

# Synthesis and Magnetic Properties of a Tetranuclear Copper(II) Complex with a $\mu$ -1,2,3,4-Squarato Coordination Mode. Crystal Structure of ( $\mu$ -1,2,3,4-Squarato)tetrakis[tris(2-aminoethyl)amine)copper(II)] Perchlorate

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The crystal and molecular structure of  $[\text{Cu}_4(\text{tren})_4(\text{C}_4\text{O}_4)](\text{ClO}_4)_6$  (where tren and  $\text{C}_4\text{O}_4^{2-}$  are tris(2-aminoethyl)amine and the dianion of 3,4-dihydroxycyclobutenedione, respectively) has been determined by single-crystal X-ray analysis. The compound crystallizes in the monoclinic system, space group  $C2$ , with  $a = 26.972(4)$  Å,  $b = 7.910(1)$  Å,  $c = 18.293(2)$  Å,  $\beta = 132.39(1)^\circ$ , and  $Z = 2$ . The structure consists of tetranuclear  $[\text{Cu}_4(\text{tren})_4(\text{C}_4\text{O}_4)]^{6+}$  cationic units and uncoordinated perchlorate anions. The geometry of the metal ions is trigonal bipyramidal with tren terminal nitrogen atoms in the equatorial positions and the tren central nitrogen and a squarate oxygen in the axial positions. This complex is the first example of an X-ray structurally characterized tetrameric transition metal complex with the four metal cations being bridged by a single squarato ligand in a  $\mu$ -1,2,3,4-coordination mode. The magnetic behavior of the complex has been studied over the 2.5–300 K temperature range. The fitting of the experimental magnetic susceptibilities  $\chi$ s temperature to the Heisenberg–Dirac–Van Vleck  $[\hat{H} = -J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_1 \cdot \hat{S}_4 + \hat{S}_2 \cdot \hat{S}_3 + \hat{S}_3 \cdot \hat{S}_4) - j(\hat{S}_1 \cdot \hat{S}_3 + \hat{S}_2 \cdot \hat{S}_4)]$ ,  $S_1 = S_2 = S_3 = S_4 = 1/2$  spin exchange model yields  $J$  and  $j$  values of  $-19.0$  and  $-0.8$  cm<sup>-1</sup>, respectively. The value of the antiferromagnetic interaction through the OCCO fragment, which is the largest found in structurally characterized squarato-bridged copper(II) complexes, has been interpreted through theoretical calculations in the light of its structural and electronic characteristics.

## Introduction

The behavior as ligand of the squarate dianion ( $\text{C}_4\text{O}_4^{2-}$ ) has been thoroughly investigated in the last years both in solution<sup>2</sup> and in the solid state<sup>3–14</sup> due to its formal similarity with the well-known oxalate ligand. In the light of the reported results, it is clear that the usual chelating and bischelating coordination modes adopted by the oxalato ligand in its metal complexes are uncommon for the squarato ligand. In fact, the value of the bite distance for the squarato ligand is too large to allow it

to adopt either chelating or bischelating coordination modes at least with first-row transition-metal ions.<sup>7d</sup> However, these coordination modes could be achieved when metal ions with larger radii were used, such as divalent alkaline-earth and trivalent lanthanide cations.<sup>11b–d,13c,f,e</sup> Restricting ourselves to

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the squarato complexes with first-row transition metal ions, mononuclear complexes are isolated when squarate acts as a monodentate ligand<sup>7d</sup> whereas dinuclear and chain compounds result when the squarato ligand is coordinated in  $\mu$ -1,3- and  $\mu$ -1,2-bis-monodentate fashions.<sup>2f,4c,e,5b,6d,e,7b-g,8</sup> It deserves to be noted that dodecanuclear compounds,<sup>14c</sup> sheetlike polymers,<sup>4b,13a</sup> and 3D networks<sup>4d,10</sup> have been achieved when squarate acts as a tetra-monodentate ligand.

Reported magnetic measurements on the structurally characterized squarato-bridged complexes show that only weak antiferromagnetic interactions occur between paramagnetic centers. The largest interaction ( $J$ (singlet-triplet energy gap) =  $-10.3 \text{ cm}^{-1}$ ) was reported recently for the dinuclear copper(II) complex of formula  $[\text{Cu}_2(\text{SalNEt}_2)_2(\text{H}_2\text{O})(\text{C}_4\text{O}_4)] \cdot \text{H}_2\text{O}$  [SalNEt<sub>2</sub> stands for the *N*-(2-(diethylamino)ethyl)salicylidene-aminato ligand] where squarate is coordinated in a  $\mu$ -1,2-bis-monodentate fashion.<sup>7g</sup> The significant  $\sigma$  overlap between the two  $d_{x^2-y^2}$  magnetic orbitals of the copper(II) ions through the O-C-C-O fragment accounts for this antiferromagnetic coupling.

In the present work we show how the use of tris(2-aminoethyl)amine (hereafter noted tren) as blocking ligand allows the preparation of the tetranuclear copper(II) complex of formula  $[\text{Cu}_4(\text{tren})_4(\text{C}_4\text{O}_4)](\text{ClO}_4)_6$  where the squarato group acts as a tetra-monodentate ligand and the magnitude of the intramolecular antiferromagnetic coupling is the largest found in the squarato-containing copper(II) complexes. This contribution concerns the preparation and the structural and magnetic characterization of such a tetrameric system.

## Experimental Section

**Materials.** Tren, copper(II) perchlorate hexahydrate, and squaric acid were purchased from commercial sources and used as received. Elemental analyses (C, H, N) were conducted by the Microanalytical Service of the Universidad Aut3noma de Madrid.

**Synthesis. Caution!** Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with care.

**Synthesis of  $[\text{Cu}_4(\text{tren})_4(\text{C}_4\text{O}_4)](\text{ClO}_4)_6$ .** This complex was prepared by adding an aqueous solution of lithium squarate [0.114 g of  $\text{H}_2\text{C}_4\text{O}_4$  (1 mmol) and 0.084 g of  $\text{LiOH} \cdot \text{H}_2\text{O}$  (2 mmol) dissolved in a minimum amount of warm water] to an aqueous solution (50 mL) of  $\text{Cu}(\text{tren})(\text{ClO}_4)_2$  [1.482 g of  $\text{Cu}(\text{H}_2\text{O})_6(\text{ClO}_4)_2$  (4 mmol) and 0.585 g of tren (4 mmol)]. The addition of squarate was accompanied by a color change of the solution from blue to green and by the subsequent formation of a green microcrystalline solid, which was filtered off, washed with cold water, and dried in vacuo. Green needles suitable for X-ray analysis were obtained from the remaining solution by slow evaporation at room temperature. The yield was practically quantitative. Anal. Calcd for  $\text{C}_{28}\text{H}_{72}\text{Cl}_6\text{Cu}_4\text{N}_{16}\text{O}_{28}$ : C, 21.74; H, 4.65; N, 14.48. Found: C, 21.70; H, 4.60; N, 14.33.

