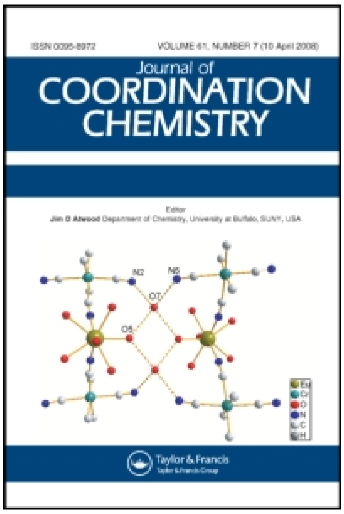

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Crystal Structure and Magnetism of (μ-Maleato)*Bis*[(*N*-(2-(Diethylamino)Ethyl)-Salicylidenaminato)Copper(II)]- Methanol

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CRYSTAL STRUCTURE AND MAGNETISM OF (μ-MALEATO)*BIS*[(*N*-(2-(DIETHYLAMINO)ETHYL)-SALICYLIDENAMINATO)COPPER(II)]-METHANOL

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The crystal and molecular structure of (μ-maleato)bis[(*N*-(2-(diethylamino)ethyl)salicylidenaminato)-copper(II)]-methanol, $[Cu_2(salNet_2)_2(\mu\text{-mal})] \cdot CH_3OH$, where $salNet_2 = N$-(2-(diethylamino)ethyl)salicylidenaminate, has been determined by single-crystal X-ray analysis. The compound crystallizes in the monoclinic space group $P2_1/c$, with $a = 11.994(1)$, $b = 14.723(1)$, $c = 20.0384(1)$ Å, and $\beta = 96.145(2)°$. In the structure two copper(II) ions are bridged by the maleato ligand, which coordinates as a monodentate through its first carboxylato group and as a *bis*-monodentate ligand through its second carboxylato group. The local geometry around the first copper(II) ion is square planar, whereas that around the second is square pyramidal. Fitting of variable-temperature magnetic susceptibility data to the HDVV ($\hat{H} = -2J\hat{S}_1\hat{S}_2$), $S_1 = S_2 = 1/2$ spin exchange model, yields of $2J$ value of $-4.56\,cm^{-1}$. The mechanism of the observed antiferromagnetic interactions is discussed in the light of extended Hückel calculations. Analysis shows an almost linear dependence of the magnitude of the exchange coupling constant, $|2J|$, upon the calculated energy difference between the two SOMOs for a series of μ-dicarboxylato-bridged *bis*-Cu(salNet$_2$) complexes.

Keywords: Copper; Schiff base; X-ray structure; Magnetism

INTRODUCTION

Materials exhibiting antiferromagnetic, ferromagnetic, or even more exotic magnetic properties have been the focus of many contemporary experimental and theoretical studies [1–3]. The target was to synthesize materials with predictable magnetic properties, achieving thus the ultimate goal of molecular engineering [4–7]. Continuing our interest on the investigation of magnetic exchange mechanism of oxygen ligand-bridged metal–metal systems [8–14], we report here the crystal structure of a new binuclear Cu(II) μ-maleato complex with the formula $[Cu_2(salNet_2)_2(\mu\text{-mal})] \cdot CH_3OH$, where salNet$_2$ stands for the anion of the *N*-(2-(diethylamino)ethyl)salicylidenaminato ligand. As far as we know, there is no report of structural or magnetic characterization of a μ-maleato-bridged binuclear copper(II) complex. IR and electronic spectra of the

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complex are discussed in relation with the structure. Experimentally depicted exchange coupling is explained in the light of extended Hückel molecular orbital calculations and compared with what has been found for analogous μ-dicarboxylato bridged *bis*-Cu(salNet$_2$) complexes.

