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Dinuclear Complexes of Copper(II) Derived from (1,3-Propanediylbis(oxamato))cuprate(II): Magneto–Structural Correlations

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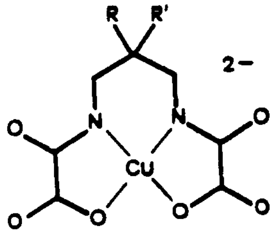
Four complexes of formula $[Cu(Me_2tn)_2][Cu(pba)]\cdot 4H_2O$ (**1**), $[Cu(tn)Cu(pba)]\cdot 4H_2O$ (**2**), $[Cu(bpy)Cu(pba)]\cdot H_2O$ (**3**), and $[Cu(dien)Cu(pba)]\cdot H_2O$ (**4**), in which Me_2tn is 2,2-dimethyl-1,3-diaminopropane, tn is 1,3-diaminopropane, bpy is 2,2′-bipyridyl, dien is diethylenetriamine, and pba is 1,3-propanediylbis(oxamato), have been synthesized. Crystal structures of $[Cu(Me_2tn)_2][Cu(pba)]\cdot 4H_2O$ (**1**) and $[Cu(tn)Cu(pba)]\cdot 4H_2O$ (**2**) have been solved. Compound **1** crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 13.196$ (3) Å, $b = 11.088$ (2) Å, $c = 11.501$ (2) Å, $\alpha = 116.39$ (2)°, $\beta = 116.89$ (3)°, $\gamma = 79.52$ (2)°, and $Z = 2$. The structure consists of an ionic packing of $[Cu(H_2O)(Me_2tn)_2]^{2+}$ cations and $[Cu(pba)]^{2-}$ anions. Compound **2** crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 10.135$ (4) Å, $b = 11.209$ (4) Å, $c = 9.836$ (3) Å, $\alpha = 116.15$ (3)°, $\beta = 80.36$ (2)°, $\gamma = 116.55$ (3)°, and $Z = 2$. The structure consists of molecular $Cu^{II}Cu^{II}$ units in which the Cu(II) ions are bridged by an oxamato group. The Cu(II) ions in the $[Cu(H_2O)(tn)]$ and $[Cu(H_2O)(pba)]$ parts are in square-pyramidal environments. The magnetic properties of all complexes have been investigated. Extended Huckel MO calculations on **2** have shown an asymmetric electronic distribution in the singlet state. Compound **1** follows the Curie law in accordance with its mononuclear nature. The other three compounds exhibit an antiferromagnetic coupling with $J = -345$ (1) cm^{-1} for **2**; $J = -350$ (2) cm^{-1} for **3**, and $J = -100$ (1) cm^{-1} for **4**. The Hamiltonian used was $H = -JS_1S_2$. The EPR spectra of dinuclear compounds indicate that the zero-field-splitting tensor is essentially determined by the dipolar contribution, due to the inefficiency of the oxamato bridge in transmitting the anisotropic exchange interactions.

Introduction

Many studies have been made in order to establish magneto-structural correlations in transition-metal polynuclear complexes.[2] One of the most thoroughly studied families of bridging ligands has been that of the oxalato anion and its derivatives. Dinuclear[3] and polynuclear[4] species containing these bridges show interesting magnetic properties due to the character of oxalato derivatives (monodentate, chelating, bischelating). In recent works, Kahn and co-workers[5,6] have investigated the possibilities of a Cu complex with another bis-bidentate oxalato-like ligand, (1,3-propanediylbis(oxamato))cuprate(II), hereafter abbreviated as $[Cu(pba)]^{2-}$:



(I) R = R′ = H

(II) R = H; R′ = OH

With this complex ligand, Kahn has reported polymetallic systems with high spin multiplicity imposing antiferromagnetic interactions between nearest-neighbor magnetic centers.[5,6] For example, $Mn^{II}Cu^{II}Mn^{II}$ and $Ni^{II}Cu^{II}Ni^{II}$ trinuclear complexes displaying this magnetic behavior were the first ones to be synthesized.[5] They were obtained from the reaction of the copper(II) precursor $[Cu(pba)]^{2-}$ with $[M(Me_6\text{-}14\text{-}ane\text{-}N_4)]^{2+}$, M being Mn or Ni. For these two compounds, no single crystal suitable for X-ray determination was obtained. A single crystal of $Ni^{II}Cu^{II}Ni^{II}$ with $Ni(bapa)^{2+}$ (bapa = bis(3-aminopropyl)amine) has been recently obtained and its magnetic behavior reported by Kahn and Ribas.[7] With the same ligands I and II, several $M^{II}Cu^{II}$ 1-D polymeric systems, with M(II) = Ni(II) and Mn(II), have been reported;[8,9] one of them, $Mn^{II}Cu^{II}$ derived from ligand II, was one of the first low-temperature molecular magnets.[9,10]

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On the other hand, the ability of this kind of ligand to form trinuclear complexes has allowed the synthesis of new trinuclear $Cu^{II}Cu^{II}Cu^{II}$ with tunable magnetic intearctions, blocking the two terminal Cu(II) ions with selected amines that produce different environments.[11]

