Contribution from the Laboratoire de Spectrochimie des Eléments de Transition, UA No. 420, Université de Paris-Sud, 91405 Orsay, France, and Laboratoire de Chimie de Coordination, CNRS, 31400 Toulouse, France

Interaction between Copper(II) Ions Separated by 7.6 Å. Crystal Structure and Magnetic Properties of (μ-Iodanilato)bis[(*N,N,N',N'*-tetramethylethylenediamine)copper(II)] Diperchlorate

Fabrice Tinti,[1a] Michel Verdaguer,[1a,b] Olivier Kahn,*[1a] and Jean-Michel Savariault[1c]

Received December 16, 1986

The compounds of formula $[Cu_2(tmen)_2(XA)](ClO_4)_2$ have been synthesized. tmen is *N,N,N',N'*-tetramethylethylenediamine and XA^{2-} a derivative of the dianion of 2,5-dihydroxy-1,4-benzoquinone with two X groups in the 3,6-positions. X may be H (**1**), Cl (**2**), Br (**3**), I (**4**), or NO_2 (**5**). The crystal structure of **4** has been solved. **4** crystallizes with two methanol molecules in the monoclinic system, space group $P2_1/n$, with a = 15.00 (1) Å, b = 10.121 (6) Å, c = 24.19 (3) Å, β = 103.07 (5)°, and Z = 4. The structure consists of $[Cu_2(tmen)_2(IA)(CH_3OH)_2]^{2+}$ dinuclear cations and perchlorate anions. The copper surroundings are square pyramidal, and within the same dinuclear unit, the two basal planes are almost coplanar. The Cu⋯Cu separations in the two crystallographically independent units are 7.587 (2) and 7.592 (2) Å. The magnetic behaviors of all the compounds have been studied in the 4.2–300 K temperature range. They exhibit an intramolecular antiferromagnetic interaction with singlet–triplet energy gaps ranging from -17.4 cm^{-1} for X = NO_2 to -25.9 cm^{-1} for X = I. For the halogeno derivatives, the magnitude of the interaction varies as I > Br > Cl. The X-band powder EPR spectra were also investigated. The zero-field splittings within the triplet states are too small to be detected. Both the magnetic and the EPR properties are discussed.

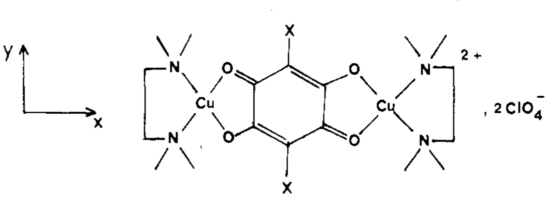
Introduction

Numerous studies are now available on the magnetic properties of copper(II) dinuclear complexes, in which the nature and the magnitude of the interaction are related to the molecular structure. Recently, a new step has been reached in that field, namely the design of compounds exhibiting predictable magnetic properties.[2] In spite of all these studies, some questions remain partly or totally unsolved, one of them being the following: Is there an upper limit for the magnitude of the interaction between two magnetic ions separated by a given distance? Another question deriving from the previous one follows: If such a limit does exist, how does it vary vs. the Cu⋯Cu separation and for what separation does it vanish?[3]

Recently, we have investigated in a thorough manner the various ways to maximize the interaction between two copper(II) ions separated by 5.4 ± 0.3 Å. Such a separation is obtained with bis-bidentate bridging ligands such as oxalato,[4,5] oxamato,[6] oxamido,[6,7] and dithiooxamido.[8] The strongest interaction for the compounds of this kind was achieved with a dithiooxamido compound, with a singlet–triplet (S–T) energy gap of -730 cm^{-1} and a Cu⋯Cu distance of 5.67 Å.[8] An even stronger interaction was reported for a bis(μ-(1,3-azido) compound with a Cu⋯Cu separation of 5.14 Å[9] and was observed for a μ-tetrathiooxalato compound with a Cu⋯Cu separation of 6.1 Å.[10] For those last two cases, the S–T gap is so large that, even at room temperature, the excited triplet state is almost totally depopulated.

From the studies mentioned above, some requirements emerge concerning the possibility of maximizing the interaction between two copper(II) ions far away from each other. These requirements are the following: (i) The copper(II) ions must be in planar or square-pyramidal surroundings. In this latter case, the apical bond length must be as large as possible. (ii) The two basal planes around the copper(II) ions must be as coplanar as possible. (iii) The highest occupied molecular orbitals of the bridge(s) must be largely delocalized on the coordinating atoms and symmetry-adapted to interact with the singly occupied metal orbitals. The HOMO's must also be as high in energy as possible. This latter condition is fulfilled when the bridge contains weakly electronegative groups.[2,6] So, everything else being unchanged, sulfur is better than oxygen and iodine better than chlorine. These requirements are valid when the magnetic orbitals are of the *xy* type (see the reference axis below). When they are obeyed, the two magnetic orbitals ϕ_A and ϕ_B centered on the copper(II) ions are essentially located in the plane of the bridging network and are strongly delocalized (in an antibonding fashion) on the bridging atoms so that the overlap integral $\langle\phi_A|\phi_B\rangle$ may be large, which favors an antiferromagnetic interaction.

The purpose of this paper is to apply these rules to a new series of copper(II) dinuclear compounds containing derivatives of the 2,5-dihydroxy-1,4 benzoquinone dianion as bridging ligands. In these compounds, the Cu⋯Cu separation is expected to be around 7.5 Å. One of the questions at hand is to see to what extent the interaction is reduced with regard to the situation encountered with μ-oxalato compounds. More precisely, we report the synthesis and the magnetic and EPR properties of the compounds



noted $[Cu_2(tmen)_2(XA)](ClO_4)_2$ with X = H (**1**), Cl (**2**), Br (**3**), I (**4**), and NO_2 (**5**), and we describe the structure of one of them, namely the iodanilato derivative **4**·$2CH_3OH$.

