27.17 kK (log $\epsilon = 3.98$) with a shoulder at 33.90 kK is observed in the solution spectrum, which is found at 25.44 kK in Nujol mull.

Magnetic properties and exchange mechanism

The plot of μ_{eff} as a function of temperature, shown in Fig. 2, is essentially linear except for a small decrease near the liquid helium temperature. On cooling the system the μ_{eff} decreases slightly from a value of 1.79 BM at room temperature to 1.62 BM at 4.9 K. This slight decrease of μ_{eff} is suggestive of weak antiferromagnetic interactions leading to a singlet ground

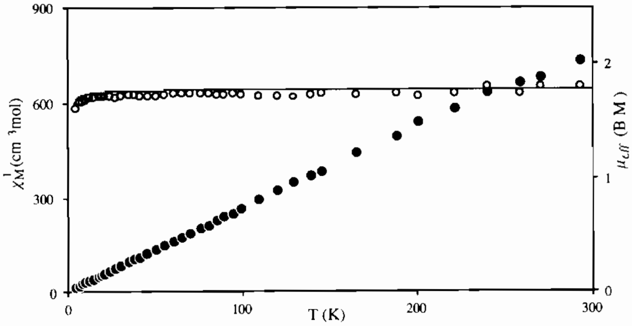

Fig. 2 Plots of inverse magnetic susceptibility, χ_{Cu}^{-1}, and μ_{eff} of [$Cu_2(SalNEt_2)_2(C_4H_2O_4)$] as a function of temperature The solid line represents the best fit to data.

state. The data reveals a linear χ_{Cu}^{-1} versus T relation down to 4.9 K. Least-squares fitting of the data to the Curie-Weiss law gave $C=0.388$ cm^3 mol^{-1} K, $\theta=-0.9$ K and $R=2.9\times10^{-6}$ ($R=\Sigma(\chi_i^{obs}-\chi_i^{calc})^2$).

The energy separation, $2J$, between the ground singlet and excited triplet states can be derived from the Bleaney–Bowers equation [23] for the magnetic susceptibility of an isotropic exchange between two copper(II) ions ($\hat{H}=-2J\hat{S}_1\hat{S}_2$). The observed experimental magnetic susceptibility data were fitted by the least-squares method to the above model and the best fit values obtained were $2J=-1.8$ cm^{-1}, $g=2.02$ and agreement factor $R=2.9\times10^{-6}$.

In order to determine the structural and electronic parameters which influence the exchange phenomenon in this complex, we performed extended Hückel calculations on a simplified model using charge iteration on all atoms and standard atomic and iteration parameters [24, 25]. According to Hoffmann's model [26] concerning the superexchange interactions in symmetric binuclear complexes bridged by multiatomic ligands, the initially degenerate in- and out-of-phase d-orbital combinations interact with the non-degenerate symmetry-adapted bridging-ligand orbitals. This interaction results in the two SOMOs, whose energy gap Δ accounts for the antiferromagnetic interactions. In our case, the interaction between Cu(II) d AOs and the proper delocalized bridge MOs is very weak due to both overlap and energy reasons. Actually, as can be seen in Fig. 3, the SOMOs are not delocalized over the bridge, their energy difference being very small ($\Delta=0.079$ eV). Thus, the antiferromagnetic contribution should be very small, and since the ferromagnetic term is usually considered to fall our more quickly than the antiferromagnetic one [27], the overall result is a very weak antiferromagnetic interaction.

EHMO calculations on the fumarate dianion show that the energy difference δ between the symmetric and antisymmetric MOs of the fumarato bridge, capable of interacting with the degenerate single-occupied in- and out-of-phase combinations of the d_{xy} metal orbitals, decreases as the angle α between the planes of the carboxylato groups and the plane of the fumarato double bond, increases (Fig. 4). The maximum energy difference corresponds to a planar or nearly planar configuration, whereas the crystallographic value of this angle is c. 5°. Consequently, a sign reversal of $2J$ could be achieved if an increase of α is obtained, probably by using a Schiff base with the appropriate steric effect.

The magnitude of $2J$ for our complex is about half the value of -3.2 cm^{-1} found in (μ-fumarato)-bis(dicyclopentadienyltitanium(III)) [10]. According to the above discussion, the stronger antiferromagnetic coupling of the latter compound could not be explained by a different value of the corresponding angle α. However, the magnitude of interaction may be influenced by the local geometry of the paramagnetic centres. Accordingly, as it was demonstrated in the case of terephthalato-bridged complexes [2], the energy difference between the SOMOs is expected to be lower for the square-planar geometry, found in our complex, than the tetrahedral one adopted by the Ti(III) analogue.

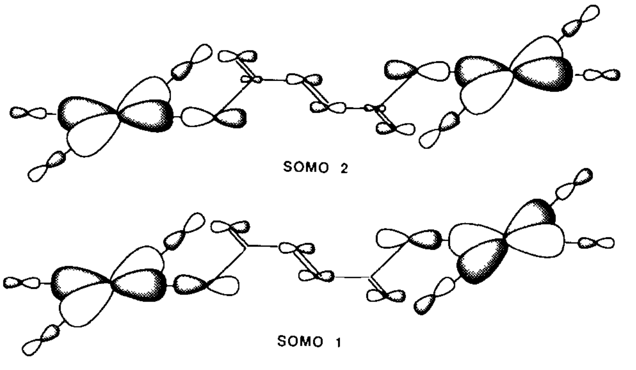

Fig. 3 Schematic representation of the two SOMOs of the model compound

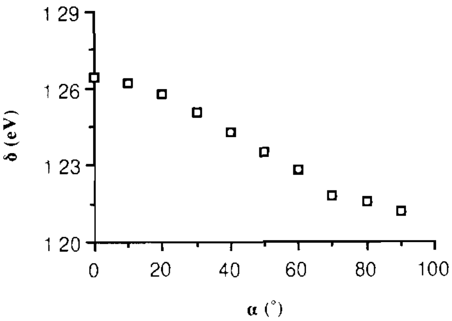

Fig 4 Variation of the energy difference, δ, between the symmetric and antisymmetric MOs of the bridging ligand with the angle, α, between the planes of the carboxylato groups and the fumarato double bond.

Supplementary material

Tables of anisotropic temperature coefficients U_{ij} for the non-hydrogen atoms, structure factor listing and the least-squares planes with displacements of selected atoms from the plane, as well as Tables of experimental and calculated magnetic susceptibility data, are available from the authors on request.

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