During the synthesis of the $Ni^{II}Cu^{II}Ni^{II}$ and $Cu^{II}Cu^{II}Cu^{II}$ trinuclear species, a $Ni^{II}Cu^{II}$ dinuclear complex[7] and some $Cu^{II}Cu^{II}$ dinuclear compounds were also obtained. In this paper, we report the four $Cu^{II}Cu^{II}$ compounds so synthesized, $[Cu(Me_2tn)_2][Cu(pba)]\cdot 4H_2O$ (**1**), $[Cu(tn)Cu(pba)]\cdot 4H_2O$ (**2**), $[Cu(bpy)Cu(pba)]\cdot H_2O$ (**3**), and $[Cu(dien)Cu(pba)]H_2O$ (**4**), in which Me_2tn is 2,2-dimethyl-1,3-diaminopropane, tn is 1,3-diaminopropane, bpy is 2,2′-bipyridyl, dien is diethylenetriamine, and pba is 1,3-propanediylbis(oxamato). We describe the synthesis and magnetic properties of these compounds, the crystal structures of **1** and **2**, and extended Hückel calculations of **2**. We must point out that all our efforts to synthesize other dinuclear $Cu^{II}Cu^{II}$ complexes with either I and another amine or with II have been unsuccessful. In all attempts we have obtained either trinuclear species already reported[11] or the starting complexes.

Experimental Section

Syntheses. $[Cu(H_2O)(Me_2tn)_2][Cu(pba)]\cdot 3H_2O$ (1). A 0.045-g (0.58-mmol) amount of Me_2tn was added with continuous stirring to a solution of 0.215 g (0.58 mmol) of copper perchlorate hexahydrate in 15 mL of water. A 0.250-g (0.58-mmol) sample of sodium (1,3-propanediylbis(oxamato))cuprate(II)[12,13] dissolved in 20 mL of hot water was then added slowly to the rapidly stirred solution. After filtration, the blue solution was left to stand at room temperature. Well-shaped blue single crystals were obtained by slow evaporation of this aqueous solution. Anal. Calcd for $C_{17}H_{42}N_6O_{10}Cu_2$: C, 33.05; H, 6.85; N, 13.60; Cu, 20.57. Found: C, 33.1; H, 6.9; N, 13.4; Cu, 20.3.

$[Cu(H_2O)(tn)Cu(H_2O)(pba)]\cdot 2H_2O$ (2). A 0.043-g (0.58-mmol) amount of tn was added with continuous stirring to a solution of 0.215 g (0.58 mmol) of copper perchlorate hexahydrate in 15 mL of water. A 0.250-g (0.58-mmol) sample of sodium (1,3-propanediylbis(oxamato))cuprate(II)[12,13] dissolved in 20 mL of hot water was then added slowly to the rapidly stirred solution. A slight blue impurity was removed by filtration, and the concentrated solution was left to stand at room temperature. After 2 days, well-shaped blue single crystals were obtained by slow evaporation of the aqueous solution. Anal. Calcd for $C_{10}H_{24}N_4O_{10}Cu_2$: C, 26.64; H, 4.92; N, 11.49; Cu, 26.10. Found: C, 24.7; H, 4.9; N, 11.6; Cu, 26.3.

$[Cu(bpy)Cu(pba)]\cdot H_2O$ (3). A 0.090-g (0.58-mmol) amount of bpy was added with continuous stirring to a solution of 0.215 g (0.58 mmol) of copper perchlorate hexahydrate in 10 mL of water/acetone (1/1). A 0.250-g (0.58-mmol) amount of sodium (1,3-propanediylbis(oxamato))cuprate(II)[12,13] dissolved in 20 mL of hot water was then added slowly to the rapidly stirred solution. After previous filtration, the concentrated solution was allowed to cool in an iace bath. The CuCu complex precipitates as a microcrystalline green powder, which was filtered and dried under vacuum. The new complex is insoluble in all common solvents. Anal. Cacld for $C_{17}H_{16}N_4O_7Cu_2$: C, 39.61; H, 3.11; N, 10.87; Cu, 24.67. Found: C, 39.8; H, 3.2; N, 11.0; Cu, 24.8.

$[Cu(dien)Cu(pba)]\cdot H_2O$ (4). A 0.060-g (0.58-mmol) sample of dien was added with continuous stirring to a solution of 0.215 g (0.58 mmol) of copper perchlorate hexahydrate in 20 mL of water. A 0.25-g (0.58-mmol) amount of sodium (1,3-propanediylbis(oxamato))cuprate(II)[12,13] dissolved in 20 mL of hot water was then added slowly to the rapidly stirred solution. After previous filtration to remove any impurities, the concentrated solution was poured into 50 mL of cool acetone with constant stirring. The new dinuclear complex precipitated as a microcrystalline powder, which was filtered and dried under vacuum. $[Cu(dien)Cu(pba)]\cdot H_2O$ is soluble in water but with slow decomposition. Anal. Calcd for $C_{11}H_{21}N_5O_7Cu_2$: C, 28.57; H, 4.52; N, 15.15; Cu, 27.50. Found: C, 28.6; H, 4.5; N, 15.1; Cu, 27.7.

