

# Synthesis and Magnetic Properties of a Binuclear Copper(II) Complex with a $\mu$ -1,2-Squarato Coordination Mode. Crystal Structure of ( $\mu$ -1,2-Squarato)bis[*N*-(2-(diethylamino)ethyl)salicylideneaminato]aquacopper(II) Hydrate

C. E. Xanthopoulos,<sup>1a</sup> M. P. Sigalas,<sup>1a</sup> G. A. Katsoulos,<sup>1a</sup> C. A. Tsipis,<sup>\*1a</sup> C. C. Hadjikostas,<sup>1b</sup> A. Terzis,<sup>1c</sup> and M. Mentzafos<sup>1c</sup>

Department of Chemistry, Aristotle University, 540 06 Thessaloniki, Greece, and Institute of Material Science, NRCPS "Demokritos", 153 10 Athens, Greece

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The crystal and molecular structure of ( $\mu$ -1,2-squarato)bis[*N*-(2-(diethylamino)ethyl)salicylideneaminato]aquacopper(II) hydrate,  $[\text{Cu}_2(\text{SalNET}_2)_2(\text{H}_2\text{O})(\text{C}_4\text{O}_4)] \cdot \text{H}_2\text{O}$ , where  $\text{SalNET}_2 = N$ -(2-(diethylamino)ethyl)salicylideneamine, has been determined by single-crystal X-ray analysis. The compound crystallizes in the monoclinic system, space group  $P2_1$ , with  $a = 10.6616(9)$  Å,  $b = 11.761(1)$  Å,  $c = 13.712(1)$  Å,  $\beta = 70.678(2)^\circ$ , and  $Z = 2$ . The structure consists of binuclear units built by two nonequivalent copper(II) moieties, namely  $[\text{Cu}(\text{SalNET}_2)\text{H}_2\text{O}]$  and  $[\text{Cu}(\text{SalNET}_2)]$ , bridged by a squarato ligand coordinated to the copper(II) ions in a  $\mu$ -1,2 mode. The geometry of the first copper(II) ion is distorted square pyramidal, whereas that of the second one is approximately square planar. This complex is the first example of an X-ray structurally characterized binuclear transition metal complex with the two metal cations being intervened by a single squarato ligand in a  $\mu$ -1,2-coordination mode. The intramolecular Cu(1)–Cu(2) distance (5.210(6) Å) is the shortest found in squarato-bridged copper(II) complexes. The magnetic behavior of the complex has been studied over the 4.6–295 K temperature range. The fitting of experimental magnetic susceptibilities vs temperature 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  $-10.3$  cm<sup>-1</sup>. The magnitude of the observed antiferromagnetic interaction, which is one of the largest found in copper(II) squarato complexes, has been interpreted in terms of the structural and electronic characteristics of the complex.

## Introduction

Magnetic exchange interactions in transition-metal complexes propagated through extended bridging ligands have attracted the interest of many researchers in the last decade. Among the intervening ligands used so far, particular interest has attracted the squarate dianion  $(\text{C}_4\text{O}_4)^{2-}$ , in hope of correlating the magnetic properties of squarato-bridged bi- and polymetallic systems with the corresponding complexes of the extensively studied oxalate dianion  $(\text{C}_2\text{O}_4)^{2-}$ .<sup>2</sup> However, in spite of the apparent structural similarity of the two ligands, the squarate dianion gave rise to binuclear and chain transition metal complexes with a variety of molecular structures,<sup>3–8</sup> which deviate significantly from the corresponding ones of the oxalato complexes. Apart from some cases where it acts as tetramonodentate,<sup>9,10</sup> in the majority of the structurally characterized squarato-bridged complexes of Fe(III), Ni(II), and Cu(II), the ligand is coordinated in a  $\mu$ -1,3-

bismonodentate fashion giving binuclear and chain structures.<sup>11–15</sup> The  $\mu$ -1,2-bismonodentate coordination mode has been reported only for chain complexes of Cu(II) and Ni(II).<sup>12,16,17</sup>

