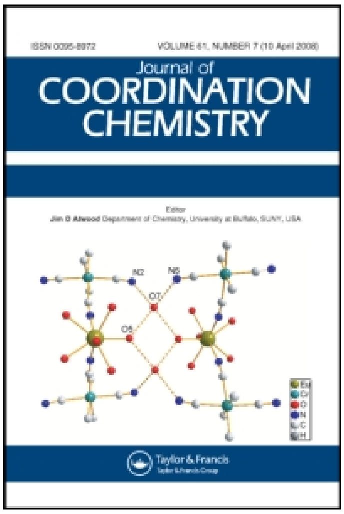

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Molecular Structure and Magnetic Properties of the Binuclear Phthalato-Bridged Species *Bis*[(*N*-(2-(Diethylamino)Ethyl)Salicylidenaminato)-Copper(II)] Trihydrate

C. E. Xanthopoulos[a]; C. C. Hadjikostas[a]; G. A. Katsoulos[a]; A. Terzis[b]; M. P. Sigalas[a]
[a] Department of Chemistry, Aristotle University, Thessaloniki, Greece [b] Institute of Material Science, NRCPS, Athens, Greece

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MOLECULAR STRUCTURE AND MAGNETIC PROPERTIES OF THE BINUCLEAR PHTHALATO-BRIDGED SPECIES *BIS*[(*N*-(2-(DIETHYLAMINO)ETHYL)SALICYLIDENAMINATO)-COPPER(II)] TRIHYDRATE

C.E. XANTHOPOULOS[a], C.C. HADJIKOSTAS[a],
G.A. KATSOULOS[a], A. TERZIS[b] and M.P. SIGALAS[a,*]

[a]*Department of Chemistry, Aristotle University, 540 06 Thessaloniki, Greece;*
[b]*Institute of Material Science, NRCPS "Demokritos", 153 10 Athens, Greece*

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The crystal structure of (μ-phthalato)*bis*[(*N*-(2-(diethylamino)ethyl)-salicylidenaminato)-copper(II)-trihydrate, $[Cu_2(salNEt_2)_2(\mu-phthal)] \cdot 3H_2O$, where $salNEt_2 = N$-(2-(diethylamino)-ethyl)salicylidenaminate, has been determined by single-crystal X-ray analysis. It crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 19.9109(9)$, $b = 10.0465(4)$, $c = 18.5837(8)$ Å, and $\beta = 100.625(1)°$. In the molecular structure the two copper(II) ions are bridged by the phthalato ligand coordinated in an amphimonodentate mode and the local geometry around both copper(II) ions is 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 $-0.34\,cm^{-1}$. An orbital interpretation of the observed weak antiferromagnetic interactions is presented based on the results of extended Hückel calculations on a model molecule.

Keywords: Copper; Complex; Structure; Magnetic properties

INTRODUCTION

In the arsenal of magnetic exchange interactions in transition-metal complexes, dicarboxylato ligands have been the subject of intense interest [1] serving as the propagators of such interactions and providing the means to design molecular systems with expected magnetic properties [2–4]. In

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*Corresponding author.

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the course of our investigations on the magnetic exchange interactions in binuclear copper(II) complexes with dicarboxylates as bridging ligands [5–8], we report here the synthesis and magnetic properties of a new binuclear Cu(II) μ-phthalato complex of formula $[Cu_2(salNet_2)_2(\mu\text{-phthal})] \cdot 3H_2O$, where $salNet_2$ stands for the anion of the *N*-(2-(diethylamino)ethyl)salicylidenaminato ligand. According to published data the phthalato ligand can propagate both ferromagnetic and antiferromagnetic interactions. A $2J$ value of $-5.6\,cm^{-1}$ has been reported by Hedrickson *et al.* [9] for $[Ti_2(cp)_2(\mu\text{-phthal})]$, whereas Tsipis *et al.* [10] have synthesized the chain compound $[Cu(dien)(\mu\text{-phthal})]_n$. Spectroscopic data for the new complex are discussed in relation with its crystal structure. The experimentally depicted exchange coupling is explained in the light of extended Hückel molecular orbital calculations.

