Articles

Crystal and Molecular Structure and Magnetism of
(μ-Terephthalato)bis[(N-(2-(diethylamino)ethyl)salicylidenaminato)copper(II)]–Water–Methanol

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The crystal and molecular structure of (μ-terephthalato)bis[(N-(2-(diethylamino)ethyl)salicylidenaminato)copper-(II)–water–methanol, $[Cu_2(SalNEt_2)_2(C_8H_4O_4)] \cdot H_2O \cdot CH_3OH$, where $SalNEt_2$ = N-(2-(diethylamino)ethyl)-salicylidenaminate, has been determined by single-crystal X-ray analysis. The compound crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 7.379(1)$ Å, $b = 7.546(2)$ Å, $c = 33.783(6)$ Å, and $\beta = 100.40(1)°$. In the molecular structure of this centrosymmetric compound the two equivalent copper(II) ions are bridged by the terephthalato ligand coordinated in an amphimonodentate mode. The local geometry around both copper(II) ions is square planar, whereas two noncoordinated molecules, namely a water and a methanol molecule, are also present. The fitting of the variable-temperature magnetic susceptibility data to the HDVV ($\hat{H} = 2J\hat{S}_1 \cdot \hat{S}_2$), $S_1 = S_2 = \frac{1}{2}$, spin exchange model yields a $2J$ value of 0.6 cm⁻¹. The results of extended Hückel calculations on a model compound are consistent with the existense of accidental orthogonality between the magnetic orbitals.

Introduction

Molecular magnetism has certainly been one of the most active fields in modern inorganic chemistry. Materials exhibiting antiferromagnetic, ferromagnetic, or even more exotic magnetic properties have been the focus of many contemporary experimental and theoretical studies.[2,3] The target of these studies was to synthesize materials with predictable magnetic properties, achieving thus the ultimate goal of molecular engineering. As far as the antiferromagnetic materials are concerned this goal has been partially accomplished;[4] still considerably less information exists about molecular ferromagnetism, although some recent results are very promising in this respect.[5,6]

Continuing our interest on the investigation of magnetic exchange mechanism of oxygen ligand-bridged metal–metal systems,[7] we specifically aimed to synthesize complexes, stable under ambient conditions, with extended dicarboxylate bridges. Obviously, these compounds should present very small antiferromagnetic coupling, if any at all, and consequently they could 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. The terephthalato dianion has been proved to be the appropriate bridging unit to design very interesting magnetic systems with a separation of

11–12 Å between the magnetic centers.[8–11] We report here the crystal structure of a new binuclear Cu(II) μ-terephthalato complex with the formula $[Cu_2(SalNEt_2)_2(C_8H_4O_4)] \cdot H_2O \cdot CH_3OH$, where $SalNEt_2$ stands for the anion of the N-(2-(di-ethylamino)ethyl)salicylidenaminato ligand. IR and UV–visible spectra of the complex are discussed in relation with the solved crystal structure, and the experimentally depicted exchange coupling is explained in the light of extended Hückel molecular orbital calculations.

Experimental Section

Synthesis. The complex was prepared by adding a methanolic solution of the terephthalic acid [0.166 g (1 mmol) in 5 mL of methanol] to a methanolic solution of the Cu(SalNEt₂)(Sal) complex[12] [0.807 g (2 mmol) in 20 mL of methanol]. The dark green resulting solution was refluxed for 1 h, cooled at room temperature, and left to stand for 24 h. The dark green microcrystalline solid precipitated was filtered off, washed with cold methanol, and dried in vacuo. Recrystallization was carried out from warm methanol. Olive-green crystals suitable for X-ray analysis were obtained by slow evaporation of a methanol solution. Anal. Calcd for $C_{35}H_{48}N_4O_8Cu_2$: C, 54.01; H, 6.10; N, 7.16. Found: C, 53.90; H, 6.20; N, 7.18.

Physical Measurements. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 elemental analyzer. Infrared spectra were recorded on a Perkin-Elmer 1463 spectrophotometer (200–4000 cm⁻¹) using KBr pellets. UV–vis spectra of methanol solutions and Nujol mull samples were measured on a Perkin-Elmer Hitachi Model 200 spectrophotometer.