Table I. Crystallographic Data for $[Cu(H_2O)(Me_2tn)_2][Cu(pba)]\cdot 3H_2O$ (**1**) and $[Cu(H_2O)(tn)Cu(H_2O)(pba)]\cdot 2H_2O$ (**2**)

	1	**2**
chem formula	$C_{17}H_{42}N_6O_{10}Cu_2$	$C_{10}H_{24}N_4O_{10}Cu_2$
fw	617.14	487.08
space group	$P\bar{1}$	$P\bar{1}$
T, K	298	298
a, Å	13.196 (3)	10.135 (4)
b, Å	11.088 (2)	11.209 (4)
c, Å	11.501 (2)	9.836 (3)
α, deg	116.39 (2)	116.15 (3)
β, deg	116.89 (3)	80.36 (2)
γ, deg	79.52 (2)	116.55 (3)
V, Å^3	1344.0 (7)	896.6 (9)
Z	2	2
d_{calcd}, g cm^{-3}	1.570	1.790
λ, Å	0.71069 (Mo Kα)	0.71069 (Mo Kα)
μ(Mo Kα), cm^{-1}	17.10	25.23
$R(F_o)$	0.049	0.064
$R_w(F_o)$	0.051	0.064

Table II. Final Atomic Coordinates ($\times 10^4$) of $[C_{17}H_{37}N_6O_7Cu_2]\cdot 3H_2O$ (**1**)

	x/a	y/b	z/c	B_{EQ},[a] Å^2
Cu(1)	11337 (3)	11009 (4)	64054 (4)	2.25 (2)
O(1)	2665 (2)	653 (3)	6623 (3)	3.52 (12)
C(2)	3021 (3)	1205 (4)	6105 (4)	2.65 (14)
O(3)	3927 (2)	978 (3)	6016 (3)	4.01 (13)
O(4)	2525 (2)	2859 (3)	5087 (3)	3.31 (12)
C(5)	2209 (3)	2178 (3)	5517 (3)	2.29 (13)
N(6)	1261 (2)	2235 (3)	5591 (3)	2.37 (11)
C(7)	396 (3)	3142 (4)	5113 (4)	2.99 (15)
C(8)	−352 (3)	3620 (4)	5917 (4)	2.99 (15)
C(9)	−1048 (3)	2528 (4)	5703 (4)	2.94 (15)
N(10)	−353 (2)	1562 (3)	6274 (3)	2.33 (11)
C(11)	−672 (3)	1073 (3)	6930 (3)	2.11 (12)
O(12)	−1566 (2)	1259 (3)	7076 (3)	3.73 (13)
O(13)	62 (2)	−324 (3)	8254 (3)	3.22 (11)
C(14)	233 (3)	179 (4)	7580 (3)	2.45 (13)
O(15)	1139 (2)	64 (3)	7415 (3)	2.72 (10)
Cu(2)	28510 (3)	1372 (4)	11528 (4)	2.31 (2)
N(16)	1868 (2)	1445 (3)	2009 (3)	2.77 (12)
C(17)	1259 (3)	2435 (4)	1395 (4)	3.21 (16)
C(18)	2049 (3)	3393 (3)	1497 (4)	2.73 (14)
C(181)	1282 (4)	4323 (5)	815 (6)	5.39 (26)
C(182)	2814 (3)	4199 (4)	3029 (4)	3.79 (17)
C(19)	2682 (3)	2638 (4)	567 (4)	3.17 (15)
N(20)	3487 (2)	1649 (3)	1071 (4)	2.98 (13)
N(21)	1808 (2)	−1388 (3)	454 (3)	2.58 (12)
C(22)	2208 (3)	−2804 (4)	210 (4)	3.15 (16)
C(23)	2954 (3)	−3313 (3)	−600 (4)	2.56 (13)
C(231)	2343 (4)	−3249 (4)	7944 (4)	3.98 (18)
C(232)	3229 (4)	−4766 (4)	−770 (5)	3.91 (18)
C(24)	4045 (3)	−2535 (4)	284 (4)	3.32 (16)
N(25)	3947 (2)	−1100 (3)	455 (3)	2.97 (13)
OW(1)	4180 (2)	568 (3)	3523 (3)	4.46 (14)
OW(2)	3649 (3)	−2337 (3)	4133 (4)	4.89 (15)
OW(3)	4620 (3)	4163 (3)	6580 (4)	5.18 (16)
OW(4)	4019 (2)	−800 (3)	8091 (3)	3.64 (12)
OW(5)	4391 (3)	6628 (4)	6380 (4)	5.31 (16)

[a] $B_{EQ} = (8\eta^2/3)U_{ij}A_i{}^*A_j{}^*A_iA_j$.