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 tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard [15]. Diamagnetic corrections of the constituent atoms were calculated from Pascal's constants. The value of 60×10^{-6} cm^3 mol^{-1} was used for the temperature-independent paramagnetism of the copper(II) ion. No field-dependent magnetism was found for the samples.

Materials

Maleic acid (H$_2$mal), salicylaldehyde (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 [16].

Synthesis

The complex was prepared by the addition of 1×10^{-3} mol of maleic acid in 5 cm^3 of methanol to 2×10^{-3} mol of Cu(salNet$_2$)(sal) in 20 cm^3 of methanol, under continuous stirring at room temperature; the mixture was refluxed for 1 h. The green microcrystalline precipitate that formed were 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 $C_{31}H_{44}N_4O_7Cu_2$(%): C, 52.32; H, 6.23; N, 7.87. Found: C, 52.46; H, 6.55; N, 7.88.

X-ray Data Collection and Refinement

The crystal system and space group were determined from preliminary oscillation and Weissenberg photographs. Unit shell dimensions were determined and refined 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

TABLE I Summary of data for the complex

Formula	$C_{31}H_{44}N_4O_7Cu_2$
Formula weight	711.78
T (K)	293
λ (Mo Kα) (Å)	0.71070
Space group	$P2_1/c$
a (Å)	11.994 (1)
b (Å)	14.723 (1)
c (Å)	20.038 (1)
β (°)	96.145 (2)
V(Å^3)	3518.2 (4)
Z	4
Reflections collected	5275
D_m (g cm^{-1})	1.33
D_c (g cm^{-1})	1.344
μ (cm^{-1})	12.56
R_{int}	0.0175
Data used	4995
$\Delta\rho_{max}$ (e Å^{-3})	0.675
$\Delta\rho_{min}$ (e Å^{-3})	− 0.276
R^a	0.057
R_w^b	0.159

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

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 [17] and refined by full-matrix least-squares techniques with SHELXL93 [18]. Final positional and equivalent thermal parameters for the non-hydrogen atoms are given in Table II. Several parts of the structure, i.e. ethyls, ethylene groups, are conformationally disordered. We included two models for these groups during refinement. Data for both models are included in the supplementary material. In Table II we report only the atoms with the largest site occupancy 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 two Cu(II) ions are bridged by a maleate dianion acting as a monodentate ligand through its first carboxylato group, C(30)O(5)O(6), and as a *bis*-monodentate ligand through its second carboxylato group, C(27)O(1)O(2). As far as we know, this is the first time that this peculiar coordination mode of the maleato ligand has been observed. The chromophore of the first copper cation, Cu(1), consists of O(1) and O(5) atoms of the maleato ligand as well as the two nitrogen atoms (N(1), N(2)) and the oxygen atom O(3) of a salNet$_2$ ligand. Its local geometry is square pyramidal with O(1) in the apical position. The chromophore of the second copper cation, Cu(2), involves O(2) of the maleato ligand as well as the two nitrogen atoms (N(3), N(4)) and the oxygen atom O(4) of the second salNet$_2$ ligand. Cu(2) adopts square planar geometry. The largest deviation from planarity of the basal atoms ligated to