Reported magnetic measurements of the structurally characterized  $\mu$ -squarato–Cu(II) complexes revealed extremely weak antiferromagnetic interactions compared to those of the corresponding oxalato complexes. Actually, in binuclear Cu(II) complexes containing oxalate, squarate, and dihydroxybenzoquinone dianions,<sup>18</sup> the largest exchange interaction was found for the  $\mu$ -oxalato complex, but the next largest interaction was found for the dihydroxybenzoquinone complex and not the squarato one, as expected on the basis of the Cu–Cu separation.<sup>4b</sup> Apparently, there should be several structural and electronic factors influencing the propagation of magnetic phenomena in the latter complex, accounting as well for the observed discrepancy. In order to rationalize the peculiar magnetic behavior of  $\mu$ -squarato complexes, we report here the synthesis, magnetism, and crystal structure of a new binuclear Cu(II) squarato complex of formula  $[\text{Cu}_2(\text{SalNET}_2)_2(\text{H}_2\text{O})(\text{C}_4\text{O}_4)] \cdot \text{H}_2\text{O}$ , where  $\text{SalNET}_2$  stands for the anion of the *N*-(2-(diethylamino)ethyl)salicylideneaminato ligand. To our knowledge, this complex is the first example of a binuclear transition metal complex with the two

- (1) (a) Laboratory of Applied Quantum Chemistry, Aristotle University. (b) Laboratory of Inorganic Chemistry, Aristotle University. (c) Institute of Material Science, NRCPS "Demokritos".
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**Table I.** Crystallographic Data Collection Parameters

chem formula	C <sub>30</sub> H <sub>42</sub> N <sub>4</sub> O <sub>8</sub> Cu <sub>2</sub>	space group	P2 <sub>1</sub>
a, Å	10.6616(9)	T, °C	25
b, Å	11.761(1)	λ, Å	0.71069
c, Å	13.712(1)	μ, cm <sup>-1</sup>	13.71
β, deg	70.678(2)	ρ <sub>obsd</sub> , g cm <sup>-3</sup>	1.44
V, Å <sup>3</sup>	1622.63(9)	ρ <sub>calcd</sub> , g cm <sup>-3</sup>	1.456
Z	2	F <sub>o</sub>	>3.0σ(F <sub>o</sub> )
fw	711.76	R(obsd) <sup>a</sup>	0.0283
data used	3458	R <sub>w</sub> (obsd) <sup>b</sup>	0.0377

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

metal cations being intervened by a single squarato ligand in a μ-1,2-coordination mode.

### Experimental Section

**Synthesis.** The complex was prepared by adding a methanolic solution of the squaric acid [0.114 g of H<sub>2</sub>C<sub>4</sub>O<sub>4</sub> (1 mmol) in 5 mL of methanol] to a methanolic solution of the Cu(SalNEt<sub>2</sub>)(Sal) complex<sup>19</sup> [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 green microcrystalline solid precipitated was filtered off, washed with cold methanol, and dried in vacuo. Recrystallization was carried out from warm methanol. The yield of the reaction was about 75%. Olive-green crystals suitable for X-ray analysis were obtained by slow evaporation of an acetone solution. Anal. Calcd for C<sub>30</sub>H<sub>42</sub>N<sub>4</sub>O<sub>8</sub>Cu<sub>2</sub>: C, 50.60; H, 5.88; N, 7.73. Found: C, 50.48; H, 5.93; N, 7.84.

**Physical Measurements.** Infrared spectra were recorded on a Perkin-Elmer 1463 spectrophotometer (200–4000 cm<sup>-1</sup>) using KBr pellets. UV-vis spectra of methanol solutions and Nujol mull samples were measured on a Perkin-Elmer Hitachi Model 200 spectrophotometer. Elemental analyses (C, H, N) were performed on a Perkin-Elmer Model 240 elemental analyzer. 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 and found to be -308 × 10<sup>-6</sup> cm<sup>3</sup> mol<sup>-1</sup>. The value 60 × 10<sup>-6</sup> cm<sup>3</sup> mol<sup>-1</sup> was used for the temperature-independent paramagnetism of copper(II) ion. Magnetism of sample was found to be field independent.

**Crystal Structure Determination and Refinement.** 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 30 automatically centered reflections in the range 11° < 2θ < 23° on a Syntex P<sub>21</sub> 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 ψ-scan absorption corrections were applied. Cell parameters and other relevant details are quoted in Table I. The structure was solved by direct methods using SIR88 and refined in two blocks by full-matrix least squares in which Σw<sup>2</sup> was minimized with SHELX76.<sup>20,21</sup> All hydrogen atoms were located from difference Fourier map, but due to insufficient number of observed data, only the positions of the water hydrogens, H(91) and H(92), were refined isotropically. The rest were placed at calculated positions riding on carbon atoms at a distance of 0.96 Å. The alternative model with all coordinates changed in sign was refined to R = 0.0330 and R<sub>w</sub> = 0.0445. 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 hydrogen atom positions, and a complete listing of bond distances and angles have been deposited and are given in Tables SI–SV, respectively.<sup>22</sup>

### Results and Discussion

**Description of the Structure.** The compound crystallizes in the monoclinic space group P2<sub>1</sub>. A perspective view of the complex along with the atom-labeling scheme is presented in Figure 1. Selected bond lengths and angles are given in Table III.