**Physical Measurements.** The infrared spectrum was recorded on a Perkin-Elmer 1750 FTIR spectrophotometer as KBr pellets in the 4000–300  $\text{cm}^{-1}$  region, and electronic spectra of aqueous solutions and Nujol mull samples were measured on a Perkin-Elmer Lambda 9 spectrophotometer. Variable-temperature EPR spectra were measured with a Bruker ER 200D spectrometer equipped with a nitrogen cryostat. The magnetic susceptibility of a polycrystalline sample was measured over the temperature range 2.5–300 K in a field of 1 T by using a Metronique Ingenierie MS03 SQUID magnetometer. 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  $-740 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ . The value

**Table 1.** Crystallographic Data for  $[\text{Cu}_4(\text{tren})_4(\text{C}_4\text{O}_4)](\text{ClO}_4)_6$

chem formula	$\text{C}_{28}\text{H}_{72}\text{Cl}_6\text{Cu}_4\text{N}_{16}\text{O}_{28}$	space group	<i>C2</i>
<i>a</i> , Å	26.972(4)	<i>T</i> , °C	21
<i>b</i> , Å	7.910(1)	$\lambda$ , Å	0.710 73
<i>c</i> , Å	18.293(2)	$Q_{\text{calcd}}$ , $\text{g cm}^{-3}$	1.783
$\beta$ , deg	132.39(1)	$\mu$ , $\text{cm}^{-1}$	18.34
<i>Z</i>	2	$R^a$	0.059
fw	1547.85	$R_w^b$	0.051

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

$60 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$  was used for the temperature-independent paramagnetism of the copper(II) ion.

**Crystal Structure Determination and Refinement.** A crystal of dimensions  $0.18 \times 0.10 \times 0.09 \text{ mm}$  was selected, and X-ray diffraction data were collected at 21 °C with an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized Mo K $\alpha$  radiation,  $\lambda = 0.710 73 \text{ \AA}$ . Unit cell parameters were determined from least-squares refinement of the setting angles of 25 reflections with  $2\theta$  angles in the range 17–38°. A summary of the crystallographic data and structure refinement is given in Table 1, and a more complete list of crystallographic data is reported in Table S1.<sup>15</sup> A total of 3305 unique reflections were recorded in the range  $2 < \theta < 55^\circ$  using the  $\omega$ -scan technique. Of them, 2398 were considered as observed ( $I > 2\sigma(I)$ ) and used for the structure refinement. The intensities of three reference reflections monitored throughout the data collection decreased slightly, on average 1.1%. The data were corrected for Lorentz and polarization effects and for linear decay. An experimental absorption correction based on  $\psi$  scans of seven reflections was carried out, the minimum and maximum transmission correction factors being 0.8997 and 0.9987, respectively.

The noncentrosymmetric space group *C2* was chosen on the basis of the intensity distribution and was later confirmed during the structure determination. The structure was solved by direct methods using the SIMPLE programs. The *E* map gave starting positions for Cu, Cl, and the atoms of the squarato group; the remaining atoms were located through successive Fourier synthesis. Localization of atoms and refinement proceeded with some difficulty, probably due to pseudo-4-fold symmetry of the structure. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included at calculated positions and were not refined. The absolute configuration was determined by refining both enantiomers; *R*, *R<sub>w</sub>*, and *s* (goodness of fit) values are lower by 0.002, 0.002, and 0.061 for the chosen enantiomer. The full-matrix least-squares refinement, minimizing  $\sum w(|F_o| - |F_c|)^2$  with  $w = 4F_o^2/(\sigma_c^2 + k(F_o)^2)$  (where  $\sigma_c$  is the standard deviation in  $F^2$  based on counting statistics and  $k = 0.03$ ) and refining 370 parameters, converged at  $R = 0.059$ ,  $R_w = 0.051$ , and  $s = 1.530$ . The final difference Fourier showed residual densities between +0.65 and  $-0.17 \text{ e \AA}^{-3}$ . All calculations were carried out with programs in the MolEN structure determination system.<sup>16</sup> The scattering curves, with anomalous scattering terms included, were those of Cromer and Waber.<sup>17</sup> Final fractional coordinates and selected bond distances and angles are listed in Tables 2 and 3, respectively. Anisotropic thermal parameters, hydrogen atom coordinates, intramolecular bond distances and angles, hydrogen bond parameters, torsion angles, and least-squares planes are given in the supporting information.

## Results and Discussion

**Description of the Structure.** The crystal structure of the title compound is composed of cationic tetranuclear  $[\text{Cu}_4(\text{tren})_4(\text{C}_4\text{O}_4)]^{6+}$  complex units, where the squarate bridges the metal ions in a  $\mu$ -1,2,3,4-mode (Figure 1), and uncoordinated perchlorate counterions. The cation has crystallographic 2-fold symmetry, and a pseudo-4-fold inversion axis. The two crystallographically independent copper(II) ions have approximately trigonal bipyramidal coordination geometries with tren

(15) Supporting information.

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**Table 2.** Final Atomic Fractional Coordinates and Equivalent Isotropic Displacement Parameters<sup>a,b</sup> for Non-Hydrogen Atoms of [Cu<sub>4</sub>(tren)<sub>4</sub>(C<sub>4</sub>O<sub>4</sub>)](ClO<sub>4</sub>)<sub>6</sub>