Experimental Section

Synthesis. Hydranilic, chloranilic, and bromanilic acids were commercially available. Iodanilic and nitranilic acids were prepared according to reported procedures.[11,12] All the compounds but the nitranilato derivative were synthesized in a similar way. We describe the preparation of the chloranilato derivative $[Cu_2(tmen)_2(ClA)](ClO_4)_2$. First, the chain compound Cu(ClA) was prepared as previously described.[13,14] A solution of 10^{-3} mol of copper(II) perchlorate and 2 ×

---

[1] (a) Université de Paris-Sud. (b) Permanent address: ENS, Le Parc, 92211, Saint Cloud, France. (c) Laboratoire de Chimie de Coordination.

[2] Kahn, O. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 834 and references therein.

[3] Hendrickson, D. N. in *Magneto-Structural Correlations in Exchange Coupled Systems*; Willett, R. D., Gatteschi, D., Kahn, O., Eds. Reidel: Dordrecht, Holland, 1985; p 523.

[4] Julve, M.; Verdaguer, M.; Kahn, O.; Gleizes, A.; Philoches-Levisalles, M. *Inorg. Chem.* **1984**, *23*, 3808.

[5] Charlot, M. F.; Verdaguer, M.; Journaux, Y.; de Loth, P.; Daudey, J. P. *Inorg. Chem.* **1984**, *23*, 3802.

[6] Verdaguer, M.; Kahn, O.; Julve, M.; Gleizes, A. *Nouv. J. Chim.* **1985**, *9*, 325.

[7] Journaux, Y.; Sletten, J.; Kahn, O. *Inorg. Chem.* **1985**, *24*, 4063.

[8] Veit, R.; Girerd, J. J.; Kahn, O.; Robert, F.; Jeannin, Y.; El Murr, N. *Inorg. Chem.* **1984**, *23*, 4448.

[9] Agnus, Y.; Louis, R.; Weiss, R. *J. Am. Chem. Soc.* **1979**, *101*, 3381.

[10] Vicente, R.; Ribas, J.; Alvarez, S.; Segui, A.; Verdaguer, M. *Inorg. Chem.*, in press.

[11] Meyer, H. O. *Ber. Dtsch. Chem. Ges.* **1924**, *57*, 326.

[12] Torney, H. A.; Hunter, W. H. *J. Am. Chem. Soc.* **1912**, *34*, 702.

[13] (a) Kanda, S. *Bull. Chem. Soc. Jpn.* **1960**, *81*, 1347; **1962**, *82*, 2843. (b) Coble, H. D.; Holtzclaw, H. F., Jr. *J. Inorg. Nucl. Chem.* **1974**, *36*, 1049.

0020-1669/87/1326-2380$01.50/0

Table I. Physical Properties and Main Data Relating to Measurement and Refinement of Structure

1. Physical and Crystallographic Properties	
formula	$[(C_6H_{16}N_2)(CH_3OH)Cu]_2(C_6O_4I_2)(ClO_4)_2$
mol wt	1012.35
cryst system	monoclinic
space group	$P2_1/n$
Z	4
cell	$a = 15.00$ (1) Å, $b = 10.121$ (6) Å, $c = 24.19$ (3) Å, $\beta = 103.07$ (5)°
vol	3576.8 (7) Å^3
ρ_{measd}	1.63 (1) g·cm^{-3}
ρ_{calcd}	1.621 g·cm^{-3}
$\mu_{Mo\ K\alpha}$	31.12 cm^{-1}
cryst shape	nearly spherical ($r = 0.1$ mm)
2. Data Pertinent to Measurement	
temp	293 K
radiation	λ(Mo Kα) = 0.71069 Å
monochromator	graphite (220)
Takeoff angle	4.0°
cryst–detector dist	207 mm
detector aperture	4 mm × 4 mm
scan type	$\omega/x\theta$ ($x = {}^4/_3$)
scan width	$(0.8 + 0.35 \tan\theta)°$
θ range	1–25°
std reflcns	
intensity (period 1 h)	(6,0,−2), (2,2,−8), (140)
orientation (period 100 reflcns)	(4,0,−18), (0,5,12), (0,−5,−12)
no. of reflcns measd	6935
3. Data Treatment and Refinement	
abs	min–max transmission factor = 0.55–0.56
no. of reflcns used with $I > 2\sigma_I$	NO = 3806
no. of variables	NV = 397 (+160 for H atoms)
weighting scheme	$w = 1/[\sigma_I^2 + (0.03I)^2]^{1/2}$
agreement factors	
$R = (\sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)/(\sum\lvert F_o\rvert)$	0.044
$R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$	0.042
$s = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(NO - NV)]^{1/2}$	1.24