**Table II.** Final Atomic Fractional Coordinates<sup>a</sup> and Equivalent Thermal Parameters<sup>b</sup> (Å<sup>2</sup>) for the Non-Hydrogen Atoms in [Cu<sub>2</sub>(SalNEt<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)(C<sub>4</sub>O<sub>4</sub>)·H<sub>2</sub>O

atom	x/a	y/b	z/c	U <sub>eq</sub>
Cu(1)	0.38056(3)	0.99997(5)	0.20569(3)	0.0357
OW(1)	0.5822(3)	0.9307(3)	0.0954(3)	0.0580
O(51)	0.4322(3)	0.9818(2)	0.3260(2)	0.0492
C(31)	0.4892(3)	1.0576(3)	0.3663(3)	0.0373
C(41)	0.5283(4)	1.0251(4)	0.4513(3)	0.0518
C(51)	0.5859(5)	1.1017(5)	0.4998(3)	0.0662
C(61)	0.6089(5)	1.2141(5)	0.4677(3)	0.0673
C(71)	0.5746(4)	1.2477(4)	0.3840(3)	0.0516
C(81)	0.5156(3)	1.1714(3)	0.3318(3)	0.0380
C(91)	0.4942(3)	1.2134(3)	0.2399(3)	0.0376
N(11)	0.4478(3)	1.1537(2)	0.1821(2)	0.0386
C(101)	0.4385(3)	1.2003(3)	0.0856(3)	0.0457
C(111)	0.3025(4)	1.1667(3)	0.0814(3)	0.0451
N(21)	0.2792(3)	1.0439(3)	0.1036(2)	0.0388
C(121)	0.3315(4)	0.9750(3)	0.0069(3)	0.0508
C(131)	0.2617(4)	0.9888(4)	-0.0725(3)	0.0617
C(141)	0.1345(3)	1.0211(3)	0.1538(3)	0.0484
C(151)	0.0827(4)	1.0603(4)	0.2642(4)	0.0587
O(1)	0.2842(2)	0.8550(2)	0.2339(2)	0.0441
O(4)	0.5740(2)	0.7301(3)	0.1899(2)	0.0509
C(1)	0.3274(3)	0.7569(3)	0.2429(2)	0.0324
C(2)	0.2602(3)	0.6514(3)	0.2751(2)	0.0324
C(3)	0.3851(3)	0.5910(3)	0.2539(3)	0.0360
C(4)	0.4567(3)	0.7008(3)	0.2229(2)	0.0359
O(2)	0.1384(2)	0.6197(2)	0.3071(3)	0.0412
O(3)	0.4167(3)	0.4899(2)	0.2547(2)	0.0526
Cu(2)	0.00819(3)	0.69572(4)	0.26128(2)	0.0393
O(52)	0.1082(2)	0.6572(3)	0.1227(2)	0.0497
C(32)	0.0887(3)	0.6929(4)	0.0381(3)	0.0459
C(42)	0.1729(4)	0.6534(4)	-0.0590(3)	0.0547
C(52)	0.1596(4)	0.6904(5)	-0.1490(3)	0.0615
C(62)	0.0633(4)	0.7707(5)	-0.1493(4)	0.0722
C(72)	-0.0221(4)	0.8090(4)	-0.0569(4)	0.0613
C(82)	-0.0128(3)	0.7714(3)	0.0379(3)	0.0484
C(92)	-0.1102(3)	0.8129(4)	0.1306(3)	0.0527
N(12)	-0.1152(3)	0.7900(3)	0.2232(3)	0.0506
C(102)	-0.2252(4)	0.8323(4)	0.3117(4)	0.0653
C(112)	-0.2519(4)	0.7433(5)	0.3949(4)	0.0653
N(22)	-0.1262(3)	0.7064(3)	0.4075(2)	0.0515
C(122)	-0.1429(5)	0.5966(5)	0.4622(5)	0.0804
C(132)	-0.1597(6)	0.4977(6)	0.3981(6)	0.1077
C(142)	-0.0743(5)	0.7946(5)	0.4647(4)	0.0705
C(152)	-0.1646(7)	0.8298(8)	0.5696(5)	0.1065
OW(2)	0.7378(3)	0.9532(3)	-0.1110(3)	0.0790

<sup>a</sup> Estimated standard deviations in the last significant digits are given in parentheses. <sup>b</sup> U<sub>eq</sub> = (U<sub>11</sub> + U<sub>22</sub> + U<sub>33</sub>)/3.