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Table I. Crystallographic Data Collection Parameters

chem formula	$C_{35}H_{48}N_4O_8Cu_2$	space group	$P2_1/c$
a, Å	7.379(1)	T, °C	25
b, Å	7.546(2)	λ, Å	0.71069
c, Å	33.783(6)	μ, cm^{-1}	12.05
β, deg	100.40(1)	ρ_{obsd}, g cm^{-3}	1.38
V, Å^3	1850.2(6)	ρ_{calcd}, g cm^{-3}	1.398
Z	2	F_o	$>5.5\sigma(F_o)$
fw	778.87	$R(obsd)^a$	0.0518
data used	2654	$R_w(obsd)^b$	0.0729

^{a} $R = \sum|\Delta F|/\sum|F_o|$. ^{b} $R_w = [\sum w(\Delta F)^2/\sum w|F_o|^2]^{1/2}$.

Table II. Final Atomic Fractional Coordinates^a and Equivalent Thermal Parameters^b (Å^2) for the Non-Hydrogen Atoms in [Cu$_2$(SalNEt$_2$)$_2$(C$_8$H$_4$O$_4$)]·H$_2$O·CH$_3$OH

atom	x/a	y/b	z/c	U_{eq}
Cu	0.41639(7)	0.16072(7)	0.13012(1)	0.0398
N(1)	0.5749(5)	0.0242(5)	0.1709(1)	0.0423
N(2)	0.6174(5)	0.1123(5)	0.0959(1)	0.0438
O(1)	0.2830(5)	0.3205(5)	0.0907(1)	0.0665
O(3)	0.2457(5)	0.2093(5)	0.1648(1)	0.0553
C(2)	0.1624(6)	0.2544(8)	0.0625(1)	0.0557
C(1)	0.0785(6)	0.3826(6)	0.0300(1)	0.0472
O(2)	0.1153(6)	0.0979(6)	0.0604(1)	0.0737
C(3)	0.2516(6)	0.1554(6)	0.2017(1)	0.0443
C(4)	0.1014(7)	0.1958(7)	0.2213(2)	0.0554
C(5)	0.0999(8)	0.1428(8)	0.2599(2)	0.0661
C(6)	0.2460(9)	0.0484(8)	0.2816(2)	0.0666
C(7)	0.3875(8)	0.0043(7)	0.2640(2)	0.0589
C(8)	0.3965(6)	0.0547(6)	0.2239(1)	0.0437
C(9)	0.5512(6)	-0.0028(6)	0.2071(1)	0.0453
C(10)	0.7371(7)	-0.0533(8)	0.1573(2)	0.0556
C(11)	0.7855(7)	0.0676(9)	0.1254(2)	0.0600
C(12)	0.5486(7)	-0.0428(7)	0.0700(2)	0.0557
C(13)	0.6750(10)	-0.1130(9)	0.0425(2)	0.0834
C(14)	0.6532(9)	0.2659(9)	0.0705(2)	0.0663
C(15)	0.6970(10)	0.4339(9)	0.0935(3)	0.1050
C(16)	-0.0402(7)	0.3210(7)	-0.0037(2)	0.0520
C(17)	0.1180(7)	0.5609(8)	0.0336(2)	0.0539
O(W)	0.2560(20)	-0.1600(20)	0.1139(6)	0.1707
O	0.2000(10)	-0.2990(10)	0.1478(3)	0.0926
C	0.0950(10)	-0.4380(10)	0.1563(4)	0.0675

^{a} Estimated standard deviations in the last significant digits are given in parentheses. ^{b} $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

Magnetic susceptibilities of polycrystalline samples were measured over the temperature range 4.6–300 K, using a Princeton Applied Research Model PAR 155 vibrating-sample magnetometer. The applied magnetic field was 10 kOe. Mercury tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard. Diamagnetic corrections of the constituent atoms were calculated from Pascal's constants. The value 60 ×10^{-6} cm^3 mol^{-1} was used for the temperature-independent paramagnetism of copper-(II) ion.