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

Atom	x/a	y/b	z/c	U_{eq}
Cu(1)	3783 (1)	2202 (1)	1612 (1)	50 (1)
Cu(2)	3569 (1)	3311 (1)	3715 (1)	58 (1)
O(1)	3623 (5)	3166 (4)	2459 (2)	69 (4)
O(2)	2870 (5)	4205 (4)	3064 (3)	79 (4)
O(3)	2287 (5)	2193 (4)	1173 (2)	64 (3)
O(4)	4995 (4)	3877 (4)	3765 (2)	60 (3)
O(5)	4450 (17)	3103 (23)	1048 (13)	61 (4)
N(1)	3504 (5)	1164 (4)	2159 (3)	61 (4)
N(2)	5462 (6)	1870 (6)	1875 (3)	78 (4)
N(3)	4141 (6)	2242 (5)	4178 (3)	62 (4)
N(4)	2000 (25)	3049 (13)	3878 (15)	61 (11)
C(1)	1438 (6)	1719 (6)	1337 (4)	59 (5)
C(2)	360 (8)	1886 (9)	1008 (5)	85 (7)
C(3)	− 557 (9)	1437 (11)	1152 (6)	117 (7)
C(4)	− 508 (9)	768 (11)	1627 (6)	126 (7)
C(5)	517 (9)	556 (9)	1955 (5)	94 (7)
C(6)	1515 (7)	1044 (6)	1827 (4)	65 (5)
C(7)	2551 (18)	787 (6)	2204 (4)	67 (6)
C(8)	4508 (9)	826 (8)	2584 (6)	101 (6)
C(9)	5434 (15)	1419 (15)	2499 (12)	108 (11)
C(10)	6031 (9)	1588 (9)	1268 (6)	107 (6)
C(11)	5282 (11)	1123 (8)	712 (5)	104 (10)
C(12)	6135 (24)	2433 (18)	2271 (14)	88 (15)
C(13)	7389 (21)	2183 (19)	2582 (16)	106 (14)
C(14)	5959 (6)	3520 (5)	3993 (3)	49 (4)
C(15)	6942 (7)	4059 (6)	3972 (4)	66 (5)
C(16)	7984 (7)	3728 (8)	4191 (5)	81 (5)
C(17)	8104 (8)	2858 (9)	4442 (5)	94 (6)
C(18)	7173 (8)	2320 (8)	4481 (5)	81 (6)
C(19)	6089 (6)	2641 (5)	4257 (4)	56 (4)
C(20)	5178 (8)	2059 (6)	4357 (4)	64 (7)
C(21)	3285 (10)	1571 (8)	4335 (5)	92 (8)
C(22)	2175 (21)	2348 (17)	4459 (17)	60 (14)
C(23)	1382 (32)	2715 (25)	3225 (21)	112 (16)
C(24)	172 (36)	2540 (37)	3206 (26)	234 (29)
C(25)	1405 (20)	3830 (15)	4127 (15)	82 (11)
C(26)	2122 (12)	4221 (12)	4680 (7)	112 (9)
C(27)	3068 (8)	3879 (6)	2498 (4)	78 (6)
C(28)	2824 (20)	4459 (12)	1831 (12)	61 (17)
C(29)	3356 (26)	4402 (21)	1241 (13)	50 (18)
C(30)	4400 (22)	3935 (20)	1090 (8)	58 (13)
O(6)	5196 (14)	4468 (10)	968 (8)	101 (11)
O(7)	6333 (15)	4469 (9)	512 (7)	122 (15)
C(31)	9101 (22)	4291 (18)	1030 (17)	163 (19)

[a] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

Cu(1) is 0.10 Å for N(2) with Cu(1) being 0.22 Å out of this plane towards the apical O(1). The largest deviation from planarity of the atoms ligated to Cu(2) is 0.26 Å for N(3) with Cu(2) lying 0.02 Å out of this plane. The monodentate nature of the first carboxylato group is reflected in the elongation of the C(30)–O(5) bond with respect to C(30)–O(6). In contrast, the *bis*-monodentate mode of the second carboxylato group leads to elongation of both C(27)–O(1) and C(27)–O(2) bonds. The non planarity of the maleato ligand is described by the dihedral angle between the mean plane formed by C(27)–C(28)–C(29)–C(30) and the plane of the first carboxylate group, C(30)O(5)O(6). 61.7°, and that with the plane of the second carboxylate group,