Crystal Data Collection and Refinement. Single crystals of **1** and **2** were selected and mounted on Enraf-Nonius (**1**) and on Philips PW-1100 (**2**) four-circle diffractometers. Unit cell parameters were determined from automatic centering of 25 reflections ($12 \leq \theta \leq 16$ in **1** and $4 \leq \theta \leq 12$ in **2**) and refined by least-squares methods. Intensities were collected with graphite-monochromatized Mo Kα, radiation by using the ω-2θ scan technique in **1** and ω scan technique in **2**. Three reflections were measured every 2 h as an orientation and intensity control; significant intensity decay was not observed. Lorentz–polarization but no absorption corrections were made. The crystallographic data, conditions employed for the intensity data collection, and some features of the structure refinements are listed in Table I.

The structures were solved by direct methods, with the MULTAN system of computer programs[14] and refined by full-matrix least-squares methods,

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Table III. Final Atomic Coordinates ($\times 10^4$) of $[C_{10}H_{20}N_4O_8Cu_2]\cdot 2H_2O$ (**2**)

	x/a	y/b	z/c	B_{EQ},[a] Å^2
Cu(1)	69208 (8)	46228 (7)	53293 (8)	1.83 (4)
Cu(2)	26403 (8)	−3842 (7)	21808 (7)	1.85 (4)
O(1)	8668 (5)	6059 (5)	4805 (5)	2.45 (18)
C(2)	992 (6)	2639 (6)	4179 (6)	1.60 (22)
O(3)	−12 (5)	1522 (5)	4249 (5)	2.53 (18)
C(4)	1900 (6)	2481 (6)	2725 (6)	1.69 (23)
O(5)	1521 (5)	1219 (5)	1650 (5)	2.41 (18)
N(6)	7014 (6)	6290 (5)	7188 (6)	1.98 (21)
C(7)	6053 (7)	6268 (7)	8472 (7)	2.38 (25)
C(8)	4485 (7)	5062 (8)	7998 (8)	2.59 (28)
C(9)	4346 (8)	3524 (7)	7190 (7)	2.56 (26)
N(10)	5040 (6)	3253 (6)	5713 (6)	1.97 (21)
C(11)	4371 (7)	2081 (7)	4504 (7)	1.86 (25)
O(12)	3142 (5)	1011 (5)	4367 (5)	2.15 (18)
O(13)	4669 (5)	964 (5)	1875 (5)	2.31 (19)
C(14)	5269 (7)	2040 (7)	3069 (6)	1.71 (24)
O(15)	6520 (5)	3068 (5)	3206 (5)	2.16 (18)
N(16)	580 (6)	−1375 (6)	2711 (6)	2.04 (20)
C(17)	−266 (7)	−2945 (7)	1710 (8)	2.67 (28)
C(18)	−261 (7)	−3224 (8)	51 (8)	3.00 (29)
C(19)	1222 (8)	−3061 (7)	−653 (8)	2.98 (28)
N(20)	2333 (6)	−1511 (6)	−54 (6)	2.19 (21)
O(21)	3598 (6)	1889 (6)	2337 (7)	3.38 (25)
O(22)	8202 (6)	3419 (6)	5775 (6)	3.10 (24)
O(23)	6477 (6)	229 (6)	3754 (6)	3.13 (24)
O(24)	8298 (7)	−330 (7)	1388 (6)	4.26 (27)

[a] $B_{EQ} = {}^8/_3 U_{ij} A_i^* A_j^* A_i A_j$.

Table IV. Main Bond Lengths (Å) and Angles (deg) for $[Cu(H_2O)(Me_2tn)_2][Cu(pba)]\cdot 3H_2O$ (**1**)

O(1)–Cu(1)	1.918 (3)	N(20)–Cu(2)	2.061 (4)
N(6)–Cu(1)	1.937 (4)	N(21)–Cu(2)	2.009 (3)
N(10)–Cu(1)	1.889 (3)	N(25)–Cu(2)	1.992 (3)
O(15)–Cu(1)	1.961 (4)	OW(1)–Cu(2)	2.357 (3)
N(16)–Cu(2)	1.989 (3)		

N(6)–Cu(1)–O(1)	83.5 (1)	N(21)–Cu(2)–N(20)	157.2 (1)
N(10)–Cu(1)–O(1)	177.6 (1)	N(25)–Cu(2)–N(16)	175.1 (1)
N(10)–Cu(1)–N(6)	97.9 (1)	N(25)–Cu(2)–N(20)	88.2 (1)
O(15)–Cu(1)–O(1)	93.4 (1)	N(25)–Cu(2)–N(21)	92.8 (1)
O(15)–Cu(1)–N(6)	174.0 (1)	OW(1)–Cu(2)–N(16)	86.3 (1)
O(15)–Cu(1)–N(10)	85.0 (1)	OW(1)–Cu(2)–N(20)	94.1 (1)
N(20)–Cu(2)–N(16)	90.4 (1)	OW(1)–Cu(2)–N(21)	108.7 (1)
N(21)–Cu(2)–N(16)	90.3 (1)	OW(1)–Cu(2)–N(25)	89.2 (1)