The structure consists of binuclear units built by two non-equivalent copper(II) moieties, namely [Cu(SalNEt<sub>2</sub>)H<sub>2</sub>O] and [Cu(SalNEt<sub>2</sub>)], bridged by a squarato ligand coordinated to the copper(II) ions in a μ-1,2 mode. Cu(1) adopts a square pyramidal geometry. The equatorial plane of the pyramid includes two nitrogen atoms (N(11), N(21)) and an oxygen atom O(51) of the SalNEt<sub>2</sub> ligand, as well as an oxygen atom O(1) from the squarato ligand. The larger deviation from the mean plane is -0.094 Å for the O(1) atom. An oxygen atom OW(1) from a water molecule occupies the apical position. The Cu(1) atom lies 0.206 Å above the mean equatorial plane. The Cu(2) coordination polyhedron is described as a slightly deformed square plane consisting of two nitrogen atoms (N(12), N(22)) and an oxygen atom O(52) of the SalNEt<sub>2</sub> ligand, as well as an oxygen atom O(2) from the squarato ligand. The larger deviation from the mean plane is -0.195 Å for O(52), and the corresponding deviation of the Cu(2) atom is 0.047 Å. The Cu(1)–OW(1) bond length (2.329(3) Å) is somewhat longer than the reported bonds in analogous Cu(II) complexes.<sup>11,12</sup> The Cu(2)–O(2) bond (1.923(3) Å) is shorter than the Cu(1)–O(1) bond (1.962(2) Å), mainly due to the apical coordination of the water molecule to Cu(1). Quite in line, the bonds between the Cu(1) atom and the ligating atoms of SalNEt<sub>2</sub> are slightly longer than the corresponding bonds for Cu(2).

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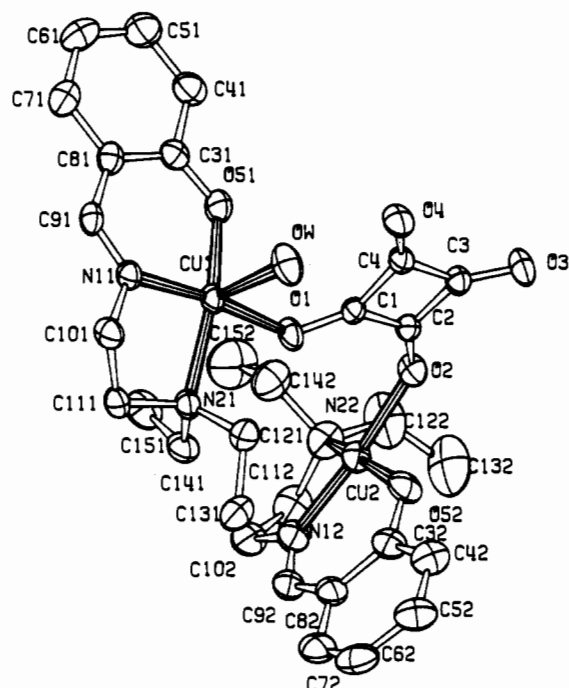


Figure 1. Perspective view of [Cu<sub>2</sub>(SalNEt<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)(C<sub>4</sub>O<sub>4</sub>)]·H<sub>2</sub>O along with the atom-labeling scheme.