atom	X/a	Y/b	Z/c	B <sub>eq</sub> , Å <sup>2</sup>
Cu(1)	0.47412(4)	0.5265(2)	0.67657(6)	2.39(2)
Cu(2)	0.31517(3)	0.4741(2)	0.28681(6)	2.38(2)
Cl(1)	0.500	1.000	0.500	2.89(7)
Cl(2)	0.500	0.1259(8)	1.000	6.3(1)
Cl(3)	0.34689(8)	1.0177(4)	0.5770(1)	3.83(6)
Cl(4)	0.71861(9)	0.9591(4)	0.8753(1)	3.96(6)
O(1)	0.4360(2)	0.5057(9)	0.5401(3)	2.6(1)
O(2)	0.4052(2)	0.5001(9)	0.3341(3)	2.9(1)
O(11)	0.4477(3)	0.898(1)	0.4679(7)	9.7(4)
O(12)	0.5166(4)	1.106(1)	0.5729(6)	10.5(3)
O(21)	0.5551(5)	0.233(2)	1.0585(9)	13.1(6)
O(22)	0.4986(5)	0.050(2)	1.0608(6)	15.7(4)
O(31)	0.3647(4)	0.895(2)	0.5438(6)	12.5(4)
O(32)	0.3775(4)	0.998(3)	0.6722(5)	19.5(5)
O(33)	0.2854(4)	1.068(3)	0.5211(7)	17.6(6)
O(34)	0.3768(8)	1.147(2)	0.579(1)	22.6(9)
O(41)	0.6942(4)	0.828(1)	0.8902(7)	12.0(4)
O(42)	0.6747(5)	1.088(2)	0.819(1)	14.9(6)
O(43)	0.7514(4)	0.912(2)	0.8473(6)	13.8(4)
O(44)	0.7690(6)	1.035(3)	0.9647(9)	20.2(8)
N(11)	0.3800(2)	0.509(1)	0.6342(4)	3.7(2)
N(12)	0.5171(3)	0.759(1)	0.7003(5)	3.5(2)
N(13)	0.5263(3)	0.299(1)	0.7286(4)	3.5(2)
N(14)	0.5104(3)	0.555(1)	0.8171(4)	2.9(2)
N(21)	0.2706(3)	0.475(1)	0.1413(4)	3.7(2)
N(22)	0.3152(3)	0.696(1)	0.3484(5)	3.4(2)
N(23)	0.3350(3)	0.242(1)	0.3563(5)	4.0(2)
N(24)	0.2214(2)	0.442(1)	0.2330(4)	2.8(2)
C(1)	0.4712(3)	0.506(1)	0.5174(4)	2.3(2)
C(2)	0.4570(3)	0.502(1)	0.4259(4)	2.1(2)
C(11)	0.3934(3)	0.484(2)	0.7252(5)	5.4(3)
C(12)	0.4525(4)	0.585(2)	0.8079(6)	5.3(3)
C(13)	0.5336(4)	0.832(1)	0.7880(6)	4.0(3)
C(14)	0.5574(4)	0.699(1)	0.8632(7)	4.3(3)
C(15)	0.5780(4)	0.318(2)	0.8392(6)	4.4(3)
C(16)	0.5472(5)	0.397(2)	0.8738(7)	5.0(3)
C(21)	0.1970(4)	0.484(2)	0.0784(6)	4.9(3)
C(22)	0.1782(4)	0.394(2)	0.1281(7)	5.4(4)
C(23)	0.2581(4)	0.688(1)	0.3403(6)	4.0(3)
C(24)	0.2008(4)	0.601(1)	0.2469(6)	4.2(3)
C(25)	0.2710(4)	0.172(2)	0.3158(7)	4.8(3)
C(26)	0.2232(4)	0.301(2)	0.2872(7)	4.9(3)

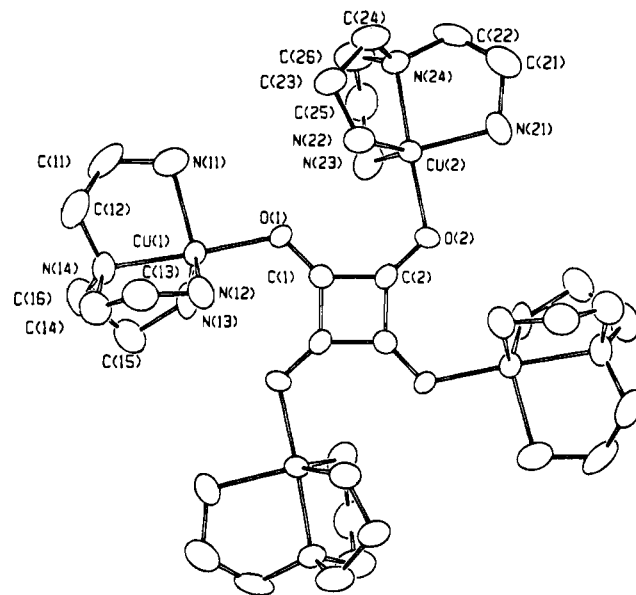
<sup>a</sup> Estimated standard deviations in the last significant digits are given in parentheses. <sup>b</sup>  $B_{eq} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_i a_j$ .

terminal nitrogen atoms in the equatorial positions (Cu–N distances ranging from 2.053 to 2.101 Å) and tren central nitrogen and squarato oxygen atoms in the axial ones (2.056–(7) and 2.018(7) Å for Cu(1)–N(14) and Cu(2)–N(24) and 1.964(5) and 1.962(5) Å for Cu(1)–O(1) and Cu(2)–O(2)). This axially compressed structure is similar to that encountered in other trigonal bipyramidal Cu(II) complexes. The angles in the equatorial planes are close to the ideal trigonal angle of 120° (equatorial N–Cu–N angles ranging from 112.8(3) to 124.5–(3)° at Cu(1) and from 118.5(4) to 120.3(4)° at Cu(2)). Cu(1) and Cu(2) are displaced by 0.182 and 0.177 Å, respectively, from the corresponding equatorial planes toward the axial oxygen atoms. The value of the axial N–Cu–O angle is very close to 180° (177.4(3) and 177.5(3)° for Cu(1) and Cu(2), respectively). Cu–N and Cu–O bond distances are in agreement with previously reported values for tren- and squarato-containing copper(II) complexes.<sup>2f,7b–d, f,g,18</sup> The tren chelate ring conformations are  $\lambda\lambda\lambda$  and  $\delta\delta\delta$  for the Cu(1) and the Cu-

**Table 3.** Selected Bond Lengths (Å) and Interbond Angles (deg) for [Cu<sub>4</sub>(tren)<sub>4</sub>(C<sub>4</sub>O<sub>4</sub>)](ClO<sub>4</sub>)<sub>6</sub><sup>a</sup>