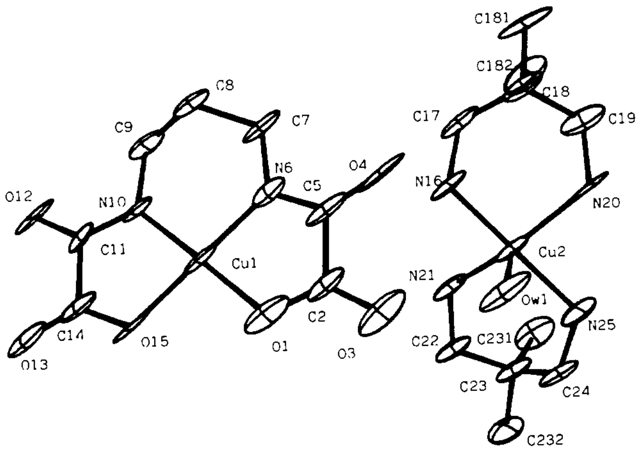

Figure 1. ORTEP diagram for the two complex Cu(II) ions in compound **1**, showing the atom-labeling scheme.

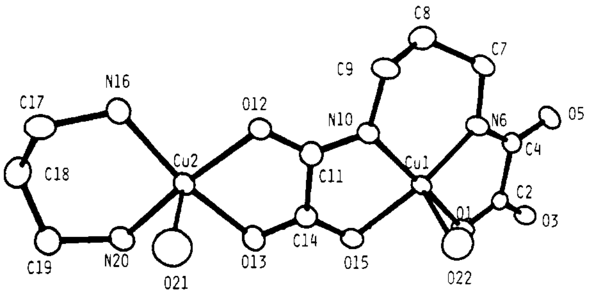

Figure 2. Molecular structure for the binuclear complex **2**, showing the atom-labeling scheme.

Table V. Main Bond Lengths (Å) and Angles (deg) for $[Cu(H_2O)(tn)Cu(H_2O)(pba)]\cdot 2H_2O$ (**2**)

O(1)–Cu(1)	1.967 (4)	O(12)–Cu(2)	2.005 (4)
N(6)–Cu(1)	1.932 (5)	O(13)–Cu(2)	2.004 (4)
N(10)–Cu(1)	1.946 (5)	N(16)–Cu(2)	1.984 (5)
O(15)–Cu(1)	2.002 (4)	N(20)–Cu(2)	1.989 (5)
O(22)–Cu(1)	2.445 (5)	O(21)–Cu(2)	2.356 (5)

N(6)–Cu(1)–O(1)	84.8 (2)	N(16)–Cu(2)–O(12)	89.7 (2)
N(10)–Cu(1)–O(1)	172.4 (2)	N(16)–Cu(2)–O(13)	169.2 (2)
N(10)–Cu(1)–N(6)	95.4 (2)	N(20)–Cu(2)–O(12)	171.5 (2)
O(15)–Cu(1)–O(1)	94.0 (2)	N(20)–Cu(2)–O(13)	89.4 (2)
O(15)–Cu(1)–N(6)	164.9 (2)	N(20)–Cu(2)–N(16)	96.8 (2)
O(22)–Cu(1)–O(1)	96.7 (2)	O(21)–Cu(2)–O(12)	93.1 (2)
O(22)–Cu(1)–N(6)	108.5 (2)	O(21)–Cu(2)–O(13)	90.3 (2)
O(22)–Cu(1)–N(10)	90.4 (2)	O(21)–Cu(2)–N(16)	98.3 (2)
O(22)–Cu(1)–O(15)	86.6 (2)	O(21)–Cu(2)–N(20)	91.4 (2)
O(13)–Cu(2)–O(12)	83.3 (2)		

with the SHELX76 computer program.[15] The function minimized was $w||F_o| - |F_c||^2$, where $w = (\sigma^2|F_o| + 0.054|F_o|^2)^{-1}$ and f, f' and f'' were taken from ref 16. In **1** the positions of 26 hydrogen atoms were computed and refined with an overall isotropic temperature factor by using a riding model, while the remaining atoms were anisotropically refined. For **2**, the positions of 12 hydrogen atoms bonded to C atoms were computed, while 7 H atoms linked to O of water molecules were obtained from a difference synthesis. All H atoms were refined with an overall isotropic temperature factor by using a riding model for H atoms linked to C atoms. The non-hydrogen atoms were refined anisotropically. In both structures were assumed $P1$ and $P\bar{1}$ space groups. $P\bar{1}$ was definitively assumed as the space group according to refinement results. Final atomic coordinates for **1** and **2** are given in Tables II and III, respectively.

Magnetic Measurements. Measurements were carried out with a Faraday type magnetometer equipped with a helium continuous-flow cryostat working in the 5–300 K range. The field strength was 15 000 G, approximately. For all complexes, the independence of the magnetic susceptibility versus the applied field was checked. Mercury tetrakis(thiocyanato)cobaltate(II) were used as a susceptibility standard. Diamagnetic corrections were estimated from Pascal tables.

EPR Spectra. Polycrystalline powder X-band (9.42 GHz) EPR spectra of **2**–**4** were recorded in the 300–16 K temperature range with a Varian E9 spectrometer equipped with an Oxford Instruments continuous-flow cryostat, with a 100-kHz field modulation. Diphenylpicrylhydrazyl (dpph) was used as a suitable field marker [g_{iso}(dpph) = 2.0037, w_0 = 9.42 GHz].