Table III. Bond Lengths (Å) and Angles (deg)<sup>a</sup>

Copper Chromophores			
OW(1)—Cu(1)	2.329(3)	N(22)—Cu(2)	2.047(3)
O(51)—Cu(1)	1.916(3)	O(2)—Cu(2)	1.923(3)
N(11)—Cu(1)	1.932(3)	O(52)—Cu(2)	1.900(2)
N(21)—Cu(1)	2.096(3)	N(12)—Cu(2)	1.920(4)
O(1)—Cu(1)	1.962(2)		
N(11)—Cu(1)—O(51)	93.0(1)	N(12)—Cu(2)—O(52)	94.3(1)
O(1)—Cu(1)—N(21)	89.6(1)	N(22)—Cu(2)—O(2)	93.2(1)
O(1)—Cu(1)—OW(1)	97.7(1)	N(22)—Cu(2)—N(12)	84.9(1)
O(1)—Cu(1)—O(51)	90.8(1)	O(52)—Cu(2)—O(2)	89.4(1)
N(21)—Cu(1)—N(11)	84.4(1)		
Squarato Bridge			
C(1)—O(1)	1.264(4)	C(3)—C(2)	1.451(5)
C(4)—O(4)	1.230(4)	O(2)—C(2)	1.281(4)
C(2)—C(1)	1.428(4)	C(4)—C(3)	1.489(5)
C(4)—C(1)	1.470(4)	O(3)—C(3)	1.237(4)
C(3)—C(2)—C(1)	91.7(2)	C(4)—C(3)—C(2)	89.0(2)
C(4)—C(1)—C(2)	90.7(3)	C(3)—C(4)—C(1)	88.6(2)

<sup>a</sup> Estimated standard deviations in the last significant digits are given in parentheses.

The squarato ligand is almost planar, and the largest deviation from the mean plane is  $-0.068$  Å for O(3). The aforementioned shortening of the Cu(2)—O(2) bond results in a longer C(2)—O(2) bond length (1.281(4) Å) with respect to the C(1)—O(1) bond (1.264(4) Å). The C(1)—O(1) and C(2)—O(2) bonds for the squarato ligand are longer than the C(3)—O(3) and C(4)—O(4) bonds (1.237(4) and 1.230(4) Å, respectively). Both the former "hydroxylic" and the latter "ketonic" C—O bond lengths are close to those reported for the free squaric acid and its monolithium salt.<sup>23,24</sup> A larger double bond character was found in the C(1)—C(2) bond (1.428(4) Å) than in the remaining C(2)—C(3), C(3)—C(4), and C(4)—C(1) bonds (mean value 1.470(19) Å). No such deviation has been reported in chain  $\mu$ -1,2-squarato-

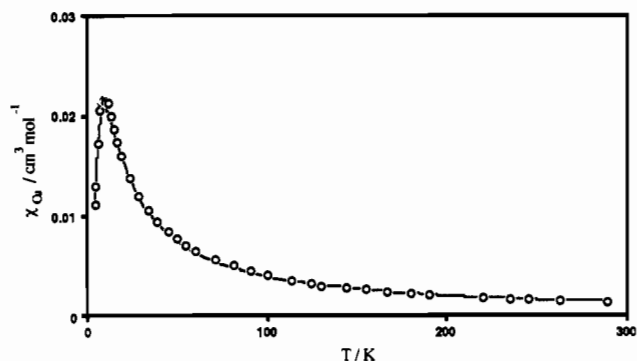


Figure 2. Plot of molar magnetic susceptibility,  $\chi_{Cu}$ , of [Cu<sub>2</sub>(SalNEt<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)(C<sub>4</sub>O<sub>4</sub>)]·H<sub>2</sub>O as a function of temperature. The solid line represents the best fit to the data.

bridged copper(II) and nickel(II) complexes.<sup>12,17</sup> The mean values of C—C—C and O—C—C bond angles are 90.9(14) and 135.0(19) Å, respectively, very close to those reported for nonchelating squarate.<sup>11,12</sup> The dihedral angle between the squarate plane and the Cu(1) basal plane is 58.8°, and the one with the plane of the Cu(2) chromophore is 70.06°. The Schiff bases are planar and coordinate to both copper(II) cations in a tridentate mode. Their geometry and the bond lengths Cu—N and Cu—O and the angles N—Cu—N and N—Cu—O are similar to those reported for the [Cu(SalNEt<sub>2</sub>)(Sal)] and [Cu(SalNMe<sub>2</sub>)<sub>2</sub>] complexes<sup>25,26</sup> and will, therefore, not be discussed in detail here.

There is an intramolecular hydrogen bond, OW(1)—H1—(W1)···O(4). Three other intermolecular H-bonds, OW(1)—H2—(W1)···OW(2), OW(2)—H1(W1)···O(3)<sup>1</sup>, and OW(2)—H2—(W2)···O(52)<sup>1</sup>, as well as van der Waals forces are responsible for the molecular packing. Distances and angles for these hydrogen bonding interactions are listed in Table SVI.<sup>22</sup>