Table II. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	B/Å^2
I(1)	0.10825 (4)	−0.21937 (5)	−0.07705 (2)	4.30 (1)
I(2)	0.38761 (3)	0.31085 (5)	0.08585 (2)	4.88 (1)
Cu(1)	−0.04017 (7)	0.2386 (1)	−0.12413 (4)	4.50 (2)
Cu(2)	0.45347 (6)	0.22979 (8)	−0.11167 (3)	4.82 (2)
Cl(1)	0.7304 (2)	0.4551 (3)	0.1422 (1)	5.30 (6)
Cl(2)	0.2711 (2)	0.5560 (3)	0.3610 (1)	6.02 (6)
O(1)	0.0201 (4)	0.0692 (5)	−0.1029 (2)	4.3 (1)
O(2)	−0.0633 (4)	0.2296 (5)	−0.0478 (2)	4.2 (1)
O(3)	0.1025 (5)	0.3494 (7)	−0.0862 (3)	6.5 (2)
O(4)	0.5140 (3)	0.4027 (4)	−0.1002 (2)	4.8 (1)
O(5)	0.4364 (3)	0.2608 (4)	−0.0350 (2)	4.8 (1)
O(6)	0.5975 (4)	0.1236 (7)	−0.0753 (3)	8.4 (2)
O(7)	0.7059 (6)	0.408 (1)	0.1897 (4)	10.2 (3)
O(8)	0.6874 (7)	0.389 (1)	0.0939 (4)	12.9 (3)
O(9)	0.8271 (5)	0.4469 (8)	0.1478 (3)	6.7 (2)
O(10)	0.7062 (6)	0.5899 (9)	0.1346 (4)	10.7 (3)
O(11)	0.2950 (7)	0.644 (1)	0.3241 (5)	13.2 (3)
O(12)	0.2997 (7)	0.432 (1)	0.3500 (5)	13.1 (3)
O(13)	0.1742 (5)	0.5555 (8)	0.3561 (3)	7.3 (2)
O(14)	0.3126 (7)	0.584 (1)	0.4163 (4)	13.7 (4)
N(1)	−0.1186 (5)	0.3989 (7)	−0.1472 (3)	5.0 (2)
N(2)	−0.0264 (5)	0.2246 (8)	−0.2047 (3)	5.1 (2)
N(3)	0.4571 (4)	0.2176 (6)	−0.1942 (2)	5.6 (1)
N(4)	0.3730 (4)	0.0682 (5)	−0.1222 (3)	5.7 (1)
C(1)	0.0127 (5)	0.0291 (7)	−0.0547 (3)	3.1 (2)
C(2)	−0.0358 (5)	0.1228 (7)	−0.0223 (3)	3.1 (2)
C(3)	0.0462 (5)	−0.0917 (7)	−0.0309 (3)	3.0 (2)
C(4)	−0.0845 (9)	0.514 (1)	−0.1138 (6)	9.7 (4)
C(5)	−0.2094 (8)	0.382 (1)	−0.1389 (8)	12.9 (5)
C(6)	−0.115 (1)	0.419 (1)	−0.2061 (5)	11.8 (5)
C(7)	−0.0747 (9)	0.336 (1)	−0.2335 (4)	11.2 (4)
C(8)	−0.067 (1)	0.105 (1)	−0.2318 (5)	12.8 (4)
C(9)	0.0663 (7)	0.229 (1)	−0.2100 (4)	7.7 (3)
C(10)	0.1484 (8)	0.344 (1)	−0.0298 (5)	8.5 (4)
C(11)	0.5101 (4)	0.4552 (6)	−0.0536 (2)	3.5 (1)
C(12)	0.4631 (4)	0.3730 (6)	−0.0159 (2)	3.6 (1)
C(13)	0.4538 (4)	0.4238 (6)	0.0359 (2)	3.4 (1)
C(14)	0.5490 (6)	0.237 (1)	−0.2037 (3)	7.1 (2)
C(15)	0.3950 (6)	0.315 (1)	−0.2278 (4)	8.8 (3)
C(16)	0.4266 (6)	0.0775 (9)	−0.2084 (3)	8.1 (2)
C(17)	0.3478 (6)	0.0459 (9)	−0.1838 (4)	8.2 (2)
C(18)	0.2884 (6)	0.0901 (9)	−0.1017 (4)	8.2 (3)
C(19)	0.4205 (7)	−0.0447 (9)	−0.0911 (5)	9.4 (3)
C(20)	0.6672 (6)	0.183 (1)	−0.0353 (4)	9.5 (3)

10^{-3} mol of tmen in 100 mL of methanol was added to a suspension of 10^{-3} mol of Cu(ClA) in 300 mL of methanol. After stirring, the mixture became limpid. A 10^{-2}-mol sample of sodium perchlorate in 100 mL of methanol was then added. The solution was filtered. Slow evaporation affords well-shaped, dark green single crystals. The crystals of **4** must be kept in the mother solution. $[Cu_2(tmen)_2(NO_2A)](ClO_4)_2$ (**5**) was obtained as follows: To a solution of 2 × 10^{-3} mol of tmen and 2 × 10^{-3} mol of copper(II) pechlorate in 100 mL of methanol was added 10^{-3} mol of solid nitranilic acid. After stirring, the solution turned from blue to green and became limpid. A 10^{-2}-mol sample of sodium perchlorate in 100 mL of methanol was then added. The solution was filtered, and **5** was obtained by slow evaporation as a green powder.

Anal. Calcd for $C_{18}H_{34}N_4O_{12}Cl_2Cu_2$ (**1**): C, 31.06; H, 4.88; N, 8.04; O, 27.57; Cl, 10.19; Cu, 18.26. Found: C, 31.20; H, 4.96; N, 7.85; O, 27.39; Cl, 10.32; Cu, 17.85. Calcd for $C_{18}H_{32}N_4O_{12}Cl_4Cu_2$ (**2**): C, 28.24; H, 4.21; N, 7.32; O, 25.08; Cl, 18.53; Cu, 16.60. Found: C, 28.16; H, 4.27; N, 7.52; O, 25.57; Cl, 18.14; Cu, 16.21. Calcd for $C_{18}H_{32}N_4O_{12}Cl_2Br_2Cu_2$ (**3**): C, 25.31; H, 3.77; N, 6.56; O, 22.47; Cl, 8.30; Br, 18.71; Cu, 14.87. Found: C, 25.07; H, 3.64; N, 6.58; O, 22.65; Cl, 8.21; Br, 17.96; Cu, 14.15. Calcd for $C_{18}H_{36}N_4O_{14}Cl_2I_2Cu_2$ (**4**·$2H_2O$): C, 21.97; H, 3.68; N, 5.69; O, 22.76; Cl, 7.20; I, 25.79; Cu, 12.91. Found: C, 21.47; H, 3.69; N, 5.62; O, 24.24; Cl, 7.17; Cu, 11.55. Calcd for $C_{18}H_{36}N_6O_{18}Cl_2Cu_2$ (**5**·$2H_2O$): C, 26.28; H, 4.38; N, 10.22; O, 35.04; Cl, 8.62; Cu, 15.46. Found: 25.23; H, 4.49; N, 10.33; O, 35.67; Cl, 8.45; Cu, 16.25.