Results and Discussion

Description of the Structures. The unit cell of **1** contains two $[Cu(pba)]^{2-}$ anions, two $[Cu(H_2O)(Me_2tn)_2]^{2+}$ cations, and six molecules of H_2O. Main bond lengths and angles are gathered in Table IV. A view of the two units with an atom-labeling scheme is presented in Figure 1. Both copper atoms are in different environments. The Cu(1) atom is in a quasi-square-planar environment. The distortion of the structure from square planar to tetrahedral can be evaluated through the parameter Δ introduced by Galy et al.[17] and very recently applied by Ribas and Kahn[7] in other similar compounds. This distortion is then found to be 3% only.

The Cu(2) environment is strongly distorted from the square-pyramidal geometry. With application of the same parameter Δ, the distortion is 26%.

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The interionic separation between metal ions is Cu(1)⋯Cu(2) = 6.967 (1) Å. Intermolecular hydrogen-bond distances (Å) involving water hydrogen atoms are as follows: OW(3)⋯OW(2) = 2.943 (7), OW(5)⋯OW(2) = 2.938 (7), OW(5)⋯OW(3) = 2.794 (7), OW(5)⋯OW(4) = 2.762 (7), OW(1)⋯O(3) = 2.741 (6), OW(2)⋯O(12) = 2.783 (6), OW(3)⋯O(4) = 2.763 (6), and OW(4)⋯O(1) = 2.698 (6).

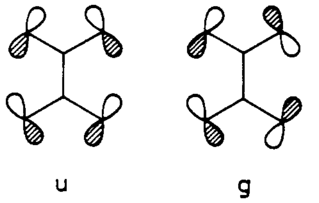
The unit cell of compound **2** contains two dinuclear units and two sets of two molecules of water. Main bond lengths and angles are gathered in Table V. A view of the molecular entity with atom-labeling scheme is presented in Figure 2.

Both Cu(II) atoms are in a quasi-symmetrical square-pyramidal environment, with O(21)(H_2O) and O(22)(H_2O) in apical positions. The Cu(1) atom deviates by 0.193 Å and Cu(2) by 0.116 Å from the mean equatorial planes toward the apical O(H_2O) atoms. The dihedral angle between both mean planes is 20.94°. The environments of both copper atoms are slightly distorted from square planar to tetrahedral, as can be seen from the angles and distances. With the parameter Δ described above, the calculated distortions are 7% for Cu(1) and 3.5% for Cu(2). It is important to point out that in a recently reported [NiCuNi] complex,[7] derived from the same $[Cu(pba)]^{2-}$ anion, the found distortion was 20%. The Cu(1)⋯Cu(2) distance is 5.22 (7) Å.

MO Calculations. The usual molecular orbital studies of superexchange interactions in dinuclear Cu(II) complexes with oxalato and related bridging ligands have been restricted to symmetric bridges,[3v,18-20] i.e., oxalato, oxamidato, and their di- and tetrathio derivatives. Verdaguer et al.[3w] carried out extended Huckel calculations on a model μ-oxamato dinuclear compound and compared the resulting singlet–triplet gap to those of complexes with related bridges. However, a qualitative analysis of the orbital interactions between two Cu(II) ions and an asymmetric bridging ligand such as oxamato has not been published so far.

We have performed MO calculations of the EH type[21] with modified Wolfsberg–Helmholtz formula,[22] in order to analyze the effect that the asymmetry of the bridging ligand has on the electronic structure of the dinuclear complex. In our model calculations, the tn ligand was replaced by NH_3 molecules, and only the two oxamato residues ($C_2O_3NH^{2-}$) of the pba ligand were retained. Bond distances and angles were taken from Table V. The atomic parameters used for Cu were taken from the literature,[18] while those for C, O, N, and H were the standard ones.

For a symmetric bridge, two combinations of the lone-pair orbitals g and u



have the appropriate symmetry to interact with the corresponding combinations of the $d_{x^2-y^2}$ orbitals. The different energies of those g and u orbitals result in a stronger interaction of one of them with the d orbitals and an energy gap between the resulting molecular orbitals: the metal–ligand antibonding HOMO and LUMO. These energy differences are ultimately responsible for the singlet–triplet gap, hence for the magnitude of the antiferromagnetic coupling constant. Since both sides of the bridging ligand are equivalent by symmetry, the two copper atoms participate with the same weight in the HOMO or in the LUMO.

The asymmetry of the bridging oxamato ligand introduces important differences in the qualitative description of the orbital interactions just outlined. The relevant lone pair MO's are represented in Figure 3 (n_1, n_2, n_3). One such orbital, n_3, has a negligible contribution of the N atom and most of its electron density on the opposite O atom (50%). The localization of this orbital is due to electronegativity reasons, so most of its electron density lies at the right-hand side of the C–C bond. Hence, n_3 interacts preferentially with Cu(2). The n_1 orbital, on the other hand, is essentially localized at the N atom (78%) and hybridized toward Cu(1).