**Spectroscopic Characterization.** The two weak bands at 1777 and 1640 cm<sup>-1</sup> in the IR spectrum of the complex, found also in the spectrum of the free squaric acid,<sup>27</sup> have been assigned to stretching vibrations of localized C=O and C—O bonds.<sup>4</sup> In addition to these bands, a group of strong bands are found at lower energies (1542, 1510, 1478, 1743, 1440 cm<sup>-1</sup>) corresponding to the strong broad band at ca. 1500 cm<sup>-1</sup> found in K<sub>2</sub>C<sub>4</sub>O<sub>4</sub> and are assigned to a combination of C—O and C—C bond stretching vibrations.<sup>28</sup> Both the splitting and the shift of this vibration suggest that the symmetry of the squarato ligand is lower than D<sub>4h</sub>, in line with its X-ray structure observed. Furthermore, the IR spectrum of the complex shows a broad band at 3420 cm<sup>-1</sup> with a shoulder at 3260 cm<sup>-1</sup> associated with the presence of the hydrogen bonds already discussed.

The electronic spectra of a mull sample and methanol solution of the complex show a band at ca. 25 × 10<sup>3</sup> cm<sup>-1</sup> and a clearly charge-transfer intense band (27.17 × 10<sup>3</sup> cm<sup>-1</sup> ( $\epsilon_{max}$  = 9500) in solution and 25.84 × 10<sup>3</sup> cm<sup>-1</sup> in the mull sample).<sup>4</sup> The visible region of the solution spectrum shows also a ligand field band at 15.95 × 10<sup>3</sup> cm<sup>-1</sup> ( $\epsilon_{max}$  = 260). The splitting of this band in an envelope of shoulders at ca. 15.94 × 10<sup>3</sup>, 14.57 × 10<sup>3</sup>, and 13.54 × 10<sup>3</sup> cm<sup>-1</sup> in the solid state-spectrum is indicative of the different geometry of each copper chromophore revealed from the X-ray solved structure.

**Magnetic Properties and Exchange Mechanism.** The molar magnetic susceptibility,  $\chi_{Cu}$ , versus temperature plot is shown in Figure 2. On cooling of the system,  $\chi_{Cu}$  exhibits an increase from 1.39 × 10<sup>-3</sup> cm<sup>3</sup> mol<sup>-1</sup> at 295 K and reaches a maximum of 20.96 × 10<sup>-3</sup> cm<sup>3</sup> mol<sup>-1</sup> at 9.3 K. Further temperature lowering results

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Table IV. Structure and Magnetic Properties of ( $\mu$ -Squarato)copper(II) Complexes<sup>a</sup>

compd	squarato mode/ complex type	copper environ.	Cu—Cu, Å		$\Delta(\text{C—C}), \text{Å}$	$\Delta(\text{C—O}), \text{Å}$	$2J, \text{cm}^{-1}$	ref
			intramol	intermol				
[Cu <sub>2</sub> (bpy) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> (C <sub>4</sub> O <sub>4</sub> )](C <sub>4</sub> O <sub>4</sub> H) <sub>2</sub> ·4H <sub>2</sub> O	$\mu$ -1,3/binucl	4 + 1 <sup>b</sup>	7.465		0.007	0.003	0.00	11
[Cu(im) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (C <sub>4</sub> O <sub>4</sub> )]	$\mu$ -1,3/chain	4 + 2 <sup>c</sup>	7.851		0.060	0.010	0.00	11
[Cu <sub>2</sub> (bpy) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> Br <sub>2</sub> (C <sub>4</sub> O <sub>4</sub> )]	$\mu$ -1,3/binucl	4 + 1 <sup>b</sup>	7.654		0.020	0.010	0.00	11
[Cu <sub>2</sub> (bpy) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> (C <sub>4</sub> O <sub>4</sub> )](NO <sub>3</sub> ) <sub>2</sub>	$\mu$ -1,3/binucl	4 + 1 <sup>b</sup>	7.690	5.441	0.001	0.009	0.00	12
[Cu <sub>2</sub> (bpca) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (C <sub>4</sub> O <sub>4</sub> )]	$\mu$ -1,3/binucl	4 + 1 <sup>b</sup>	7.833	5.740	0.018	0.023	0.00	10
[Cu(terpy)(H <sub>2</sub> O)(C <sub>4</sub> O <sub>4</sub> )]·H <sub>2</sub> O	$\mu$ -1,2/chain	4 + 2 <sup>c</sup>	7.770		0.014	0.030	-0.35	12
[Cu <sub>2</sub> (terpy)(H <sub>2</sub> O) <sub>2</sub> (C <sub>4</sub> O <sub>4</sub> )]·(ClO <sub>4</sub> ) <sub>2</sub>	$\mu$ -1,3/binucl	4 + 1 <sup>b</sup>	7.770		0.025	0.025	-3.60	12
[Cu <sub>2</sub> (SalNEt <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O)(C <sub>4</sub> O <sub>4</sub> )]·H <sub>2</sub> O	$\mu$ -1,2/binucl	4/4 + 1 <sup>b</sup>	5.210	7.474	0.061	0.051	-10.3	this work