Copper Chromophores			
Cu(1)–O(1)	1.964(5)	Cu(2)–O(2)	1.962(5)
Cu(1)–N(11)	2.101(7)	Cu(2)–N(21)	2.053(7)
Cu(1)–N(12)	2.055(8)	Cu(2)–N(22)	2.084(9)
Cu(1)–N(13)	2.080(8)	Cu(2)–N(23)	2.087(9)
Cu(1)–N(14)	2.056(7)	Cu(2)–N(24)	2.018(7)
O(1)–Cu(1)–N(11)	93.4(2)	O(2)–Cu(2)–N(21)	92.3(3)
O(1)–Cu(1)–N(12)	94.6(3)	O(2)–Cu(2)–N(22)	97.1(3)
O(1)–Cu(1)–N(13)	97.0(3)	O(2)–Cu(2)–N(23)	95.2(3)
O(1)–Cu(1)–N(14)	177.4(3)	O(2)–Cu(2)–N(24)	177.5(3)
N(11)–Cu(1)–N(12)	120.4(3)	N(21)–Cu(2)–N(22)	119.1(4)
N(11)–Cu(1)–N(13)	112.8(3)	N(21)–Cu(2)–N(23)	118.5(4)
N(11)–Cu(1)–N(14)	84.7(3)	N(21)–Cu(2)–N(24)	85.5(3)
N(12)–Cu(1)–N(13)	124.5(3)	N(22)–Cu(2)–N(23)	120.3(4)
N(12)–Cu(1)–N(14)	84.9(3)	N(22)–Cu(2)–N(24)	85.0(3)
N(13)–Cu(1)–N(14)	85.4(3)	N(23)–Cu(2)–N(24)	84.8(3)
Squarato Bridge			
O(1)–C(1)	1.27(1)	O(2)–C(2)	1.27(1)
C(1)–C(2)	1.44(1)	C(1)–C(2) <sup>i</sup>	1.46(1)
Cu(1)–O(1)–C(1)	123.4(3)	Cu(2)–O(2)–C(2)	121.1(6)
O(1)–C(1)–C(2)	135.0(5)	O(2)–C(2)–C(1)	136.9(7)
O(1)–C(1)–C(2) <sup>i</sup>	134.3(6)	O(2)–C(2)–C(1) <sup>i</sup>	133.8(8)
C(2)–C(1)–C(2) <sup>i</sup>	90.7(7)	C(1)–C(2)–C(1) <sup>i</sup>	89.2(5)

<sup>a</sup> Symmetry code: (i) 1 – x, y, 1 – z.

**Figure 1.** Perspective drawing of the tetrameric [Cu<sub>4</sub>(tren)<sub>4</sub>(C<sub>4</sub>O<sub>4</sub>)]<sup>6+</sup> unit with the atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for simplicity.

(2) coordinated molecule ( $\lambda$  and  $\delta$  denote rings of left- and right-handed helicity, respectively).<sup>19</sup>

The squarato ligand is almost planar, and the largest deviation from the mean plane of the squarato carbon atoms is 0.032 Å for O(2). The mean C–C bond length (1.45(1) Å) is practically identical to the mean value found in the acid (1.456(12) Å)<sup>20</sup> and in its dipotassium salt (1.457(8) Å)<sup>21</sup> but intermediate between those reported for [Ni(C<sub>4</sub>O<sub>4</sub>)(H<sub>2</sub>O)<sub>2</sub>] (1.487(16) Å)<sup>4b</sup> and [Ce<sub>2</sub>(H<sub>2</sub>O)<sub>10</sub>(C<sub>4</sub>O<sub>4</sub>)] [Ni(S<sub>2</sub>C<sub>2</sub>O<sub>2</sub>)<sub>2</sub>]<sub>2</sub>·5.2H<sub>2</sub>O (1.438(8) Å),<sup>13a</sup> these last two compounds having the  $\mu$ -1,2,3,4-coordination

(18) (a) Duggan, D. M.; Jungst, R. G.; Mann, K. R.; Stucky, G. D.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1974**, *96*, 3443. (b) Lee, S. C.; Scott, M. J.; Kauffmann, K.; Münck, E.; Holm, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 401.

(19) The previously used symbols  $k$  and  $k'$  are equivalent to  $\lambda$  and  $\delta$ , respectively. See: Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; W. B. Saunders: Philadelphia, 1977; pp 636–644.

(20) Semmingsen, D. *Acta Chem. Scand.* **1973**, *27*, 3961.

(21) Macintyre, W. M.; Werkema, M. S. *J. Chem. Phys.* **1964**, *42*, 3563.

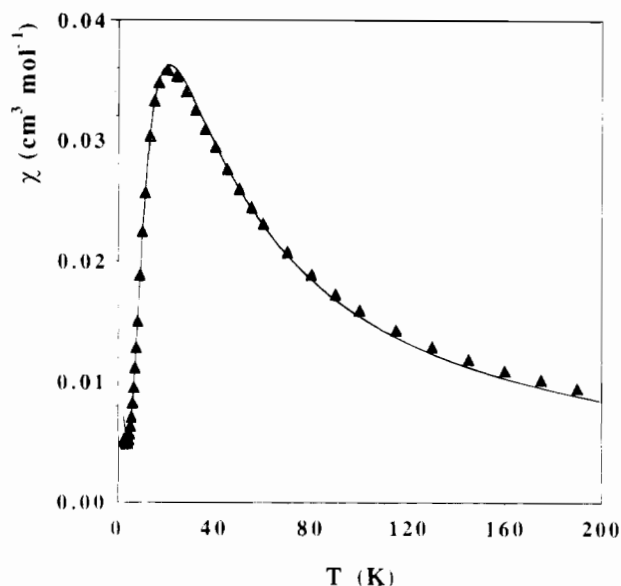
mode of squarate as in the title complex. The values of the C(1)–O(1) and C(2)–O(2) bonds are the same (1.27(1) Å) and are practically identical to the average C–O bond length in  $K_2C_4O_4 \cdot H_2O$ , but significantly shorter than the ketonic C=O bonds for the free squaric acid. The C–C–C and O–C–C bond angles vary in the ranges 89.2(5)–90.7(7) and 133.8(8)–136.9(7)°, values which are very close to those reported for nonchelating squarate. The dihedral angles between the squarate plane and the Cu(1) and Cu(2) equatorial mean planes are 83.8 and 82.9°, respectively.

The complex cation is surrounded by uncoordinated perchlorate ions, two of which are situated on a crystallographic 2-fold axis. Some amine–perchlorate  $NH \cdots O$  contacts [the shortest ones being 3.02(2) and 3.08(1) Å for  $N(11) \cdots O(34)^{ii}$  and  $N(13) \cdots O(12)^{ii}$ , respectively (symmetry code  $ii = x, y - 1, z$ )] suggest the presence of weak hydrogen bonding (supplemental Table S7). The list of close contacts also reveals that the surroundings of the two crystallographically independent tren ligands are different. Metal–metal distances within the tetranuclear entity are  $Cu(1) \cdots Cu(2) = 5.307(2)$  Å,  $Cu(1) \cdots Cu(2)^j = 5.271(2)$  Å,  $Cu(1) \cdots Cu(1)^i = 7.473(2)$  Å, and  $Cu(2) \cdots Cu(2)^j = 7.442(2)$  Å. The shortest intermolecular metal–metal separations are those due to the unit translation along the  $b$  axis (7.910 Å).