EXPERIMENTAL

Physical Measurements

IR spectra were recorded on a Perkin-Elmer 1463 spectrophotometer (4000–250 cm^{-1}) using KBr pellets. Electronic 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 instrument. Magnetic susceptibilities 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 $60 \times 10^{-6}\,cm^3\,mol^{-1}$ was used for the temperature-independent paramagnetism of the copper(II) ion. Magnetism of the sample was found to be field-independent.

Materials

Phthalic acid (H_2phthal), salicyladehyde (sal) and *N*,*N*-diethyl-ethylenediamine were obtained commercially. $Cu(salNet_2)(sal)$, where $salNet_2$ is the Schiff base derived from salicylaldehyde and *N*,*N*-diethyl-ethylenediamine, was isolated as previously described [12].

Synthesis

The complex was prepared by the addition of 1×10^{-3} mol of phthalic acid in 5 cm^3 of methanol to 2×10^{-3} mol of Cu(salNet$_2$)(sal) in 20 cm^3 of methanol with 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 80%. Single crystals suitable for the structure and magnetic determinations were obtained by slow evaporation of a methanol solution. Anal. Calc. for $C_{34}H_{48}N_4O_9Cu_2$ (%): C, 52.10; H, 6.17; N, 7.15. Found: C, 52.47; H, 6.05, N, 7.36.

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 determined and refined by using the angular settings of 24 automatically centred reflections in the range $11 < 2\theta < 24°$ on a Syntex P2$_1$ diffractometer upgraded by Crystal Logic using Zr-filtered MoKα radiation. Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz-polarization and absorption correction were applied using Crystal Logic software. Cell parameters and other relevant details are quoted in Table I. The structure was solved by direct methods using SHELXS86 [13] and refined by full-matrix least-squares techniques with SHELXL93 [14]. The final positional and equivalent thermal parameters of the non-hydrogen atoms are given in Table II. For this complex hydrogen atoms were not included in the refinement because the quality of the data did not allow it. All non-hydrogen atoms, except N(3), C(29), C(30) and C(31) which were disordered, were refined anisotropically. In Table II we report only the atoms with the largest site occupation factors.

RESULTS AND DISCUSSION

Description of the Structure

A perspective view of the complex along with the atom labelling scheme is presented in Fig. 1 and selected bond lengths and angles are given in Table III. The structure consists of binuclear units in which an amphimonodentate phthalate dianion bridges the two Cu(II) ions through oxygen atoms

TABLE I Crystallographic data for the complex

Formula	$C_{34}H_{48}N_4O_9Cu_2$
Formula weight	783.84
T (K)	293
λ (Mo Kα) (Å)	0.71070
Space group	$P2_1/c$
a (Å)	19.9109(9)
b (Å)	10.0465(4)
c (Å)	18.5837(8)
β (°)	100.625(1)
V (Å^3)	3653.7(3)
Z	4
Reflections collected	6006
D_m (g cm^{-3})	1.40
D_c (g cm^{-3})	1.425
μ (cm^{-1})	12.21
R_{int}	0.0327
N_r^{a}	443
Data used	4772
$\Delta\rho_{\max}$ (e Å^{-3})	1.265
$\Delta\rho_{\min}$ (e Å^{-3})	− 1.280
R^{b}	0.0908
R_w^c	0.1146

[a] N_r = number of refined parameters. [b] $R = \sum|\Delta F|/\sum|F_0|$.
[c] $R_w = [\sum w(\Delta F)^2/\sum w|F_0|^2]^{1/2}$.