<sup>a</sup> bpy = 2,2'-bipyridyl, im = imidazole, terpy = 2,2':6',2''-terpyridine, bpca = bis(2-pyridylcarbonyl)amide anion. <sup>b</sup> Squarato O atoms in equatorial plane. <sup>c</sup> Squarato O atoms in axial positions.

in decrease of  $\chi_{\text{Cu}}$  to  $11.04 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$  at 4.6 K. Furthermore, the  $\mu_{\text{eff}}$  decreases from a value of  $1.76 \mu_{\text{B}}$  at room temperature to a value of  $0.62 \mu_{\text{B}}$  at 4.6 K. The maximum in the susceptibility curve, as well as the  $\mu_{\text{eff}}$  versus temperature course, provide strong evidence for antiferromagnetic interactions leading to a singlet ground state. The data reveals a linear  $\chi_{\text{Cu}}^{-1}$  versus  $T$  relation down to 10 K and then shows marked anomalies near the liquid-helium temperature. Least-squares fitting of the data in the 10–259 K range to the Curie–Weiss law gave  $C = 0.439 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ ,  $\theta = -10.3 \text{ K}$ , and  $R = 6.9 \times 10^{-6}$ .

The energy separation,  $2J$ , between the ground singlet and excited triplet states can be derived from Bleaney–Bowers equation for the magnetic susceptibility of an isotropic exchange between two copper(II) ions ( $\hat{H} = -2J\hat{S}_1\hat{S}_2$ ).<sup>30</sup> The observed experimental magnetic susceptibility data were fitted by the least-squares method to the above model, and the best fit values obtained were  $2J = -10.3 \text{ cm}^{-1}$ ,  $g = 2.04$ , and agreement factor  $R = 1.3 \times 10^{-6}$ . The already discussed intermolecular hydrogen bonding via the noncoordinated water molecule forced us to consider the possibility of an intermolecular exchange interaction present in the complex. To this end, the data were fitted to the same model but with a molecular field correction included.<sup>31,32</sup> The  $2J$  value calculated was almost identical with that of the previous model, whereas the  $2J'$  value was practically zero, thus, excluding any intermolecular interaction. In any case, however, exchange via hydrogen bonds over long distances is assumed very weak.<sup>33,34</sup> The  $2J$  value obtained clearly supports a relatively strong antiferromagnetic coupling of the copper(II) ions, and its magnitude seems to be one of the highest found in squarato-bridged copper(II) complexes. Therefore, it would be interesting to define those unique structural and electronic characteristics of the complex under study which are responsible for its peculiar magnetic behavior. Along this line, literature data concerning structure and magnetic properties of several ( $\mu$ -squarato)copper(II) complexes are collected in Table IV. As can be seen from this table in [Cu<sub>2</sub>(SalNEt<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)(C<sub>4</sub>O<sub>4</sub>)]·H<sub>2</sub>O, the intramolecular Cu—Cu separation is shorter than those found in the remaining complexes, due to the existence of the squarato ligand in its  $\mu$ -1,2-monodentate coordination mode. Furthermore, despite the fact that this coordination mode is also adopted in the chain complex [Cu(terpy)(H<sub>2</sub>O)(C<sub>4</sub>O<sub>4</sub>)]·H<sub>2</sub>O, the Cu—Cu distance is still higher than 7.5 Å, mainly due to the axial coordination of the squarato ligand via the Jahn–Teller effect.