**Spectroscopic Characterization.** Apart from the infrared bands attributable to the presence of tren [two sharp (sh) and medium (m) intensity  $\nu(N-H)$  stretching absorptions at 3290 and 3340  $cm^{-1}$ ] and uncoordinated perchlorate (1080 s, br and 620 m, sh), the IR spectrum of the title compound presents a strong and sharp absorption at 1505  $cm^{-1}$ , which corresponds to the strong-broad band at ca. 1500  $cm^{-1}$  found in the spectrum of  $K_2C_4O_4$  and which has been tentatively assigned to a combination of C–O and C–C bond stretching vibrations.<sup>22</sup> The lack of stretching vibrations between 1800 and 1640  $cm^{-1}$  for the squarato ligand of the present complex, in contrast to what is observed in the IR spectra of squaric acid, the squarate dianion, and previously structurally characterized squarate-containing copper(II) complexes (monodentate and bis-monodentate squarato), supports the absence of localized C=O bonds in this ligand. This is in line with its quasi- $D_{4h}$  symmetry, as shown by the X-ray structure determination.

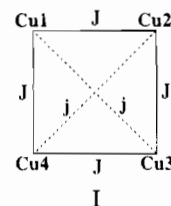
The electronic spectrum of an aqueous solution of the title compound in the UV region displays a strong band at 37 000  $cm^{-1}$  ( $\epsilon = 3.8 \times 10^4$  L  $dm^{-3}$   $cm^{-1}$ ) with a shoulder at 40 000  $cm^{-1}$ , which are attributable to squarate internal transitions. A shoulder at 25 000  $cm^{-1}$  and a very broad band centered at 11 800  $cm^{-1}$  ( $\epsilon = 529$  L  $dm^{-3}$   $cm^{-1}$ ) with a shoulder at 14 300  $cm^{-1}$  are observed in the visible region. The former corresponds to a metal–ligand charge transfer band whereas the latter corresponds to unresolved d–d transitions. The electronic spectrum of a mull sample is essentially identical to that of a solution except for the position of maximum of the very broad d–d feature, which is shifted to 10 000  $cm^{-1}$ . The position of this maximum is in agreement with a roughly trigonal bipyramidal geometry of the copper(II) ion.<sup>23</sup>

**Magnetic Properties and Exchange Mechanism.** The thermal dependence of the magnetic susceptibility for the tetrameric copper(II) unit,  $\chi_M$ , is shown in Figure 2. Cooling causes  $\chi_M$  to exhibit an increase from  $6.4 \times 10^{-3}$   $cm^3$   $mol^{-1}$  at 290 K and to a maximum of  $36.2 \times 10^{-3}$   $cm^3$   $mol^{-1}$  at 22 K. Further temperature lowering results in decrease of  $\chi_M$  to  $5.2 \times 10^{-3}$   $cm^3$   $mol^{-1}$  at 2.5 K. This curve is characteristic of



**Figure 2.** Thermal variation of the molar magnetic susceptibility for  $[Cu_4(tren)_4(C_4O_4)](ClO_4)_6$ : (▲) experimental data; (—) best theoretical fit.

antiferromagnetic interactions among the copper(II) ions ( $\mu_{eff}$  varies from  $7.69 \mu_B$  at 290 K to  $0.65 \mu_B$  at 2.5 K) leading to a singlet ground state. Assuming that the four copper(II) ions are equivalent (I), the susceptibility data can be fitted to a



theoretical expression for the magnetic susceptibility derived through the Hamiltonian

$$\hat{H} = -J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_1 \cdot \hat{S}_4 + \hat{S}_2 \cdot \hat{S}_3 + \hat{S}_3 \cdot \hat{S}_4) - j(\hat{S}_1 \cdot \hat{S}_3 + \hat{S}_2 \cdot \hat{S}_4) \quad (1)$$

where  $J = J_{12} = J_{14} = J_{23} = J_{34}$  and  $j = J_{13} = J_{24}$ . The energies  $E(S, S', S^*)$  of the low-lying states deduced from the Hamiltonian (1) are

$$\begin{aligned} E(0,0,0) &= 0 \\ E(1,1,0) &= E(1,0,1) = -j \\ E(0,1,1) &= 2(J - j) \\ E(1,1,1) &= J - 2J \\ E(2,1,1) &= -J - 2J \end{aligned} \quad (2)$$

$S$ ,  $S'$ , and  $S^*$  being the spin quantum numbers associated with the spin operators

$$\begin{aligned} \hat{S} &= \hat{S}_1 + \hat{S}_2 + \hat{S}_3 + \hat{S}_4 \\ \hat{S}' &= \hat{S}_1 + \hat{S}_3 \\ \hat{S}^* &= \hat{S}_2 + \hat{S}_4 \end{aligned} \quad (3)$$

The theoretical expression for the magnetic susceptibility is

$$\chi_M = (2N\beta^2 g^2 / kT) \frac{W}{Z} (1 - \varrho) + (N\beta^2 g^2 / kT) \varrho \quad (4)$$

(22) Ito, M.; West, B. J. *Am. Chem. Soc.* **1963**, *85*, 2580.

(23) (a) Hathaway, B. J.; Billing, D. E. *Coord. Chem. Rev.* **1970**, *5*, 143.  
(b) Hathaway, B. J. *Struct. Bonding (Berlin)* **1984**, *57*, 55.

where

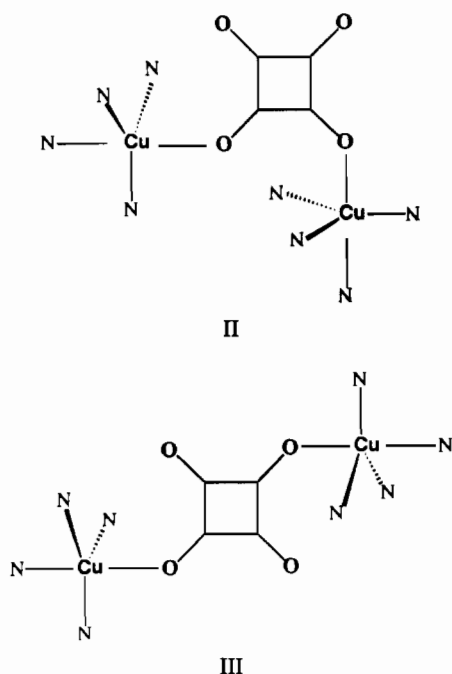
$$W = \exp[(2j - J)/kT] + 2 \exp(j/kT) + 5 \exp[(J + 2j)/kT] \quad (5)$$

and

$$Z = 1 + \exp[(2j - 2J)/kT] + 3 \exp[(2j - J)/kT] + 5 \exp[(J + 2j)/kT] + 6 \exp(j/kT) \quad (6)$$