Crystallographic Data Collection and Refinement of the Structure of 4. The crystal used was dark brown with a nearly spherical shape. It was sealed in a Lindemann capillary with one drop of methanol. The X-ray data were recorded with a CAD 4 Enraf-Nonius diffractometer using the graphite-monochromated Mo Kα radiation. Cell dimensions were obtained by least-squares fitting from the setting angles of 25 reflections with 8° $\leqslant \theta \leqslant$ 20°. Information concerning conditions for crystallographic data collection and structure refinement is summarized in Table I. No absorption correction was carried out due to the very flat shape of ψ scan. Patterson synthesis gave the starting point of the structure, which was then solved by least-squares refinement and Fourier synthesis. Introduction of anisotropic thermal parameters for all nonhydrogen atoms led to $R = 0.040$, and introduction of hydrogen atoms with isotropic thermal parameters led to $R = 0.036$. It may be noticed that the hydrogen atom bound to oxygen O(3) of the methanol molecule was not found. Anomalous dispersion was corrected. All calculations were performed on a VAX 11/730 computer using the Enraf-Nonius Structure Determination Package. Atomic parameters are given in Table II and Tables VI and VII (supplementary material). Bond lengths and bond angles are tabulated in Tables III and IV, respectively.

Magnetic Measurements. These were carried out on polycrystalline samples in the 4.2–300 K temperature range with a Faraday-type magnetometer equipped with a helium continuous-flow cryostat. Mercury (thiocyanato)cobaltate(II) was used as susceptibility standard. Magnetic susceptibility independence of the magnetic induction was checked at room temperature. Corrections for the diamagnetism were estimated as −322 × 10^{-6}, −383 × 10^{-6}, −394 × 10^{-6}, −431 × 10^{-6}, and −424 × 10^{-6} cm^3 mol^{-1} for **1**–**5**, respectively.

EPR. The powder X-band EPR spectra were recorded at various temperatures between 4.2 and 300 K with an ER 200D Bruker spectrometer equiped with a helium continuous-flow cryostat, a Hall probe, and a frequency meter.

Description of the Structure of 4

The crystals used for the structure determination contained two methanol molecules whereas the chemical analysis of a powder

---

(14) Verdaguer, M.; Michalowicz, A.; Girerd, J. J.; Alberding, N.; Kahn, O. *Inorg. Chem.* **1980**, *29*, 3271.

Table III. Bond Distances (Å)[a]

Cu(1)-O(1)	1.951 (5)	Cu(1)-O(2)	1.955 (5)
Cu(1)-O(3)	2.406 (6)	Cu(1)-O(12)	2.911 (10)
Cu(1)-N(1)	2.008 (7)	Cu(1)-N(2)	2.010 (7)
Cu(2)-O(4)	1.963 (4)	Cu(2)-O(5)	1.954 (5)
Cu(2)-O(6)	2.395 (6)	Cu(2)-O(10)	2.961 (9)
Cu(2)-N(3)	2.014 (5)	Cu(2)-N(4)	2.015 (6)
N(1)-C(4)	1.446 (14)	N(1)-C(5)	1.43 (2)
N(1)-C(6)	1.455 (15)	N(2)-C(7)	1.437 (15)
N(2)-C(8)	1.44 (2)	N(2)-C(9)	1.426 (13)
N(3)-C(14)	1.461 (11)	N(3)-C(15)	1.468 (11)
N(3)-C(16)	1.506 (10)	N(4)-C(17)	1.469 (11)
N(4)-C(18)	1.479 (12)	N(4)-C(19)	1.462 (11)
C(1)-O(1)	1.263 (9)	C(1)-C(2)	1.516 (11)
C(1)-C(3)	1.396 (10)	C(2)-O(2)	1.268 (8)
C(2)-C(3)	1.368 (9)	C(3)-I(1)	2.062 (7)
C(6)-C(7)	1.30 (2)	C(10)-O(3)	1.383 (12)
C(11)-O(4)	1.259 (7)	C(11)-C(12)	1.521 (9)
C(12)-O(5)	1.256 (7)	C(12)-C(13)	1.390 (8)
C(13)-I(2)	2.073 (6)	C(16)-C(17)	1.473 (14)
C(20)-O(6)	1.390 (11)	O(6)-H(40)	0.94 (8)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Bond Angles (deg)[a]