O(1) and O(3). The chromophore of the first copper cation, Cu(1), consists of O(1) of the phthalato ligand as well as the two nitrogen atoms (N(1), N(2)) and the oxygen atom O(5) of a salNet$_2$ ligand. Similarly, the chromophore of the second copper cation, Cu(2), involves O(3) of the phthalato ligand as well as the two nitrogen atoms (N(3), N(4)) and the oxygen atom O(6) of the second salNet$_2$ ligand. Both Cu(II) ions adopt a square planar geometry. The largest deviation from planarity of the atoms ligated to Cu(1) is 0.11 Å for N(1) with Cu(1) being 0.06 Å out of this plane, whereas for those ligated to Cu(2) atoms the largest deviation from planarity is 0.11 Å for N(3) with Cu(2) lying 0.04 Å out of this plane. The lengths of the Cu–O and Cu–N coordination bonds are in line with those found in the literature [6–8]. The monodentate nature of each carboxylato group is reflected in the elongation of the C(1)–O(1) and C(8)–O(3) bonds with respect to C(1)–O(2) and C(8)–O(4). The phthalato ligand deviates substantially from planarity. The dihedral angle between the benzene ring and the plane of the first carboxylate group, C(1)O(1)O(2), is 10.5° and that with the plane of the second carboxylate group, C(8)O(3)O(4), is 83.9°. The dihedral angle between the first carboxylate group, C(1)O(1)O(2), and the mean plane of the chromophore O(1)O(5)N(1)N(2) is 90.2° and that between the

TABLE II Positional and equivalent thermal parameters ($\times 10^4$) of the non-hydrogen atoms[a]

Atom	x/a	y/b	z/c	U_{eq}[b]
Cu(1)	1574(1)	2177(1)	351(1)	41(1)
Cu(2)	3914(1)	1079(1)	2843(1)	70(1)
O(1)	2073(3)	2940(9)	1271(3)	44(4)
O(2)	1029(3)	3703(7)	1270(3)	51(4)
O(3)	3032(3)	1936(7)	2692(3)	48(4)
O(4)	3554(4)	3505(8)	2171(4)	66(4)
O(5)	1459(4)	563(7)	863(3)	53(5)
O(6)	4189(4)	2135(11)	3695(4)	86(5)
N(1)	1060(4)	1513(8)	−551(4)	47(6)
N(2)	1817(5)	3745(9)	−300(4)	53(6)
N(3)	4786(8)	337(16)	2813(9)	49(4)
N(4)	3640(6)	−233(11)	1949(7)	89(8)
C(1)	1634(5)	3600(9)	1550(5)	40(6)
C(2)	1911(4)	4307(8)	2260(4)	34(5)
C(3)	1482(5)	5229(9)	2510(5)	46(6)
C(4)	1701(6)	5935(10)	3166(5)	56(7)
C(5)	2354(6)	5703(11)	3560(6)	63(8)
C(6)	2792(5)	4797(10)	3321(5)	54(7)
C(7)	2569(4)	4082(9)	2654(5)	39(5)
C(8)	3083(5)	3122(10)	2477(5)	43(6)
C(9)	1112(5)	−505(9)	600(5)	49(6)
C(10)	1081(6)	−1607(11)	1088(6)	58(7)
C(11)	728(6)	−2734(11)	834(6)	64(8)
C(12)	377(6)	−2854(12)	107(7)	68(8)
C(13)	388(5)	−1796(10)	−352(5)	49(6)
C(14)	762(5)	−633(9)	−129(5)	40(5)
C(15)	744(5)	402(10)	−678(5)	47(6)
C(16)	997(8)	2429(12)	−1199(5)	77(11)
C(17)	1187(7)	3849(13)	−903(7)	78(10)
C(18)	1902(7)	5047(10)	97(6)	67(9)
C(19)	1993(8)	6263(11)	−406(8)	87(13)
C(20)	2432(9)	3380(13)	−601(8)	92(14)
C(21)	3044(9)	3226(27)	−37(10)	143(11)
C(22)	4747(6)	2100(19)	4181(8)	101(7)
C(23)	4858(9)	2819(40)	4712(9)	239(11)
C(24)	5434(12)	2937(57)	5285(16)	271(15)
C(25)	5916(18)	1935(44)	5199(15)	258(32)
C(26)	5923(11)	1215(29)	4565(15)	179(15)
C(27)	5300(7)	1140(17)	4027(9)	106(9)
C(28)	5304(9)	410(17)	3353(10)	105(12)
C(29)	4891(14)	−305(27)	2110(14)	114(8)
C(30)	4281(20)	−840(40)	1828(21)	50(9)
C(31)	3049(11)	−1024(22)	2062(12)	134(7)
C(32)	3023(14)	−1437(22)	2776(13)	105(22)
C(33)	3417(11)	574(18)	1257(9)	126(20)
C(34)	3122(13)	−243(24)	550(11)	159(23)