Crystallographic Data Collection and Refinement of the Structure. The crystal system and the space group were determined from preliminary oscillation and Weissenberg photographs. Unit cell dimensions were derived from a least-squares refinement of the setting angles of 15 automatically centered 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 8% decrease during data collection, and a correction was applied during data reduction. Lorentz–polarization and a numerical absorption correction were applied. Cell parameters and other relevant details are quoted in Table I. The structure was solved by direct methods and the refinement based on F proceeded by blocked full-matrix least squares in which $\sum w\delta^2$ was minimized with SHELX76.[13] The hydrogen atoms of the methyl groups were calculated as riding on carbon atoms at a distance of 0.96 Å. Both O(W) and methanol were refined at half-occupancy. The water hydrogens could not be located from the difference map. The final positional and equivalent thermal parameters of the non-hydrogen atoms are given in Table II. A full length table of crystallographic data, listings of thermal parameters and

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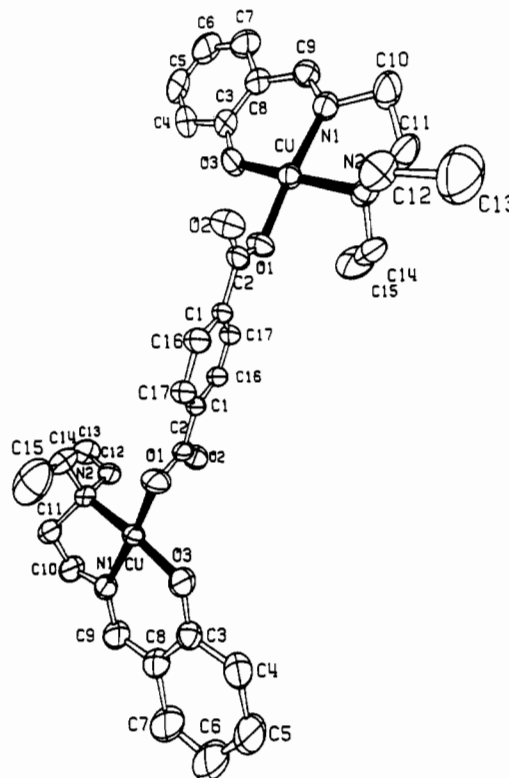
Figure 1. Perspective view of [Cu$_2$(SalNEt$_2$)$_2$(C$_8$H$_4$O$_4$)]·H$_2$O·CH$_3$OH along with the atom-labeling scheme.

Table III. Bond Lengths (Å) and Angles (deg)^a

Copper Chromophores			
Cu–N(1)	1.936(3)	N(2)–Cu–N(1)	84.4(1)
Cu–N(2)	2.070(4)	N(1)–Cu–O(3)	92.6(1)
Cu–O(1)	1.930(3)	N(2)–Cu–O(1)	93.0(2)
Cu–O(3)	1.905(3)	O(1)–Cu–O(3)	89.6(2)
Terephthalato Bridge			
C(2)–O(1)	1.278(6)	O(2)–C(2)–C(1)	120.2(4)
C(2)–O(2)	1.226(7)	O(2)–C(2)–O(1)	124.3(5)
C(2)–C(1)	1.508(6)		

^{a} Estimated standard deviations in the last significant digits are given in parentheses.

hydrogen atom positions, and a complete listing of bond distances and angles have been deposited and are given in Tables SI–SV, respectively.[14]

Results and Discussion

Description of the Structure. A perspective view of the complex crystallized in the monoclinic space group $P2_1/c$ along with the atom-labeling scheme is presented in Figure 1. Selected bond distances and angles are given in Table III.

The structure consists of centrosymmetrical binuclear units in which the two Cu(II) ions are bridged by an amphimonodentate terephthalate 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 O(3) of the SalNEt$_2$ ligand as well as an oxygen atom O(1) from the terephthalato ligand. The larger deviation from their mean plane is 0.033 Å for O(1) atom. The Cu atom lies 0.087 Å out of this plane. The Cu–O(1), Cu–O(3), Cu–N(1), and Cu–N(2) bond lengths of 1.930(3), 1.905(5), 1.936(3), and 2.070(4) Å, respectively, are in agreement with analogous literature distances.[7b] In line with the amphimonodentate coordination mode of the carboxylate groups is the marked difference of 0.052 Å between the two C–O distances, implying a partial double bond character of the C(2)–O(2) bond. Another