O(1)-Cu(1)-O(2)	83.2 (2)	O(1)-Cu(1)-O(3)	89.4 (2)
O(1)-Cu(1)-O(12)	81.0 (3)	O(1)-Cu(1)-N(1)	172.0 (3)
O(1)-Cu(1)-N(2)	92.9 (3)	O(2)-Cu(1)-O(3)	89.6 (2)
O(2)-Cu(1)-O(12)	82.0 (3)	O(2)-Cu(1)-N(1)	94.7 (3)
O(2)-Cu(1)-N(2)	172.1 (3)	O(3)-Cu(1)-O(12)	168.0 (3)
O(3)-Cu(1)-N(1)	98.3 (3)	O(3)-Cu(1)-N(2)	97.2 (3)
O(12)-Cu(1)-N(1)	91.0 (3)	O(12)-Cu(1)-N(2)	90.6 (3)
N(1)-Cu(1)-N(2)	88.3 (3)	O(4)-Cu(2)-O(5)	83.0 (2)
O(4)-Cu(2)-O(6)	89.9 (2)	O(4)-Cu(2)-O(10)	78.8 (2)
O(4)-Cu(2)-N(3)	94.5 (2)	O(4)-Cu(2)-N(4)	170.7 (2)
O(5)-Cu(2)-O(6)	91.4 (2)	O(5)-Cu(2)-O(10)	78.7 (2)
O(5)-Cu(2)-N(3)	171.8 (2)	O(5)-Cu(2)-N(4)	92.7 (2)
O(6)-Cu(2)-O(10)	165.7 (2)	O(6)-Cu(2)-N(3)	96.5 (2)
O(6)-Cu(2)-N(4)	98.5 (2)	O(10)-Cu(2)-N(3)	93.11 (3)
O(10)-Cu(2)-N(4)	92.3 (2)	N(3)-Cu(2)-N(4)	88.6 (3)
Cu(1)-N(1)-C(4)	112.7 (6)	Cu(1)-N(1)-C(5)	112.3 (7)
Cu(1)-N(1)-C(6)	103.6 (7)	C(4)-N(1)-C(5)	104 (1)
C(4)-N(1)-C(6)	110.2 (9)	C(5)-N(1)-C(6)	113 (1)
Cu(1)-N(2)-C(7)	105.3 (6)	Cu(1)-N(2)-C(8)	112.1 (7)
Cu(1)-N(2)-C(9)	113.6 (5)	C(7)-N(2)-C(8)	109.2 (8)
C(7)-N(2)-C(9)	109.1 (9)	C(8)-N(2)-C(9)	107 (1)
Cu(2)-N(3)-C(14)	112.6 (4)	Cu(2)-N(3)-C(15)	110.5 (5)
Cu(2)-N(3)-C(16)	102.1 (4)	C(14)-N(3)-C(15)	109.1 (7)
C(14)-N(3)-C(16)	109.9 (7)	C(15)-N(3)-C(16)	112.6 (6)
Cu(2)-N(4)-C(17)	105.2 (5)	Cu(2)-N(4)-C(18)	111.8 (5)
Cu(2)-N(4)-C(19)	111.2 (5)	C(17)-N(4)-C(18)	108.7 (6)
C(17)-N(4)-C(19)	112.7 (7)	C(18)-N(4)-C(19)	107.4 (7)
O(1)-C(1)-C(2)	115.4 (6)	O(1)-C(1)-C(3)	124.3 (7)
C(2)-C(1)-C(3)	120.3 (6)	O(2)-C(2)-C(1)	115.0 (6)
O(2)-C(2)-C(3)	124.1 (7)	C(1)-C(2)-C(3)	120.8 (6)
I(1)-C(3)-C(1)	119.4 (5)	I(1)-C(3)-C(2)	121.8 (5)
C(1)-C(3)-C(2)	118.8 (7)	N(1)-C(6)-C(7)	122 (1)
N(2)-C(7)-C(6)	120 (1)	O(4)-C(11)-C(12)	115.3 (5)
O(4)-C(11)-C(13)	124.3 (6)	C(12)-C(11)-C(13)	120.4 (5)
O(5)-C(12)-C(11)	115.3 (5)	O(5)-C(12)-C(13)	125.2 (6)
C(11)-C(12)-C(13)	119.5 (5)	I(2)-C(13)-C(11)	121.2 (4)
I(2)-C(13)-C(12)	118.7 (4)	C(11)-C(13)-C(12)	120.0 (5)
N(3)-C(16)-C(17)	110.0 (7)	N(4)-C(17)-C(16)	109.4 (7)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

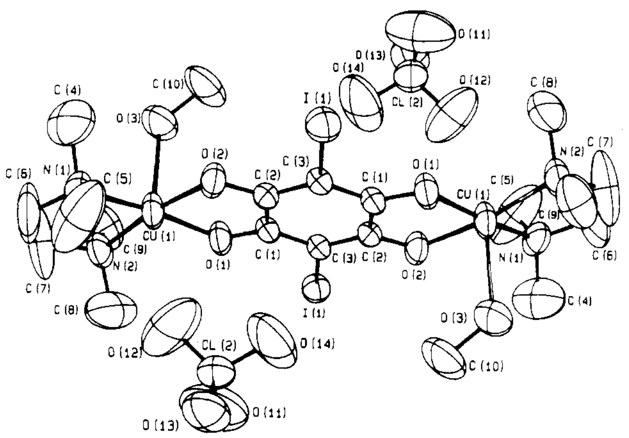


Figure 1. Perspective view of 4·2CH$_3$OH with thermal ellipsoids at the 50% probability level.

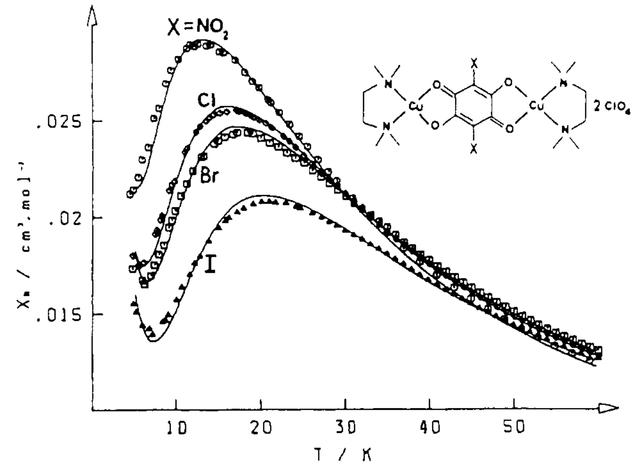


Figure 2. Experimental and calculated temperature dependences of the molar magnetic susceptibility for **2** (X = Cl), **3** (X = Br), **4** (X = I), and **5** (X = NO$_2$).

sample of **4** suggested the presence of two water molecules. The structure of **4** consists of two crystallographically independent but geometrically very similar $[Cu_2(tmen)_2(IA)(CH_3OH)_2]^{2+}$ dinuclear cations and essentially noncoordinated perchlorate anions. The dinuclear units, noted I and II, are centrosymmetric. A perspective view of I with the labeling of the atoms is shown in Figure 1. Each copper(II) ion is located in slightly distorted square-pyramidal surroundings with two nitrogen atoms of tmen and two oxygen atoms of IA^{2-} in the basal plane and the oxygen atom of a methanol molecule in apical position with an apical bond length of 2.406 (6) Å in I (2.395 (6) Å in II). The copper atom is pulled out of the basal plane toward the apical site by 0.19 (7) Å in I (0.143 Å in II). The iodanilato group IA^{2-} is almost perfectly planar with a mean deviation of 0.015 Å in I and II. The intramolecular Cu···Cu separation is 7.587 (2) in I and 7.592 (2) Å in II. The shortest Cu–O perchlorate distance is 2.911 (10) Å in I and 2.961 (9) Å in II. The dinuclear units are well separated from each other owing to the presence of methanol molecules and perchlorate anions. The shortest intermolecular Cu···Cu separation is 7.026 (3) Å.