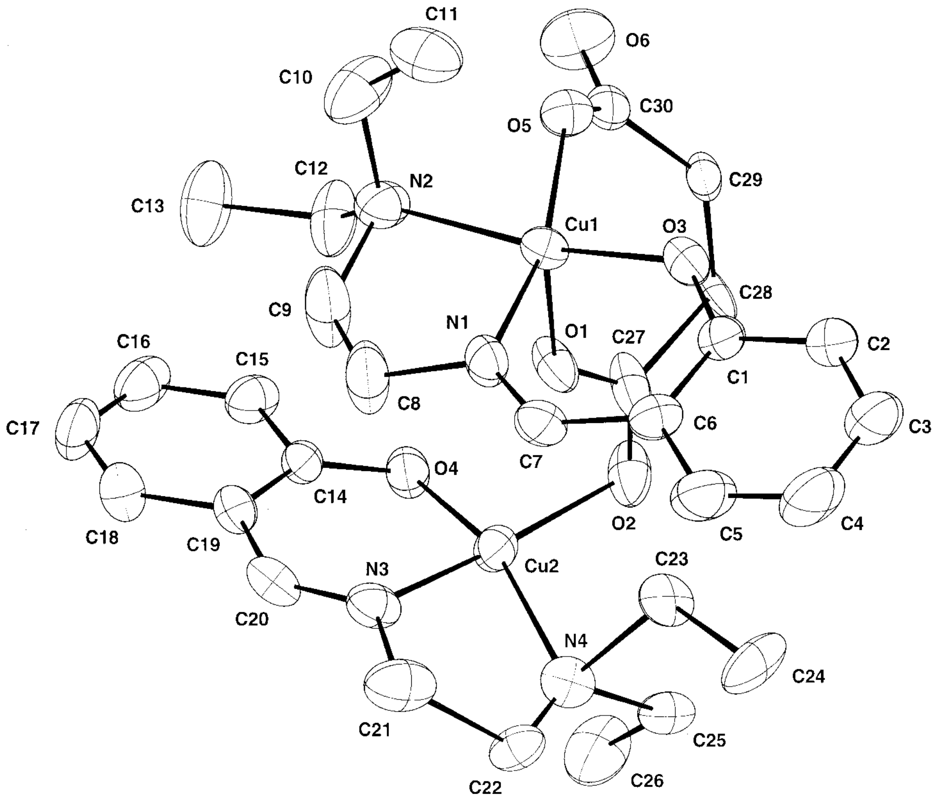

FIGURE 1 A perspective view of $[Cu_2(salNet_2)_2(\mu\text{-mal})] \cdot CH_3OH$ along with the atom labelling scheme.

C(27)O(1)O(2), 28.9°. The dihedral angle between the first carboxylate group, C(30)O(5)O(6), and the mean basal plane of the square pyramid O(5)O(3)N(1)N(2) is 52.3° and that between the second carboxylate group, C(27)O(1)O(2), and the mean plane of the square planar chromophore O(2)O(4)N(3)N(4) is 79.2°. The intramolecular Cu(1) $\cdots$ Cu(2) distance is 4.552 Å, whereas the shortest intermolecular Cu $\cdots$ Cu distance is 5.832 Å. The geometry of the $salNet_2$ Schiff base is quite normal [19,20] and need not be discussed in detail here.

Spectroscopic Characterization

The most interesting features in the IR spectrum are the positions of the $\nu_{as}(COO)$ and $\nu_s(COO)$ bands at $1635\,cm^{-1}$ and $1393\,cm^{-1}$ respectively. Their difference, $\Delta = 242\,cm^{-1}$, is characteristic of the monodentate coordination mode of maleic acid [8–14,21].