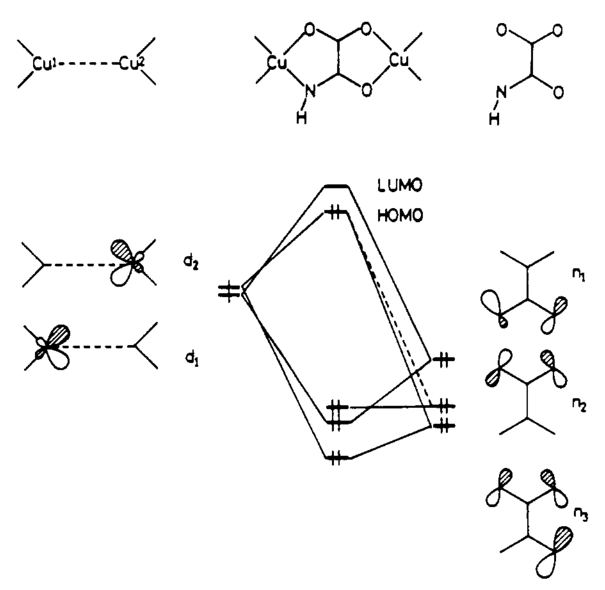


Figure 3. Orbital diagram for the interaction of the unpaired electrons of the two $Cu^{II}L_3$ fragments with the lone pairs of the oxamato bridge.

The orbital interactions between the lone pair MO's of the bridging oxamato ligand and the $d_{x^2-y^2}$ orbitals of the Cu atoms are summarized in Figure 3. The better energy match between n_1 and the $d_{x^2-y^2}$ orbital of Cu(1) results in a stronger interaction. Hence, the LUMO is formed by the antibonding combinations of $d_{x^2-y^2}$ (Cu(1)) and n_1. The HOMO is essentialy $d_{x^2-y^2}$ (Cu(2)) with antibonding contributions from n_3 (6%) and n_2 (4%). The consequence of mixing n_3 and n_2 is that the HOMO has practically all of its electron density on the right-hand side of the bridge.

There is an unexpected result directly tied to the asymmetry of the bridging ligand: since the HOMO is mostly localized at the Cu(2) atom and the LUMO at the Cu(1) atom, the calculated difference in electron density between both Cu atoms in the ground configuration of Figure 3 is practically one electron. Although the one-electron description of the singlet state would be modified by the inclusion of correlation, the ground-state configuration is expected to be the leading one, and important asymmetry in the charge distribution is expected to appear even with higher level computational methods. Changes in the thermal population of the singlet and triplet state may then result in variations of properties other than the magnetic susceptibility, such as the metal–equatorial ligand bond distances or dipole moment.

Magnetic Properties. The magnetic susceptibility measurements indicate different behavior for $[Cu(H_2O)(Me_2tn)_2][Cu(pba)]$ with respect to the other three complexes. According to its ionic nature consistent with two isolated mononuclear Cu(II) ions, complex **1** follows a Curie law with $g = 2.13$. Instead, the magnetic measurements for the other three complexes indicate a strong antiferromagnetic coupling. With application of the Hamiltonian $H = -JS_1S_2$, the J values calculated from the Bleaney–Bowers equation

$$\chi = \left(\frac{Ng^2\beta^2}{kT}\right)\left(\frac{2e^x}{1+3e^x}\right)(1-\rho) + \left(\frac{Ng^2\beta^2}{2kT}\right)\rho + N\alpha$$

$x = J/kT$ $\quad\rho$ = fraction of paramagnetic impurities

$N\alpha$ = TIP

corresponding to a $Cu^{II}Cu^{II}$ dinuclear complex are given in Table

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Table VI. Spectral and Magnetic Data

	magnetic data			EPR data	
compd	J, cm^{-1}	g	ρ	$g_\perp$	$g_\parallel$
2	−345 (1)	2.10 (2)	0.015 (2)	2.07 (2)	2.21 (2)
3	−350 (2)	2.11 (2)	0.022 (3)	2.07 (2)	2.21 (2)
4	−100 (1)	2.03 (2)	0.035 (3)	2.095 (5)	

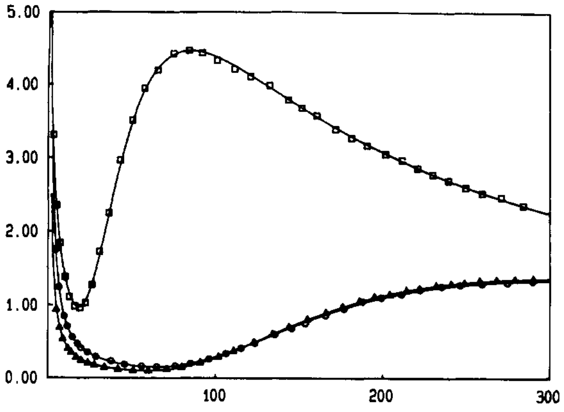

Figure 4. Experimental (○, △, □) and calculated (—) temperature dependence of χ_M for compounds 2, (△), 3 (○), and 4 (□).