[a] E.s.d.'s in parentheses. [b] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

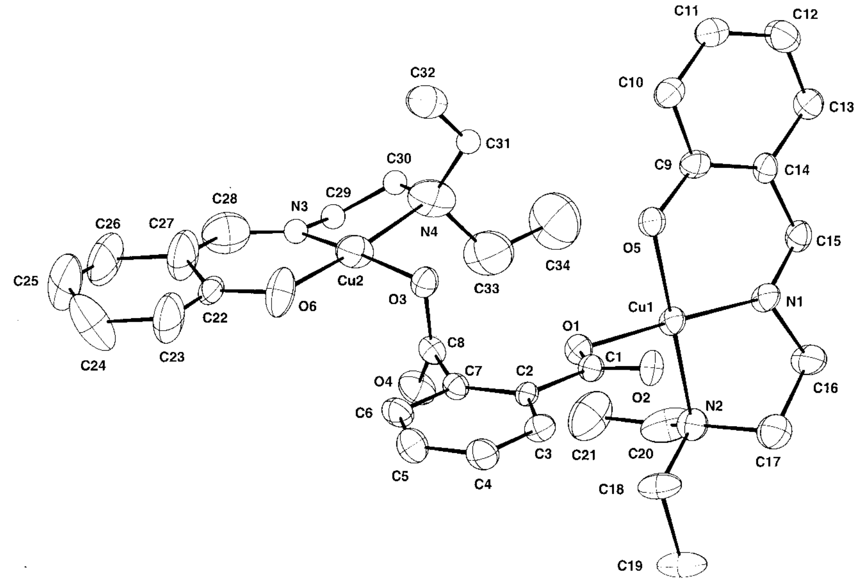

FIGURE 1 A perspective view of $[Cu_2(salNet_2)_2(\mu\text{-phthal})] \cdot 3H_2O$ along with the atom labelling scheme.

second carboxylate group, C(8)O(3)O(4), and the mean plane of the chromophore O(3)O(6)N(3)N(4) is 77.8°. The intramolecular Cu(1)$\cdots$Cu(2) contact is 6.034 Å, whereas the shortest intermolecular Cu$\cdots$Cu distance is 7.383 Å. The Schiff bases are planar and coordinate to both copper(II) ions in a tridentate mode. Their geometries are similar to those reported for the $[Cu(salNet_2)sal]$ and $[Cu(salNme_2)_2]$ complexes [15,16], as well to other $[Cu_2(salNet_2)_2(\mu\text{-dicarboxylato})]$ complexes [6–8].

Spectroscopic Characterization

The positions of $\nu_{as}(COO)$ and $\nu_s(COO)$ bands at $1577\,cm^{-1}$ and $1391\,cm^{-1}$, respectively, in the IR spectrum of the complex as well as their difference, $\Delta = 186\,cm^{-1}$, are characteristic of the monodentate coordination mode of phthalic acid [5–8,17]. The electronic spectrum of a Nujol mull sample of the complex shows a charge transfer band at 25.90 kK, found at 27.17 kK ($\log \varepsilon = 4.89$) in methanol solution. The visible region of the solution spectrum shows a ligand field band at 16.02 kK ($\log \varepsilon = 2.40$). Its position is characteristic of square-planar, four-coordinated Cu(II) chromophores [18–20]. In the solid state spectrum, the shape of this band, found at