Magnetic and EPR Properties

The variations vs. the temperature T of the molar magnetic susceptibility χ_M for compounds **1**–**5** have been studied in the 4.2–300 K range. Figure 2 shows the data below 50 K. The data for **1** are almost superimposable on those for **2** and have been omitted for the sake of clarity. For all compounds, a maximum of χ_M is observed in the 14–21 K temperature range, which is characteristic of an antiferromagnetic interaction. χ_M may then be expressed as

$$\chi_M = \frac{2N\beta^2g^2}{kT}[3 + \exp(-J/kT)]^{-1}(1 - \rho) + \frac{N\beta^2g^2}{2kT}\rho \quad (1)$$

where the symbols have their usual meaning. In (1), the eventual presence of a small proportion of uncoupled copper(II) impurity is taken into consideration. The minimization of

$$R = \sum(\chi_M^{\text{obsd}} - \chi_M^{\text{calcd}})^2/\sum(\chi_M^{\text{obsd}})^2$$

leads to the J, g, and ρ values given in Table V.

The X-band powder EPR spectra of compounds **2**–**5** have been investigated. The spectrum for **4** is shown in Figure 3. In the

Table V. Parameters Deduced from the Magnetic Data for the Compounds $[Cu_2(tmen)_2(XA)](ClO_4)_2$

X	compd	g	J/cm^{-1}	ρ
H	**1**	2.16	−20.9	0.017
Cl	**2**	2.15	−21.0	0.019
Br	**3**	2.18	−22.5	0.013
I	**4**	2.17	−25.9	0.031
NO_2	**5**	2.07	−17.4	0.020

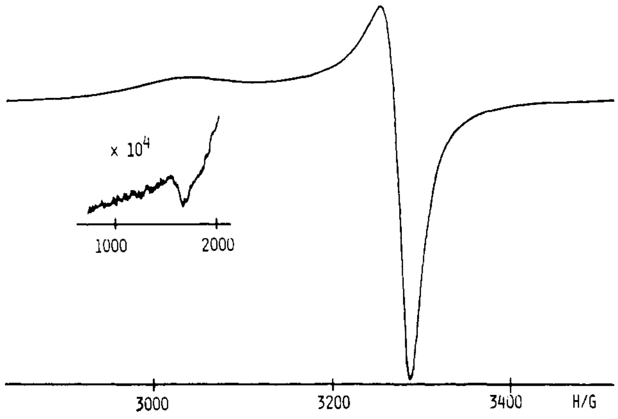


Figure 3. X-Band powder EPR spectrum of **4** at 23 K.

$g = 2$ region, all spectra appear as expected for an isolated copper(II) ion in elongated surroundings with a small rhombic component. The intensity of the signals, however, decreases upon cooling down toward 4.2 K, which confirms that the resonance occurs within the triplet excited state. Moreover, the spectra show the $\Delta M_s = 2$ forbidden transitions in the $g = 4$ region. Their intensity is however extremely weak; the ratio of the intensities $I(\Delta M_s = 1)/I(\Delta M_s = 2)$ is around 10^4. The appearance of the spectra of the $g = 2$ region and the very weak intensity of the half-field signals indicate that the zero-field splitting within the triplet states is almost negligible with regard to the incident quantum ($\sim$0.3 cm^{-1}). The principal values of the g tensors are found as follows:

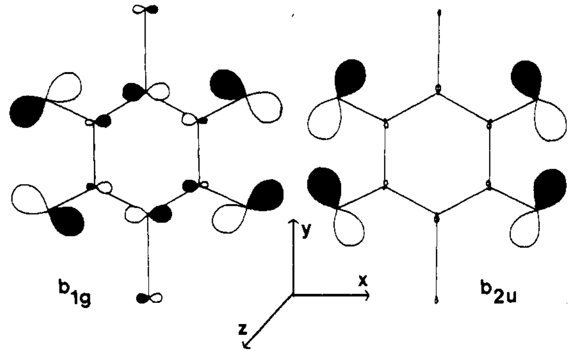
2	$g_x = 2.07$	$g_y = 2.09$	$g_z = 2.24$
3	$g_x = 2.06$	$g_y = 2.09$	$g_z = 2.23$
4	$g_x = g_y = 2.07$		$g_z = 2.23$
5	$g_x = 2.065$	$g_y = 2.09$	$g_z = 2.24$

Discussion

In spite of a Cu⋯Cu separation of about 7.6 Å, all of the compounds **1–5** exhibit a rather large S–T energy gap. The largest interaction is observed in the μ-iodanilato compound **4**, of which the crystal structure has been solved. It is worthwhile to notice that the J value in this compound (−25.9 cm^{-1}) is significantly beyond the J_{limit} value deduced from the empirical relation proposed by Coffman and Buettner[15]

$$J_{\text{limit}}/\text{cm}^{-1} = -1.35 \times 10^7 \exp(-1.80R/A) \tag{2}$$

From (2), J_{limit} is found equal to −15.7 cm^{-1} for $R = 7.59$ Å. Such large interactions in **1–5** are obtained because all requirements presented in the Introduction are fulfilled. Indeed, the choice of tmen as a terminal ligand imposes an essentially planar geometry for the compounds. It follows that the two magnetic orbitals of xy symmetry are favorably oriented to interact of either side of the bridge.[2] A same situation has been reported for the ribbon chains Cu(XA) with X = Cl and Br.[14] In contrast, in the μ-chloranilato complex described by Pierpont et al., the terminal ligands are 1,1,4,7,7-pentamethyldiethylenetriamine. The copper surroundings are again close to square pyramidal, but the basal planes are now perpendicular to the plane of the bridging network. The two magnetic orbitals are then unfavorably oriented to interact, and no interaction was detected.[16] The requirements concerning the HOMO's of the bridges XA^{2-} are also fulfilled. The two HOMO's of b_{1g} and b_{2u} symmetries, respectively, as derived from extended Hückel calculations,[17] are schematized as follows:



Both are largely delocalized toward the oxygen atoms with an orientation of the 2p oxygen orbitals favoring the overlaps with the in-phase and out-of-phase combinations of d_{xy} metal orbitals. When X is a halogen, the magnitude of the interaction varies according to the sequence I > Br > Cl. Such a sequence confirms that, everything else being unchanged, the less electronegative X is, the stronger the interaction. In the present case, however, the effect is not very pronounced. J is found as −21.0, −22.5, and −25.9 cm^{-1}, respectively. This is due to the fact that the HOMO's of XA^{2-} schematized above have a weak contribution from X atoms. From X = Cl to X = I, the energies of the b_{1g} and b_{2u} orbitals are found to increase by 0.10 and 0.14 eV, respectively. The weakest interaction is obtained with X = NO_2. This result could have two origins: either the NO_2 groups exert a strong electroattractive effect so that the b_{1g} and b_{2u} HOMO's of $(NO_2A)^{2+}$ are particularly low in energy, or owing to the polyatomic nature of NO_2, the dinuclear cation $[Cu_2(tmen)_2(NO_2A)]^{2+}$ is less planar than for the derivatives involving halogen atoms.

Another point deserving to be discussed in this section is the nondetection of zero-field splitting in the triplet state. It is now well understood that the zero-field splitting in a symmetrical copper(II) dinuclear compound may have two origins, the dipolar interaction and the anisotropic exchange.[18] In the point magnetic dipole approximation, the zero-field splitting arising from the dipolar interaction between the two local doublets separated by 7.6 Å is[18,20]

$$D = \frac{5g_{\perp}^2 + g_{\parallel}^2}{2}\frac{\beta^2}{R^3} = 5.6 \times 10^{-3}\ \text{cm}^{-1} \tag{3}$$

which is clearly undetectable owing to the line widths. As for the anisotropic interaction, it is due to the combined effect of the local spin–orbit coupling and the interaction between the ground sate of an ion and the excited states of the other.[18] It has been shown that for a quasi-planar system, the most efficient ground–excited interaction is of the type (xy)–$(x^2 - y^2)$ involving in-plane orbitals.[18,19] Such an interaction, purely ferromagnetic, may be large when the Cu⋯Cu separation is around 3 Å with monoatomic bridges.[19] It quickly vanishes when the Cu⋯Cu separation increases with extended bridges.[2]

To conclude, we want to stress that 7.6 Å is far from being a limit for the interaction betwen two copper(II) ions. In fact, the interaction propagated along such a distance may be rather large,

---

(15) Coffman, R. E.; Buettner, G. R. *J. Phys. Chem.* **1979**, *83*, 2387.

(16) Pierpont, C. G.; Francesconi, L. C.; Hendrickson, D. N. *Inorg. Chem.* **1977**, *16*, 2367.

(17) The extended Hückel calculation was performed with the FORTICON 8 program from the Quantum Chemistry Program Exchange, with method 2 (charge iteration on all atoms). The VSIE parameters for halogen atoms were calculated from: Moore, C. E. *Natl. Bur. Stand. Circ.* (*U.S.*) **1968**, *No. 476*. Those for the other elements and the exponents of the atomic orbitals were taken from ref 22.

(18) Bencini, A.; Gatteschi, D.; Zanchini, C. *Inorg. Chem.* **1985**, *24*, 700.

(19) Charlot, M. F.; Journaux, Y.; Kahn, O.; Bencini, S.; Gatteschi, D.; Zanchini, C. *Inorg. Chem.* **1986**, *25*, 1060.

(20) Abragam, A.; Bleaney, R. *Electron Paramagnetic Resonance of Transition Ions*; Clarendon: Oxford, England; p 16.

provided that the energy and orientation requirements for the involved orbitals are respected. We are currently exploring the range 10–11 Å.[21]

Safety Note. Perchlorate salts of metal complexes, with organic ligands are potentially explosive. We used in the synthesis here described only small amounts of material (the preparations were carried out on the millimole scale), and the starting perchlorate salt was an aquo complex. The dilute solutions were handled with great caution and evaporated slowly at room temperature.

When noncoordinating agents are required, every attempt should be made to substitute anions such as the fluoro sulfonates for the perchlorates.[23]

Supplementary Material Available: Listings of atomic parameters for hydrogen atoms (Table VI) and thermal parameters for non-hydrogen atoms (Table VII) (2 pages); a listing of structure factor amplitudes (41 pages). Ordering information is given on any current masthead page.

---

(21) Julve, M.; Verdaguer, M.; Faus, J.; Tinti, F.; Moratal, J.; Monge, A.; Gutierrez-Puebla, E. *Inorg. Chem.*, in press.

(22) (a) Burns, G. J. *Chem. Phys.* **1964**, *41*, 1521. (b) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.

(23) Cf.: *J. Chem. Educ.* **1973**, *50*, A335; **1985**, *62*, 1001.