(14) Supplementary material.
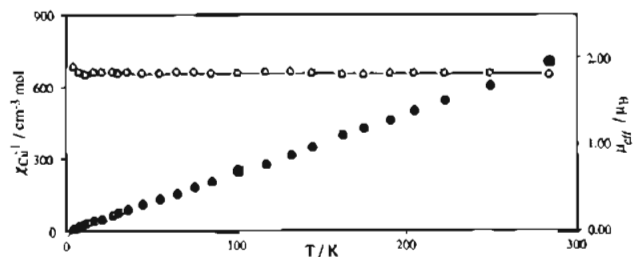
Figure 2. Plot of inverse magnetic susceptibility, χ_{Cu}^{-1}, and μ_{eff} of $[Cu_2(SalNEt_2)_2(C_8H_4O_4)]\cdot H_2O\cdot CH_3OH$ as a function of temperature. The solid line represents the best fit to data.

interesting feature of this structure is the value of 5.9° for the dihedral angle between the benzene ring and the plane of the carboxylate group, which is more acute than the corresponding ones of other amphimonodentate μ-terephthalato complexes. The dihedral between the carboxylate group and the mean plane of the chromophore is 91.0°. The intramolecular Cu⋯Cu' distance is 11.0348 Å, whereas the shorter intermolecular Cu⋯Cu' one is 8.8179(6) Å. Finally, the Schiff base geometry is quite normal[7b,15,16] and will therefore not be discussed in detail here.

Infrared and Electronic Spectra. The most interesting features of the IR spectrum of this compound are the positions of the $\nu_{as}(COO)$ and $\nu_s(COO)$ bands at 1592 and 1358 cm^{-1}, respectively. Their difference, $\Delta = 234$ cm^{-1}, is characteristic of the monodentate coordination mode of the terephthalic dianion.[7a,8,17]

The ligand field spectrum of a Nujol mull sample of the complex shows a broad band at *ca.* 16.95×10^3 cm^{-1} which is found at slightly lower energy, 16.10×10^3 cm^{-1} (log ϵ_{max} = 2.82), in methanol solution. The position of this band is characteristic of planar four-coordinated Cu(II) chromophores,[18–21] in accordance with our crystallographic results. Accordingly, the same square planar local geometry should remain in the solution, since the shape of the latter band remains unchanged. At higher energies a CT band at 27.17×10^3 cm^{-1} (log ϵ_{max} = 4.29) with a shoulder at 33.90×10^3 cm^{-1} is observed in the solution spectrum, which is found at 26.04×10^3 cm^{-1} in Nujol mull.

Magnetic Properties and Exchange Mechanism. The plot of μ_{eff} as a function of temperature, shown in Figure 2, is essentially linear except a small increase near the liquid helium temperature. On cooling of the system, the μ_{eff} increases slightly from a value of 1.83 μ_B at room temperature to a value of 1.89 μ_B at 4.6 K. This slight increase of μ_{eff} is suggestive of weak ferromagnetic interactions leading to a triplet ground state. The data reveals a linear χ_{Cu}^{-1} versus T relation down to 4.6 K. Least-squares fitting of the data to the Curie–Weiss law gave $C = 0.410$ cm^3 mol^{-1} K, $\theta = 0.5$ K, and $R = 2.9 \times 10^{-6}$.[22]

The energy separation, $2J$, between the ground singlet and excited triplet states can be derived from the Bleany–Bowers equation for the magnetic susceptibility of an isotropic exchange between two copper(II) ions ($\hat{H} = -2J\hat{S}_1\hat{S}_2$).[23] The observed experimental magnetic susceptibility data were fitted by the least-squares method to the above model, and the best fit values obtained were $2J = 0.6$ cm^{-1}, $g = 2.08$, and agreement factor $R = 2.9 \times 10^{-6}$.