TABLE III Bond lengths (Å) and angles (°)[a] for the complex

Copper chromophores			
Cu(1)–N(1)	1.916(7)	O(5)–Cu(1)–N(1)	92.7(3)
Cu(1)–N(2)	2.096(8)	O(5)–Cu(1)–O(1)	89.2(3)
Cu(1)–O(1)	1.968(6)	N(1)–Cu(1)–O(1)	177.1(3)
Cu(1)–O(5)	1.915(7)	O(5)–Cu(1)–N(2)	169.8(3)
Cu(2)–N(3)	1.900(2)	N(1)–Cu(1)–N(2)	84.2(3)
Cu(2)–N(4)	2.112(12)	O(1)–Cu(1)–N(2)	94.3(3)
Cu(2)–O(3)	1.929(6)	O(6)–Cu(2)–N(3)	96.8(5)
Cu(2)–O(6)	1.900(9)	O(6)–Cu(2)–O(3)	89.3(3)
		N(3)–Cu(2)–O(3)	169.4(5)
		O(6)–Cu(2)–N(4)	175.2(4)
		N(3)–Cu(2)–N(4)	80.6(6)
		O(3)–Cu(2)–N(4)	93.9(4)
Phthalato bridge			
C(1)–O(1)	1.280(11)	O(1)–C(1)–O(2)	124.3(8)
C(1)–O(2)	1.226(11)	O(3)–C(8)–O(4)	123.1(9)
C(8)–O(3)	1.267(11)	C(2)–C(1)–O(1)	115.5(8)
C(8)–O(4)	1.244(11)	C(2)–C(1)–O(2)	120.1(8)
C(1)–C(2)	1.511(12)	C(7)–C(8)–O(3)	116.2(8)
C(2)–C(3)	1.396(12)	C(7)–C(8)–O(4)	120.6(9)
C(2)–C(7)	1.396(12)	C(1)–C(2)–C(3)	117.1(8)
C(3)–C(4)	1.408(13)	C(1)–C(2)–C(7)	122.5(8)
C(4)–C(5)	1.390(2)	C(2)–C(3)–C(4)	120.8(9)
C(5)–C(6)	1.390(2)	C(2)–C(7)–C(6)	119.0(8)
C(6)–C(7)	1.430(13)	C(2)–C(7)–C(8)	127.4(8)
C(7)–C(8)	1.487(13)	C(3)–C(2)–C(7)	120.3(8)
		C(3)–C(4)–C(5)	118.8(10)
		C(4)–C(5)–C(6)	121.5(9)
		C(5)–C(6)–C(7)	119.5(10)
		C(6)–C(7)–C(8)	113.6(8)
		C(1)–O(1)–Cu(1)	106.2(5)
		C(8)–O(3)–Cu(2)	110.0(6)

[a] E.s.d.'s in parentheses.

16.43 kK, remains unchanged. Thus, both in the solid state and in solution, the local geometry of the two copper chromophores is square planar as revealed in the X-ray structure.

Magnetic Properties and Exchange Mechanism

The plot of μ_{eff} as a function of temperature, shown in Fig. 2 is almost linear except for a small decrease near liquid helium temperatures. The decrease of μ_{eff} from 1.87 BM to 1.75 BM upon cooling the system from room temperature down to 4.8 K suggests some weak antiferromagnetic interaction leading to a singlet ground state. Also shown in Fig. 2 is the linear χ_{Cu}^{-1} vs. T plot. Least-squares fitting of these data to the Curie–Weiss law gave $C = 0.399\,\text{cm}^3\,\text{mol}^{-1}\,\text{K}$, $\theta = -0.14\,\text{K}$ and $R = 1.0 \times 10^{-6}$ $\left[R = \sum (\chi_{\text{Cu}}^{\text{obs}} - \chi_{\text{Cu}}^{\text{calc}})^2\right]$.

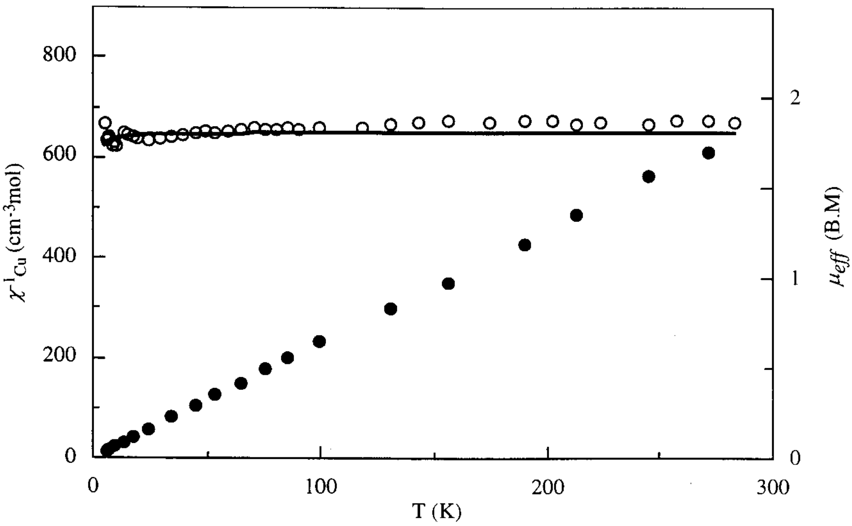

FIGURE 2 Plots of inverse magnetic susceptibility, χ_{Cu}^{-1}, and μ_{eff} of the complex as a function of temperature. The solid line represents the best fit to the data.