The electronic spectrum of a Nujol mull sample of the complex shows a charge transfer band at 25.90 kK, found at 27.24 kK ($\log \varepsilon = 3.93$; $m^{-1}\,cm^{-1}$ units) in methanol solution. The visible region of the solution spectrum shows a ligand field band at 15.92 kK ($\log \varepsilon = 2.40$). The position of this band is characteristic of square planar, four-coordinate Cu(II) chromophores [22–24]. In the solid state spectrum of the complex there is a split in the ligand field band with maximum at 15.97 kK and a shoulder

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

Copper chromophores			
Cu(1)–N(1)	1.931 (6)	N(1)–Cu(1)–N(2)	83.8 (3)
Cu(1)–N(2)	2.084 (7)	O(1)–Cu(1)–O(3)	101.6 (2)
Cu(1)–O(1)	2.236 (5)	O(1)–Cu(1)–O(5)	94.7 (9)
Cu(1)–O(3)	1.912 (5)	O(3)–Cu(1)–O(5)	99.2 (7)
Cu(1)–O(5)	1.970 (3)	N(1)–Cu(1)–O(1)	92.1 (2)
Cu(2)–N(3)	1.917 (7)	N(1)–Cu(1)–O(5)	165.0 (6)
Cu(2)–N(4)	1.980 (3)	N(2)–Cu(1)–O(1)	96.7 (2)
Cu(2)–O(2)	1.975 (6)	N(1)–Cu(1)–O(3)	92.5 (2)
Cu(2)–O(4)	1.895 (5)	N(2)–Cu(1)–O(3)	161.5 (3)
		N(2)–Cu(1)–O(5)	82.1 (6)
		N(3)–Cu(2)–N(4)	93.3 (7)
		O(2)–Cu(2)–O(4)	93.4 (2)
		N(3)–Cu(2)–O(4)	166.3 (2)
		N(3)–Cu(2)–O(4)	93.5 (2)
		N(4)–Cu(2)–O(2)	84.0 (7)
		N(4)–Cu(2)–O(4)	160.8 (8)
Maleato bridge			
C(27)–O(1)	1.250 (9)	O(1)–C(27)–O(2)	121.5 (7)
C(27)–O(2)	1.277 (10)	O(5)–C(30)–O(6)	124.0 (2)
C(30)–O(5)	1.230 (5)	C(28)–C(27)–O(1)	116.8 (11)
C(30)–O(6)	1.280 (3)	C(28)–C(27)–O(2)	120.7 (10)
C(27)–C(28)	1.590 (2)	C(29)–C(30)–O(5)	121.0 (3)
C(28)–C(29)	1.410 (4)	C(29)–C(30)–O(6)	115.0 (3)
C(29)–C(30)	1.490 (3)	C(27)–C(28)–C(29)	128.0 (2)
		C(28)–C(29)–C(30)	132.0 (2)
		C(27)–O(1)–Cu(1)	132.1 (5)
		C(27)–O(2)–Cu(2)	103.2 (5)
		C(30)–O(5)–Cu(1)	127.0 (2)

at 15.03 kK. The latter is indicative of the five membered coordination sphere of the second copper centre [25] and matches well with the crystallographic results.

Magnetic Properties and Exchange Mechanism

A plot of μ_{eff} as a function of temperature, shown in Fig. 2, is essentially linear except for a small decrease near liquid helium temperatures. On cooling the system, μ_{eff} decreases slightly from 1.81 BM at room temperature to 1.46 BM at 4.7 K. This decrease suggests the existence of weak antiferromagnetic interactions leading to a singlet ground state. The data reveal a linear χ_{Cu}^{-1} *vs.* T relation down to 4.7 K. Least-squares fitting of the data to the Curie–Weiss law gave $C = 0.435\,\text{cm}^3\,\text{mol}^{-1}\,\text{K}$, $\theta = -3.07\,\text{K}$ and $R = 1.9 \times 10^{-5}$ $[R = \sum(\chi_{\text{Cu}}^{\text{obs}} - \chi_{\text{Cu}}^{\text{calc}})^2]$. The observed experimental magnetic susceptibility data were fitted by the least-squares method to the Bleany–Bowers equation [26] for the magnetic susceptibility of an isotropic exchange between two copper(II) ions $(\hat{H} = -2J\hat{S}_1\hat{S}_2)$. The best fit values obtained were $2J = -4.60\,\text{cm}^{-1}$, $g = 2.12$; the agreement factor was $R = 1.0 \times 10^{-5}$.