$N$ ,  $\beta$ ,  $g$ ,  $k$ , and  $T$  have their usual meanings, and  $q$  is the mass portion of uncoupled species assumed to follow a Curie law. Least-squares fitting of the data to eq 4 gave  $J = -19.0 \text{ cm}^{-1}$ ,  $j = -0.8 \text{ cm}^{-1}$ ,  $g = 2.17$ , and  $q = 0.01$  with an agreement factor  $R = \sum_i [\chi_M^{\text{exptl}}(i) - \chi_M^{\text{calc}}(i)]^2 / \sum_i [\chi_M^{\text{exptl}}(i)]^2$  of  $3.6 \times 10^{-4}$ . The EPR spectrum at 120 K consists of a quasi-symmetric feature at 3157 G ( $g_{\text{av}} = 2.14$ ) and a weak half-field signal at 1600 G which decrease in intensity upon cooling, reflecting the occurrence of antiferromagnetic coupling between the copper(II) centers.

The  $J$  value obtained clearly supports a relatively strong antiferromagnetic coupling between adjacent copper(II) ions within the tetrameric  $[\text{Cu}_4(\text{tren})_4(\text{C}_4\text{O}_4)]^{6+}$  unit, and its magnitude is the largest found in structurally characterized squarato-bridged copper(II) complexes. As far as the weak antiferromagnetic coupling between nonadjacent copper(II) ions ( $j$ ) is concerned, its value is in line with the negligible coupling reported previously for  $\mu$ -1,3-squarato-bridged copper(II) complexes.<sup>2f,6e,7c,d,f</sup> Moreover, given the local trigonal-bipyramidal surrounding of the metal ion, it is worth noting that a  $d_{z^2}$  type orbital describes the unpaired electron of each copper(II) ion. In order to analyze both exchange pathways within the  $[\text{Cu}_4(\text{tren})_4(\text{C}_4\text{O}_4)]^{6+}$  unit and define its unique structural and electronic characteristics which are responsible for the much larger antiferromagnetic coupling in  $\mu$ -1,2 with respect to that in  $\mu$ -1,3, extended Hückel calculations were performed by using the CACAO program.<sup>24</sup> Calculations were performed on two model complexes consisting of two copper(II)  $d_{z^2}$  type magnetic orbitals which interact through a squarato ligand acting in  $\mu$ -1,2 (II) and  $\mu$ -1,3 (III) modes,<sup>25</sup> respectively. Atomic parameters



used are shown in Table 4.<sup>26,27</sup> The HOMOs ( $\phi_1 - \phi_6$ ) of the squarato dianion ( $D_{4h}$ ) with the appropriate symmetry to interact

**Table 4.** Orbital Exponents (Contraction Coefficients in Double- $\zeta$  Expansion Given in Parentheses) and Energies Used in the Extended Hückel Calculations

atom	orbital	$\zeta_i (c_i)$	$H_{ii}$ , eV
Cu	4s	2.200	-11.40
	4p	2.200	-6.06
	3d	5.950 (0.5933), 2.300 (0.6168)	-14.00
C	2s	1.625	-21.40
	2p	1.625	-11.40
O	2s	2.275	-32.30
	2p	2.275	-14.80
H	1s	1.300	-13.60
N	2s	1.950	-26.00
	2p	1.950	-13.40

with the  $d_{z^2}$  magnetic orbitals of the metal centers are shown in the energy level diagram in Figure 3. The SOMOs containing the unpaired electrons for the situations illustrated by diagrams II and III are depicted respectively in parts a and b of Figures 4. A comparison between them shows that a larger delocalization is observed in the SOMOs of the  $\mu$ -1,2-squarate. The calculated values of  $\Delta$  (energy gaps between the SOMOs  $\Psi_I$  and  $\Psi_{II}$  in Figure 4) are 76 and 47 meV for the  $\mu$ -1,2- and  $\mu$ -1,3-modes, respectively. According to Hoffmann's model,<sup>26</sup>  $J_{\text{AF}}$  is proportional to  $\Delta^2/(J_{\text{aa}} - J_{\text{ab}})$ , where  $J_{\text{aa}}$  and  $J_{\text{ab}}$  are the one-center and two-center Coulomb repulsion integrals, respectively. Assuming in a first approach that the values of  $(J_{\text{aa}} - J_{\text{ab}})$  are the same for both cases, the antiferromagnetic coupling in the  $\mu$ -1,2-mode would be larger than that in the  $\mu$ -1,3-mode as observed, given that the ratio  $\Delta^2(\mu$ -1,2)/ $\Delta^2(\mu$ -1,3) is ca. 4. Actually,  $J_{\text{aa}}$  must be practically constant in both model systems whereas  $J_{\text{ab}}$  must be much larger for the  $\mu$ -1,2-case. Consequently, the value of  $(J_{\text{aa}} - J_{\text{ab}})$  being much smaller for the  $\mu$ -1,2 situation contributes to an increase in the antiferromagnetic coupling in  $\mu$ -1,2 with respect to  $\mu$ -1,3. These considerations account for the significant difference between the values of  $J$  and  $j$  in our tetrameric complex. As can be observed in Figure 4, several squarato HOMOs have the appropriate symmetry to contribute to the SOMOs  $\Psi_I$  and  $\Psi_{II}$ . However, in each case only two of them (those linked with continuous line) exhibit a larger participation,  $\phi_1$  and  $\phi_4$  in  $\mu$ -1,2 (Figure 4a) and  $\phi_1$  and  $\phi_3$  in  $\mu$ -1,3 (Figure 4b). The greater value of  $\Delta$  in the  $\mu$ -1,2 case with respect to that in the  $\mu$ -1,3 situation is attributed to the greater energy gap between the  $\phi_1$  and  $\phi_4$  HOMOs (2.6 eV) in the former with respect to that between the  $\phi_1$  and  $\phi_3$  HOMOs (1.3 eV) in the latter. It deserves to be pointed out that although the metal-squarate interactions described by the  $\Psi_{II}$  molecular orbitals in parts a and b of Figure 4 are similar, that described by  $\Psi_I$  is rather different. The participation of the carbon skeleton in  $\mu$ -1,2 is much greater than that in  $\mu$ -1,3, leading to larger interaction in the former and therefore to a larger spin delocalization on the bridging squarato ligand.