VI. J is the singlet–triplet (S–T) energy gap arising from the intramolecular interaction and ρ the eventual proportion of uncoupled copper(II) contained in the sample. The other symbols have their usual meaning. The parameters J, g, ρ, and $N\alpha$ were determined by minimizing R described as $\sum(\chi^{\mathrm{obs}} - \chi^{\mathrm{calc}})^2/\sum(\chi^{\mathrm{obs}})^2$. In all three complexes R was found to be less than 10^{-4}.

Figures 4 and 5 represent the curves of χ vs T and χT vs T for the complexes **2**–**4**, respectively. The strong antiferromagnetic coupling is in agreement with the well-known ability of the oxalato-like bridges in transmitting the isotropic exchange interaction between the two paramagnetic centers.[23-26] For compound **3** there is expected a molecular structure similar to that described in this paper for **2**. The singly occupied molecular orbitals (SOMO's) of Cu(tn) and Cu(bpy) fragments lie coplanar to the bridging ligand plane, giving a very strong interaction. For compound **4**, due to the nature of the dien ligand, a slightly distorted square-pyramidal structure is expected, as found for related compounds.[25,26] As indicated by Kahn et al., the SOMO's of the Cu(dien) subunit in this kind of geometry lie quasi-perpendicular to the plane of the bridging ligand. Due to this fact the overlap between the SOMO's of the two paramagnetic ions is strongly reduced, giving a much smaller value of J (Table VI).

The polycrystalline powder room-temperature EPR spectra of **4** consist of a single symmetric signal centered at $g = 2.095$ (5) with $\Delta B_{\mathrm{pp}} = 180$ G, while the spectra of **2** and **3** are rather similar to each other with the EPR parameters reported in Table VI. Only for **2** a very weak half-field transition is observed at ~1.6 T. Such spectra could be interpreted as due to monomeric Cu(II) species exhibiting large line widths or to $S = 1$ systems with very small D values. The magnetic susceptibility measurements indicate for all the compounds under investigation a strong antiferromagnetic coupling. This is in agreement with the above-mentioned ability of the oxamato bridge in transmitting the isotropic exchange interaction between the two paramagnetic centers[23-26] and clearly indicates that the room-temperature EPR spectra of **2**–**4** must be attributed to the excited triplet state.

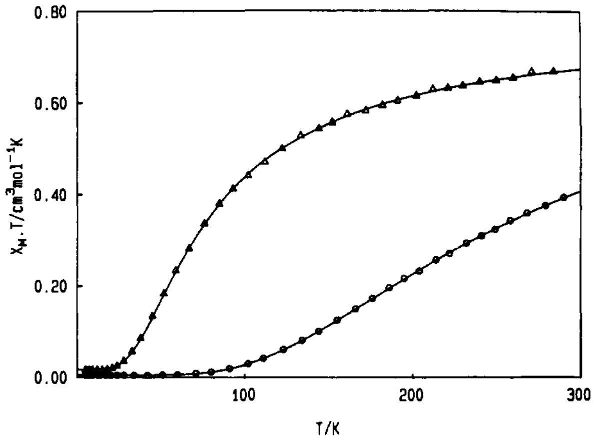

Figure 5. Experimental (○, △) and calculated (—) temperature dependence of $\chi_M T$ for compounds **2** (○) and **4** (△). The experimental values of χT for complex **3** are practically the same as for compound **2** and are not plotted.

On decreasing temperature the spectra of the dimeric species reduce in intensity and disappear, in agreement with the expected behavior, and the spectra of monomeric impurities become evident for **2** and **3**. The low-temperature EPR spectra of **4** appear to consist of a superposition of the dimeric and monomeric spectra, so confirming the magnetic results that give for **4** the smallest value of the isotropic exchange constant J.

As previously reported for other oxalato type bridging copper(II) dimers, the zero-field-splitting tensor is essentially determined by the dipolar contribution,[23,24] due to the inefficiency of the bridge ligand in transmitting the anisotropic exchange interactions. The exchange contribution to the zero-field splitting, even if very small, is every important in determining the principal direction of the **D** tensor,[28] and single-crystal EPR measurements could give definitive information, but a detailed analysis of the spectra is difficult for very small D values, due to overlap of rather broad lines.[23] In **2**, for which structural data are available, the copper–copper intradimer distance is 5.227 Å, and similar values can be expected also for the other two compounds, so that the dipolar contribution to the zero-field splitting is expected not to exceed 0.008–0.01 cm^{-1}. In fact, the polycrystalline powder EPR spectra of **2**–**4** can be nicely reproduced by using the reported analytical expression[29] for $S = 1$ systems with D values ranging from 0.003 to 0.005 cm^{-1} and E/D ranging from 0 to 0.25.

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Registry No. **1**, 131380-68-2; **2**, 131380-69-3; **3**, 131380-70-6; **4**, 131380-71-7; [Cu(pba)]Na$_2$, 61344-73-8.

Supplementary Material Available: Tables of complete crystal data, anisotropic thermal parameters, hydrogen atom coordinates, and all angles and distances (6 pages); tables of calculated and observed structure factors for **1** and **2** (27 pages). Ordering information is given on any current masthead page.

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