In order to determine 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 [27,28]. According in Hoffmann's model for the superexchange interactions in binuclear complexes [29], 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 energy gap between the two SOMOs.

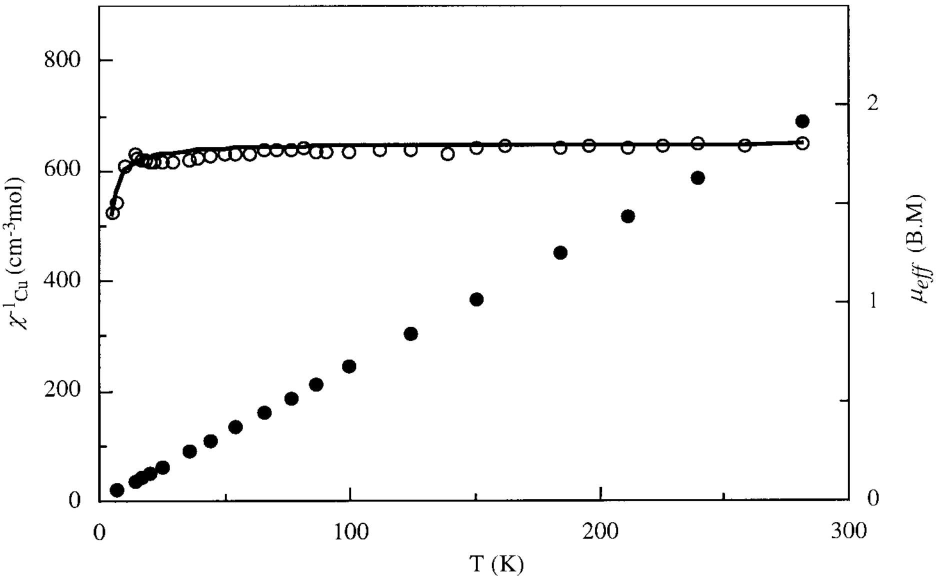

FIGURE 2 Plots of inverse magnetic susceptibility, χ_{Cu}^{-1}, and μ_{eff} of $[Cu_2(salNEt_2)_2(\mu\text{-mal})]\cdot CH_3OH$ as a function of temperature. The solid line represents the best fit to data.

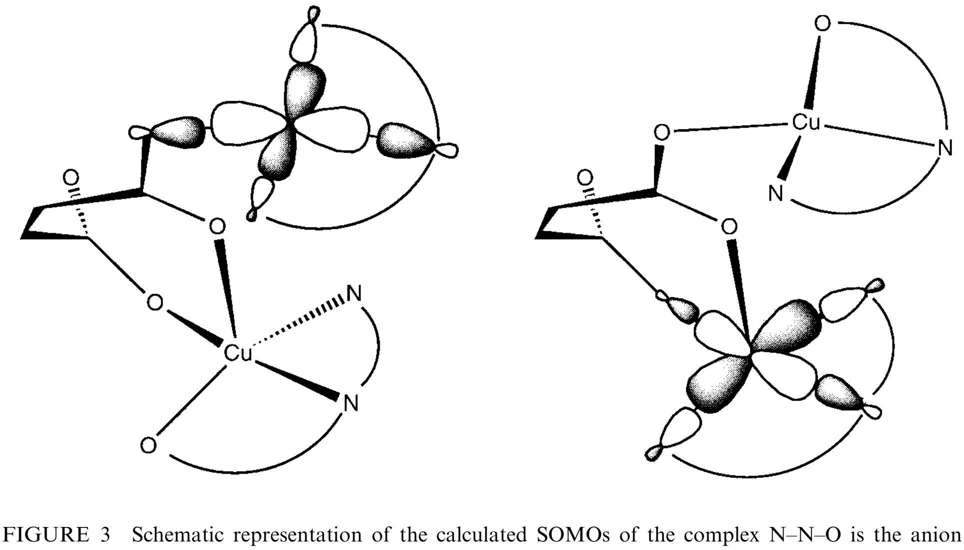

FIGURE 3 Schematic representation of the calculated SOMOs of the complex N–N–O is the anion of $salNet_2$.