Theoretical Calculations. Although we cannot conclude with certainty from the experimental data that weak ferromagnetic
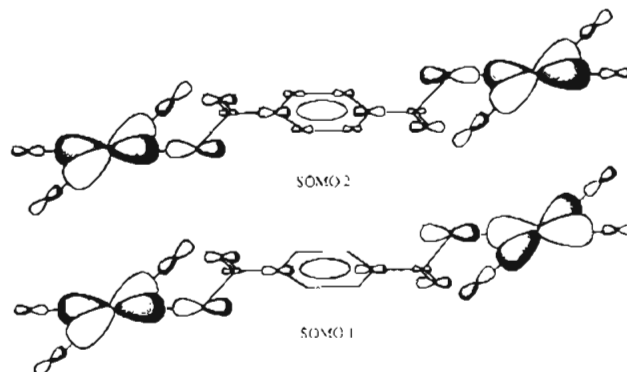

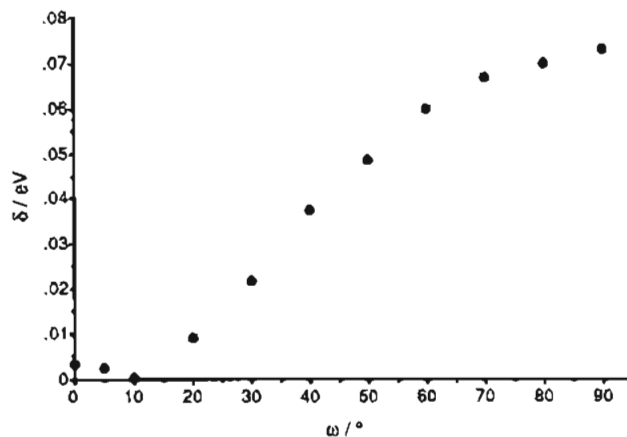**Figure 3.** Schematic representation of the two SOMOs of the model compound.

Figure 4. Variation of the energy difference, δ, between the symmetric and antisymmetric MOs of the bridging ligand with the angle, ω, between the planes of the carboxylato groups and the plane of benzene ring.

interactions do exist in this complex, we examined whether the terephthalato bridge possess suitable orbital pathways for the propagation of magnetic exchange phenomena by performing extended Hückel calculations on a model compound.[24–26] The superexchange interaction could be analyzed into an antiferromagnetic and a ferromagnetic term, J_{AF} and J_F, respectively. The magnitude of J_{AF} is related to the orbital energy splitting term ($\epsilon_1 - \epsilon_2$) (ϵ_1 and ϵ_2 being the eigenvalues of the symmetric and antisymmetric single occupied MOs, respectively) and may be used as a qualitative measure of the magnetic superexchange interaction.[27,28] For our model compound this term takes the value of 0.049 eV. As can be seen in Figure 3, where the shapes of the two SOMOs are presented, this extremely low value has its origin to the very weak overlap between Cu(II) d AOs and the proper highly delocalized bridge MOs. This situation is ideal to observe the phenomenon of accidental orthogonality. Actually, additional calculations[29,30] on the terephthalato dianion showed that the energy difference, δ, between the symmetric and antisymmetric MOs capable to interact with the degenerate single-occupied in- and out-of-phase combinations of the d_{xy} metal orbitals, is minimized as the angle, ω, between the planes of the carboxylato groups and the plane of the benzene ring, approaches

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(29) (a) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209. (b) QCPE 455, MOPAC, Indiana University, Bloomington, IN.
(30) The calculations on the terephthalato ligand were of the PM3 type with full geometry optimization using the angle ω as the reaction coordinate.

a value of 10° (Figure 4), this latter value being very close to the crystallographic one of ca. 6°.

According to the above results, the antiferromagnetic term should be negligible, leading predominantly to ferromagnetic exchange interactions. In this respect, it should be noted that the ferromagnetic term is usually considered to fall out more quickly than the antiferromagnetic one,[31] but this is not necessarily always true as it has been recently shown.[32-34] Thus, the presence of weak ferromagnetic interactions in our complex could be the result of accidental orthogonality of the magnetic orbitals. An intramolecular ferromagnetic coupling with $J = 4$ cm^{-1} was also found for the μ-terephthalato chain complex $[Cu(C_8H_4O_4)$-$(C_4H_8N_2)(H_2O)_2]_n$.[8b] However, in this case a weak interchain antiferromagnetic coupling was superimposed over an intrachain one.

Supplementary Material Available: Tables giving crystal data and details of the structure determination, anisotropic thermal parameters, hydrogen atom locations, and thermal parameters, bond lengths, and bond angles as well as experimental and calculated susceptibility data (7 pages). Ordering information is given on any current masthead page.

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