The observed experimental magnetic susceptibility data for the complex were fitted by the least-squares method to the Bleany–Bowers equation for the magnetic susceptibility of an isotropic exchange between two copper(II) ions ($\hat{H} = -2J\hat{S}_1\hat{S}_2$) [21]. The best fit values and agreement factors obtained were $2J = -0.34\,\text{cm}^{-1}$, $g = 2.06$, $R = 1.0 \times 10^{-5}$.

In order to elucidate the structural and electronic parameters which influence the exchange phenomenon in the complex, we performed extended Hückel calculations on a simplified model derived from the X-ray structure and using standard atomic parameters [22,23]. According to Hoffmann's model for super-exchange interactions in binuclear complexes [24], the degenerate in- and out-of-phase d-orbital combinations of the metal fragments interact with the symmetry-appropriate orbitals of the bridging ligands, resulting in two SOMOs. The square of the energy gap between the two SOMOs, $(e_1 - e_2)^2$, is closely related to the absolute magnitude of the antiferromagnetic term, J_{AF}, of the superexchange interaction [25,26].

The shapes of the two SOMOs are presented in Fig. 3. For the complex each SOMO is localized on one metal fragment. This is due to the geometry of the intervening bridging ligand shown in Fig. 1, in which one carboxylato group is vertical to the carbon chain. According to our calculations there are no orbitals of the bridging ligand simultaneously delocalized in both carboxylato groups. Thus, upon interaction of these orbitals with the metal

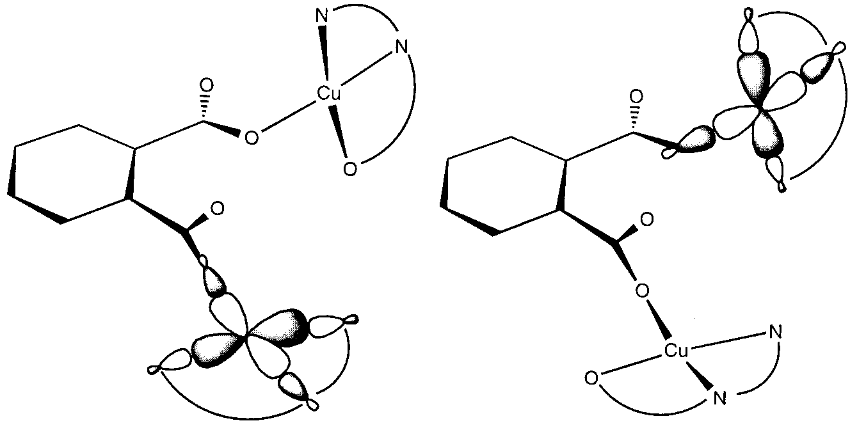

FIGURE 3 Schematic representation of the calculated SOMOs of the studied complex (the N–N–O chelate is the anion of salNet$_2$).

orbitals, each resulting SOMO is an antibonding combination of a metal d-orbital lying in the plane of the chromophore and the lone pairs of four ligating atoms. The two chromophores of the complex are almost orthogonal to each other. This situation is ideal to observe the phenomenon of accidental orthogonality between the magnetic orbitals which leads to a negligible antiferromagnetic term, J_{AF}. Furthermore, the very low value of $(e_1-e_2)^2$ for this complex ($0.0029\,eV^2$) accounts well for the observed very weak antiferromagnetic interaction.

Supplementary Material

Tables of anisotropic temperature coefficients for the non-hydrogen atoms and structure factor listings, as well as Tables of experimental and calculated magnetic susceptibility data are available from the authors on request.

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