In a very recent work, an antiferromagnetic coupling of  $-10.3 \text{ cm}^{-1}$  was determined for a  $\mu$ -1,2-squarato-bridged copper(II) dinuclear 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 the magnetic orbital on each copper atom is  $d_{x^2-y^2}$  type,<sup>7g</sup> in contrast to the present case, where the magnetic orbital is  $d_{z^2}$  and  $J = -19 \text{ cm}^{-1}$ . In order to analyze and understand the influence of the symmetry of the magnetic orbital on the value

(24) Mealli, C.; Proserpio, D. M. *Computer Aided Composition of Atomic Orbitals (CACAO Program)*, (kindly supplied by C. Mealli), *J. Chem. Educ.* **1990**, *67*, 399.

(25) The geometrical parameters used were those of the title compound.

(26) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

(27) Hay, P. J.; Thiebault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.

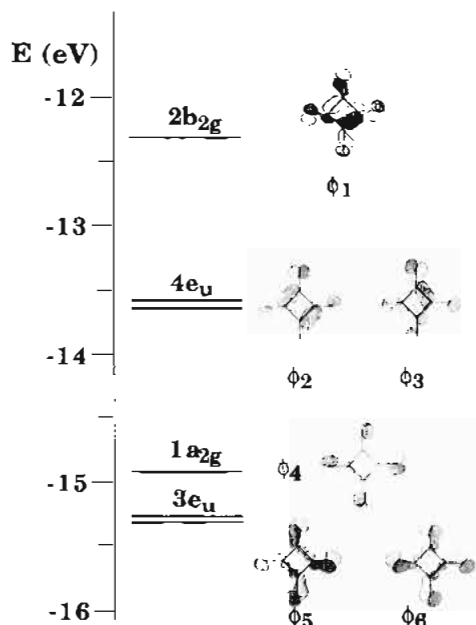
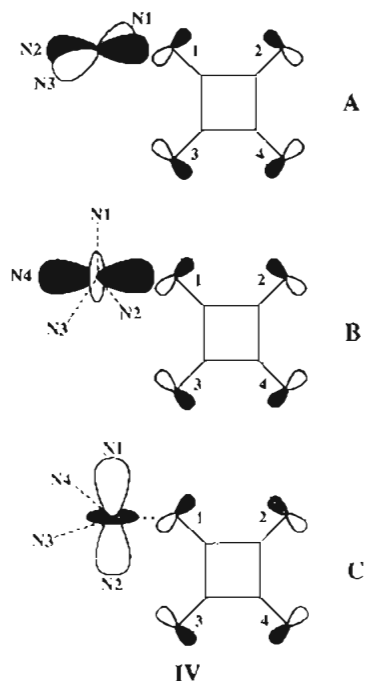


Figure 3. Energy diagram and shape of the HOMOs of the squarate dianion in  $D_{4h}$  symmetry.

of the antiferromagnetic coupling in  $\mu$ -1,2-squarato-bridged dinuclear copper(II) complexes, we have considered the three hypothetical monomeric fragments shown in diagram IV, where



the unpaired electron is defined by  $d_{x^2-y^2}$  (A) and  $d_z$  (B, C) type orbitals. The dinuclear systems may be considered as the combination of two of these monomeric fragments. In A, the four nearest neighbors are three nitrogen atoms and an oxygen atom of the squarate. The unpaired electron is thus described by the orbital

$$\Psi_A = N[d_{x^2-y^2} - \gamma\phi_B - \epsilon\phi_L] \quad (7)$$

with

$$\phi_B = \sigma(O(1)) - c_2\sigma(O(2)) - c_3\sigma(O(3)) + c_4\sigma(O(4)) \quad (8)$$

$$\phi_L = \sigma(N(1)) - \sigma(N(2)) + \sigma(N(3)) \quad (9)$$

where the  $c_i$  is the mixing coefficient of each  $\sigma$  orbital of the squarato oxygens. B and C correspond to the trigonal-bipyramidal symmetry with N(4)CuO(1) (B) and N(1)CuN(2) (C) trigonal axes and N(1)N(2)N(3) (B) and O(1)N(3)N(4) (C) equatorial planes, the magnetic orbitals orbitals would be

$$\Psi_B = N[d_{z^2} - 2(3^{-1/2})\gamma\phi_B - (3^{-1/2})\epsilon\phi_L] \quad (10)$$

$$\Psi_C = N[d_{z^2} - (3^{-1/2})\gamma\phi_B - (3^{-1/2})\epsilon\phi_L'] \quad (11)$$

with

$$\phi_L = \sigma(N(1)) + \sigma(N(2)) + \sigma(N(3)) - 2\sigma(N(4)) \quad (12)$$

$$\phi_L' = 2\sigma(N(1)) + 2\sigma(N(2)) - \sigma(N(3)) - \sigma(N(4)) \quad (13)$$

Assuming that (i)  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals have the same energy and that (ii) the geometry of squarato ligand remains constant in the series A–C, the overlap between the metal ion and squarate only depends on the nature of the d orbital, and consequently, identical values of the mixing coefficients  $\gamma$  and  $\epsilon$  are used in the magnetic orbitals  $\Psi_A$ – $\Psi_C$ .

In order to simplify the evaluation of the overlap integral  $S$  between the magnetic orbitals of all  $\mu$ -1,2-squarato-bridged dinuclear copper(II) complexes, we have neglected the two-center integrals and  $\phi_B$  is considered as a one-center orbital. Under this approximation, the values of  $S$  for the symmetric and asymmetric  $\mu$ -1,2-squarato-bridged complexes are given by

$$S_{A,A'} = \langle \Psi_A | \Psi_{A'} \rangle \propto \gamma^2 \quad (14)$$

$$S_{B,B'} = \langle \Psi_B | \Psi_{B'} \rangle \propto (4/3)\gamma^2 \quad (15)$$

$$S_{C,C'} = \langle \Psi_C | \Psi_{C'} \rangle \propto (1/3)\gamma^2 \quad (16)$$