Contribution from the Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X7, and Chemistry Division, National Research Council, Ottawa, Ontario, Canada K1A 0R6

Spontaneous Reduction of Copper(II) Complexes of the Ligand 3,6-Bis(2-pyridylthio)pyridazine. Crystal Structures of Bis[3,6-bis(2-pyridylthio)pyridazine-N^1,N^2]aquocopper(II) Diperchlorate Trihydrate and Bis[μ-3,6-bis(2-pyridylthio)pyridazine-N^4,μ-N^1,μ-N^2,N^3]dicopper(I) Diperchlorate

Sanat K. Mandal,[1a] Laurence K. Thompson,*[1a] Eric J. Gabe,†[1b] Florence L. Lee,[1b] and Jean-Pierre Charland[1b]

Received December 16, 1986

The ligand 3,6-bis(2-pyridylthio)pyridazine (PTP) forms both mononuclear and binuclear copper(II) derivatives and binuclear copper(I) derivatives. The copper(II) complexes reported are characterized by exhibiting positive reduction potentials (+0.4 to +0.6 V vs. SCE), a feature that can be exploited with respect to the redox chemistry of such systems. The complexes $[Cu(PTP)_2(H_2O)](ClO_4)_2 \cdot 3.3H_2O$ (I) and $[Cu_2(PTP)Cl_4] \cdot CH_3CH_2OH$ (III) both react with appropriate reducing agents (e.g. I^-, SO_3^{2-}) to produce derivatives containing the very stable species $[Cu_2(PTP)_2]^{2+}$, involving two four-coordinate copper(I) centers. The crystal and molecular structures of $[Cu(PTP)_2(H_2O)](ClO_4)_2 \cdot 3.3H_2O$ (I) and $[Cu_2(PTP)_2](ClO_4)_2$ (II) are reported. I crystallizes in the monoclinic system, space group $C2/c$, with $a = 25.176$ (7) Å, $b = 12.6423$ (14) Å, $c = 13.908$ (4) Å, $\beta = 122.630$ (19)°, and four formula units per unit cell. II crystallizes in the monoclinic system, space group $P2_1/a$, with $a = 8.906$ (4) Å, $b = 18.825$ (3) Å, $c = 10.157$ (2) Å, $\beta = 99.82$ (0)°, and four formula units per unit cell. Compound III exhibits moderate antiferromagnetic exchange with $g = 2.03$ and $-2J = 131$ cm^{-1}.

Introduction

The spontaneity of the reduction of copper(II) species to copper(I) is influenced to a large extent by the ligand environment at the copper center and by the metal ion stereochemistry. π-Acid ligands generate a more favorable thermodynamic situation for reduction than non-π-acid ligands, and some sulfur donors and acetonitrile generate positive enough reduction potentials that in many cases relatively stable copper(I) species can be generated.[2,3] Typically, copper(I) salts are generated in acetonitrile (e.g. $[Cu(CH_3CN)_4]X$; X = ClO_4, BF_4, etc.). Markedly positive Cu(II)/Cu(I) redox potentials (+0.10 to +0.80 V vs. SHE) are found for the type 1 copper protein centers, which contain imidazole (histidine), thioether (methionine), and thiolate (cysteine) donor groups.[4] Also, positive reduction potentials are found for binuclear copper proteins (fungal laccase, $E_{1/2}$ +0.78 V;[5] tree laccase, $E_{1/2}$ +0.43 V;[5] tyrosinase, $E_{1/2}$ +0.30 V;[6] potentials vs. SHE[2]). We have examined a number of hydroxide-bridged binuclear copper(II) complexes of tetradentate (N_4) ligands derived from pyridazine and phthalazine, and almost without exception, these systems exhibit positive redox potentials (+0.2 to +0.8 V vs. SCE), spanning the range observed for the binuclear copper proteins.[7-11]

In this report we describe some aspects of the copper coordination chemistry of the ligand PTP (3,6-bis(2-pyridylthio)pyridazine; Figure 1) and in particular the spontaneous redox reactions of both mononuclear and binuclear copper(II) complexes of PTP, which exhibit very positive redox potentials. The square-pyramidal, mononuclear complex $[Cu(PTP)_2(H_2O)](ClO_4)_2 \cdot 3.3H_2O$ (I), which has been characterized by X-ray crystallography, has a redox potential of +0.57 V (glassy carbon, CH_3CN, TEAP (tetraethylammonium perchlorate), vs. SCE)[8] and is spontaneously reduced on refluxing in methanol or acetonitrile, for an extended period of time, to $[Cu_2(PTP)_2](ClO_4)_2$ (II). This binuclear copper(I) species can be generated directly from PTP and cuprous perchlorate (CH_3CN), and an X-ray structure reveals a dimeric, binuclear structural arrangement involving two pseudotetrahedral copper(I) centers. The same product arises on reaction of I with triphenylphosphine in acetonitrile. The complex $[Cu_2(PTP)Cl_4] \cdot CH_3CH_2OH$ (III), the

---

* To whom correspondence should be addressed.

† This paper assigned NRCC Contribution No. 27819.

(1) (a) Memorial University of Newfoundland. (b) National Research Council.

(2) Phillips, C. S. G.; Williams, R. J. P. *Inorganic Chemistry*; Oxford University Press: London, 1966; Vol. II, p 316.

(3) Patterson, G. S.; Holm, R. H. *Bioinorg. Chem.* **1975**, *4*, 257.

(4) Addison, A. W. In *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*; Karlin, K. D., Zubieta, J., Eds.; Adenine: Guilderland, NY, 1984; p 109.

(5) Reinhammar, B. R. M. *Biochim. Biophys. Acta* **1972**, *275*, 245.

(6) Makino, N.; McMahill, P.; Mason, H. S. *J. Biol. Chem.* **1974**, *249*, 6062.

(7) Mandal, S. K.; Thompson, L. K.; Hanson, A. W. *J. Chem. Soc., Chem. Commun.* **1985**, 1709.

(8) Woon, T. C.; McDonald, R.; Mandal, S. K.; Thompson, L. K.; Addison, A. W. *J. Chem. Soc., Dalton Trans.* **1986**, 2381.

(9) Mandal, S. K.; Woon, T. C.; Thompson, L. K.; Newlands, M. J.; Gabe, E. J. *Aust. J. Chem.* **1986**, *39*, 1007.

(10) Thompson, L. K.; Mandal, S. K.; Gabe, E. J.; Lee, F. L.; Addison, A. W. *Inorg. Chem.* **1987**, *26*, 657.

(11) Mandal, S. K.; Thompson, L. K.; Newlands, M. J.; Lee, F. L.; LePage, Y.; Charland, J.-P.; Gabe, E. J. *Inorg. Chim. Acta* **1986**, *122*, 199.