$(e_1 - e_2)^2$, is closely related to the absolute magnitude of the antiferromagnetic term, J_{AF}, of the superexchange interaction [30,31].

The shapes of the two SOMOs are presented in Fig. 3. For this complex, each SOMO is localized to 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 with respect 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

TABLE IV Exchange coupling constants and calculated energy differences between the two SOMOs of μ-dicarboxylato bridged *bis*-Cu(salNet$_2$) complexes

Complex[a]	$(e_1-e_2)^2$ ($10^4\,eV^2$)	$2J$ (cm^{-1})	*Ref.*
$[Cu_2(salNet_2)_2(\mu\text{-ter})] \cdot H_2O \cdot CH_3OH$	24	0.60	13
$[Cu_2(salNet_2)_2(\mu\text{-phthal})] \cdot 3H_2O$	29	− 0.34	14
$[Cu_2(salNet_2)_2(\mu\text{-fum})]$	62	− 1.78	11
$[Cu_2(salNet_2)_2(\mu\text{-mal})] \cdot CH_3OH$	84	− 4.60	This work
$[Cu_2(salNet_2)_2(\mu\text{-squar})] \cdot H_2O$	324	− 10.30	10

[a] Ter: dianion of tercphthalic acid; phthal: dianion of phthalic acid; fum: dianion of fumaric acid; mal: dianion of maleic acid; squar: dianion of 1,2-squaric acid.

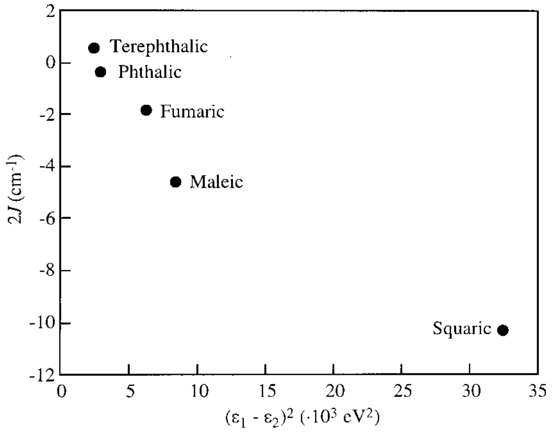

FIGURE 4 Plot of exchange coupling constant *vs.* the calculated energy differences between the two SOMOs of μ-dicarboxylato bridged *bis*-Cu(salNet$_2$) complexes.

of these orbitals with the metal orbitals, each resulting SOMO is an antibonding combination of a metal *d*-orbital lying in the basal plane of the square pyramidal chromophore and the lone pairs of four ligating atoms. However, the two metal fragments are not vertical and thus no accidental orthogonality exists. The value of $(e_1 - e_2)^2$ for the complex is $0.0084\,eV^2$.

Finally, it is worth comparing the values of the square of the energy gap between the two SOMOs, $(e_1 - e_2)^2$, with the exchange coupling constant, $2J$, for a number of carboxylato bridged bis-Cu(salNet$_2$) complexes studied by our group. Numerical values for these quantities are given in Table IV and a plot of $2J$ *vs.* $(e_1 - e_2)^2$ is shown in Fig. 4. From the data it is clear that there is an almost linear dependence of $2J$ upon $(e_1 - e_2)^2$. Taking into account that all calculations have been done with the same atomic parameters, this linear dependence confirms the abovementioned Hoffman model.

Supplementary Material

Tables of anisotropic temperature coefficients, U_{ij}, 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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