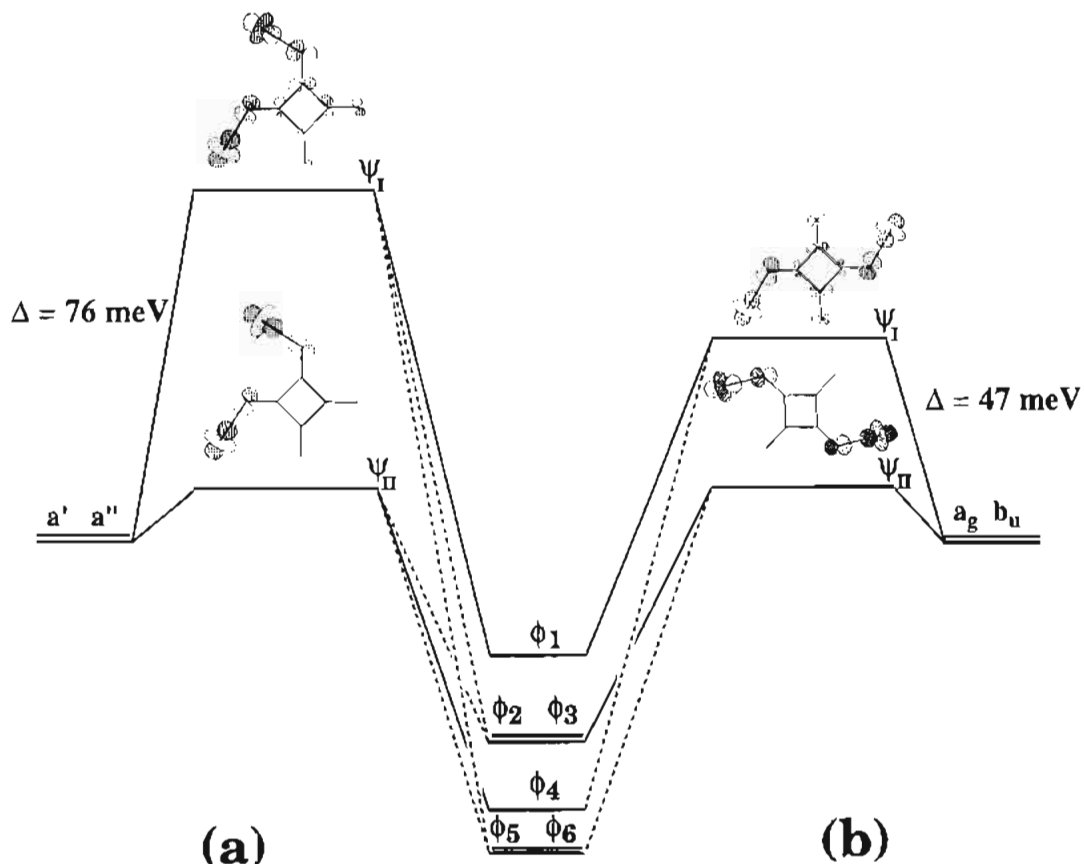
$$S_{A,B'} = \langle \Psi_A | \Psi_{B'} \rangle \propto (2/\sqrt{3})\gamma^2 \quad (17)$$

$$S_{A,C'} = \langle \Psi_A | \Psi_{C'} \rangle \propto (1/\sqrt{3})\gamma^2 \quad (18)$$

$$S_{B,C'} = \langle \Psi_B | \Psi_{C'} \rangle \propto (2/3)\gamma^2 \quad (19)$$

where the prime refers to the second magnetic orbital in the dimer. In the framework of the Kahn's orbital model it is found that  $J$  varies as  $S^2$  (the bielectronic exchange integrals being neglected) for copper(II) dinuclear complexes.<sup>28</sup> Therefore, our predictions concerning the relative magnitudes of the antiferromagnetic interaction are  $J_{B,B'}/J_{A,A'} = 16/9$ ,  $J_{C,C'}/J_{A,A'} = 1/9$ ,  $J_{A,B'}/J_{A,A'} = 4/3$ ,  $J_{A,C'}/J_{A,A'} = 1/3$ , and  $J_{B,C'}/J_{A,A'} = 4/9$ . Keeping in mind that the complex  $[\text{Cu}_4(\text{tren})_4(\text{C}_4\text{O}_4)](\text{ClO}_4)_6$  ( $-19 \text{ cm}^{-1}$ ) corresponds to the B, B' case, a value of  $J$  equal to  $-10.7 \text{ cm}^{-1}$  is calculated for the complex  $[\text{Cu}_2(\text{SalNEt}_2)_2(\text{H}_2\text{O})(\text{C}_4\text{O}_4)] \cdot \text{H}_2\text{O}$  which represents the A, A' case. In fact, the observed value of  $J$  for this complex ( $-10.3 \text{ cm}^{-1}$ )<sup>78</sup> is in excellent agreement with the predicted one in spite of the crude orbital model used. In this respect, we would like to finish the present work with an example of an application of our results to structural predictions. The syntheses and magnetic characterizations of two squarato-bridged dinuclear copper(II) complexes of formulas  $[\text{Cu}_2(\text{phen})_4(\text{C}_4\text{O}_4)](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  and  $[\text{Cu}_2(\text{bpy})_4(\text{C}_4\text{O}_4)](\text{BF}_4)_2 \cdot 3.5\text{H}_2\text{O}$  (phen = 1,10-phenanthroline and bpy = 2,2'-bipyridine) were reported by Hendrickson and co-workers 15 years ago.<sup>7a</sup> Values of  $J$  equal to ca.  $-20$  and  $-7 \text{ cm}^{-1}$  were

(28) (a) Girerd, J. J.; Charlot, M. F.; Kahn, O. *Mol. Phys.* **1977**, *34*, 1063. (b) Kahn, O.; Charlot, M. F. *Nouv. J. Chim.* **1980**, *4*, 567.



**Figure 4.** MO diagram showing the symmetry and energy of the SOMOs resulting from the interaction between two copper(II)  $d_{z^2}$  type orbitals through (a)  $\mu$ -1,2- and (b)  $\mu$ -1,3-squarato bridges. Major and minor contributions of the squarato HOMOs to the SOMOs are indicated by continuous and broken lines, respectively.

determined for the phen and bpy derivatives, respectively. Although their structures remain unknown, our results strongly support a  $\mu$ -1,2-squarato bridge for both complexes with the magnetic orbitals involved being B (phen) and A (bpy) as suggested by the authors on the basis of spectroscopic data. This orbital approach, which can be considered very satisfying for the case of squarato-copper(II) complexes, has also allowed semiquantitative predictions for the antiferromagnetic coupling between two copper(II) centers bridged by extended bridges such as oxalato,<sup>29</sup> oxamidato,<sup>30</sup> and 2,2'-bipyrimidine.<sup>31</sup>

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**Supporting Information Available:** Tables listing crystal data, anisotropic thermal parameters, hydrogen atom coordinates, intramolecular bond distances and angles, hydrogen-bonding parameters, torsion angles, and least-squares planes and a stereodrawing showing the crystal packing (11 pages). Ordering information is given on any current masthead page.

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