Next, we considered the extend of the  $\pi$ -delocalization within the squarato ring. The stabilization of the ligand orbitals due to this delocalization has been assumed to be the reason for the extremely weak antiferromagnetic interactions observed in

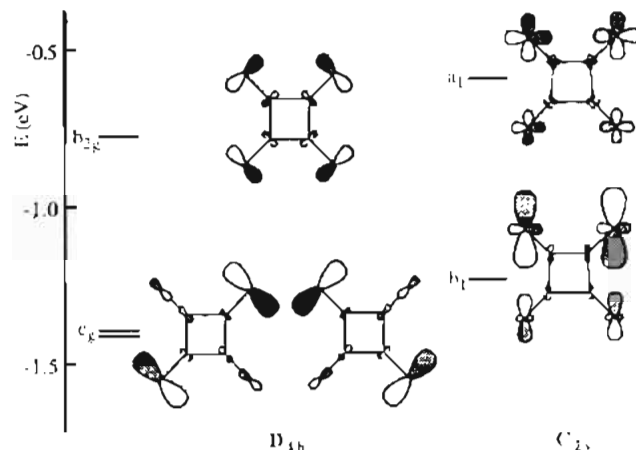


Figure 3. Energy diagram and shape of the HOMOs of the two forms of the squarato dianion.

$\mu$ -squarato–Cu(II) complexes.<sup>17,35</sup> To estimate this delocalization in all complexes shown in Table IV, we calculated the differences between the shortest and the longest C—C and C—O bonds within the squarato dianion,  $\Delta(\text{C—C})$  and  $\Delta(\text{C—O})$ , respectively. An inspection of these values proves that in all complexes there is an extensive delocalization, except in the case of [Cu<sub>2</sub>(SalNEt<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)(C<sub>4</sub>O<sub>4</sub>)]·H<sub>2</sub>O, where the bonds of the squarato ring are localized with values almost identical to those found for the squaric acid ( $\Delta(\text{C—C}) = 0.059 \text{ Å}$ ,  $\Delta(\text{C—O}) = 0.040 \text{ Å}$ ).<sup>23d</sup> In an attempt to find out whether this localization enhances the exchange coupling of the copper(II) ions, we performed extended Hückel calculations on the squarato dianion in both delocalized ( $D_{4h}$ ) and localized ( $C_{2v}$ ) forms.<sup>36–38</sup> The results, depicted in Figure 3, show that the HOMOs of the  $C_{2v}$  dianion are higher in energy and much more localized on the oxygen atoms than the corresponding ones of the  $D_{4h}$  dianion. Hence, a greater interaction of the metal orbitals with the HOMOs of the former is expected, leading to a stronger exchange interaction. Actually, calculations performed on model complexes with the squarato ligand acting either in a  $\mu$ -1,2- or in a  $\mu$ -1,3-mode confirmed these speculations. The larger localization on the oxygen atoms observed in the  $C_{2v}$  ligand is retained also when the squarato is coordinated in a  $\mu$ -1,2-bismonodentate fashion. As a result, a larger delocalization is observed in the SOMOs of  $\mu$ -1,2-squarato than those of  $\mu$ -1,3-. The calculated energy difference between them is  $\Delta E_A = 0.18 \text{ eV}$  and  $\Delta E_B = 0.084 \text{ eV}$ , respectively. According to Hoffmann's model,<sup>39</sup> the square of this energy

(29) Agreement factor calculated from equation,  $R = \sum_i |(\chi_{\text{obsd}})_i - (\chi_{\text{calcd}})_i|^2$ .

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difference can be used to rationalize the alteration in the magnitude of the exchange constant  $J$  between complexes with the same bridge. Thus, from the ratio  $\Delta E_B^2/\Delta E_A^2$ , which is *ca.* 4, it can be estimated that the  $J_A$  exchange constant is larger than  $J_B$ , in accordance with the stronger magnetic interaction observed in our complex as compared to those of the corresponding  $\mu$ -1,3-squarato complexes. Finally, it is worth mentioning that exchange interactions of comparable magnitude have been observed for  $[\text{Cu}_2(\text{bipy})_4(\text{C}_4\text{O}_4)](\text{BF}_4)_2 \cdot 3.5\text{H}_2\text{O}$  ( $2J = -6.8 \text{ cm}^{-1}$ ) and  $[\text{Cu}_2(\text{phen})_4(\text{C}_4\text{O}_4)](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  ( $2J = -20.2 \text{ cm}^{-1}$ ) complexes.<sup>4a</sup> On the basis of spectral data, it has been suggested that the squarato ligand acts in these complexes in a  $\mu$ -1,2-monodentate fashion. Although this suggestion has not been supported by

X-ray diffraction data, we believe that an analogous electron localization of the squarate dianion in these complexes should also exist.

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**Supplementary Material Available:** Tables giving crystal data and details of the structure determination, atom coordinates, bond lengths, bond angles, anisotropic thermal parameters, least-squares planes, and hydrogen atom locations as well as experimental and calculated susceptibility data (11 pages). Ordering information is given on any current masthead page.