Conclusion

This study establishes the structure of one species obtained from the aqueous solution of tungstate and phosphate mixtures with a low W/P ratio. Several other polyanions coexist in these solutions. We are currently studying some of them, using the same methods of investigation.

Registry No. $Na_{12}P_4W_{14}O_{58}$, 111933-31-4; $K_{12}P_4W_{14}O_{58}\cdot 21H_2O$, 111933-32-5; sodium tungstate, 13472-45-2; disodium hydrogen phosphate, 7558-79-4; ^{183}W, 14265-81-7.

Supplementary Material Available: A table of anisotropic temperature factors for W, P, and K atoms (1 page); a listing of structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

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Crystal Structure, Magnetic Properties, and Orbital Interactions of the [(μ-Terephthalato)(ethylenediamine)diaquocopper(II)] Zigzag Chain

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The crystal structure of $[Cu(en)(H_2O)_2(TA)]_n$, where TA^{2-} is the dianion of terephthalic acid and en is ethylenediamine, has been determined by direct X-ray methods. The complex crystallizes in the monoclinic space group *P*2/*c* with two formula units in a unit cell of dimensions $a = 5.726$ (1) Å, $b = 8.806$ (2) Å, $c = 12.866$ (4) Å, and $\beta = 101.12$ (1)° and densities *d*(calcd) = 1.693×10^3 kg·m^{-3} and *d*(exptl) = 1.694×10^3 kg·m^{-3}. The structure was refined to conventional discrepancy factors of $R = 0.041$ and $R_w = 0.049$ for 1404 observed reflections. A crystallographic inversion center is located at the center of the benzene ring of the TA bridging ligand. The Cu centers, lying on 2-fold axes, are bridged by TA in a bis-unidentate fashion. Thus, infinite zigzag chains along the *b* axis and parallel to ($\bar{1}02$) are formed. The environment of each metal ion is distorted-elongated octahedral. Variable-temperature (4.2–295 K) magnetic susceptibility data are consistent with a chain structure, the intrachain exchange parameter *J* being 4.0 cm^{-1} and the interchain exchange parameter *zJ'* being −7.0 cm^{-1}. The EPR spectrum does not exhibit any evidence for a triplet state. An orbital interpretation of the coupling is proposed.

Introduction

In recent studies[2,3] our attention has been focused on the investigation of the magnetic exchange mechanism of novel terephthalato-bridged d^9–d^9 magnetic systems. Within this framework important magnetostructural relationships have been deduced on the grounds of experimental and quantum-chemical methods. It was shown that, under certain conditions, the terephthalato dianion is an appropriate bridging unit to design magnetic systems with expected magnetic properties. These magnetic systems could be either dimeric or polymeric, depending on the reaction conditions. In the polymeric magnetic systems some specific problems exist; in only rare cases can single crystals be obtained, and therefore uncertainties in the determination of the exchange parameters of the systems are unavoidable. In our opinion these are the main reasons justifying the absence from the literature of the magnetic properties of the copper(II) μ-terephthalato chains.

In this work we report the synthesis, crystal structure, and magnetic properties of the polymeric [(μ-terephthalato)(ethylenediamine)diaquocopper(II)] complex. Moreover, a possible interpretation of its magnetic behavior in correlation with the structural data and extended Hückel LCAO–MO calculations was attempted.

Experimental Section

Synthesis. The compound was prepared as follows. A 4×10^{-3} mol sample of $Cu(NO_3)_2\cdot 3H_2O$ was added to an equimolar one of ethylenediamine in 10 mL of distilled water and 40 mL of ethanol. The dark blue, clear solution derived was added to a 2×10^{-3} mol sample of disodium terephthalate in 10 mL of distilled water and 100 mL of ethanol (under continuous stirring at room temperature). The complete mixture was refluxed for 7 h. The light blue powder precipitate formed was filtered off; the dark blue filtrate, upon staying in a refrigerator for a period of about 1 month, gave 0.2 g (31% yield) of dark blue single crystals suitable for structure and magnetic determinations. Anal. Calcd for $C_{10}H_{16}N_2O_6Cu$: C, 37.10; H, 4.98; N, 8.65; O, 29.65; Cu, 19.62. Found: C, 37.02; H, 5.09; N, 8.53; O, 29.95; Cu, 19.41.

Table I. Crystallographic Data Collection

formula	$[Cu(C_8H_4O_4)(C_4H_8N_2)(H_2O)_2]_n$
cryst color	dark blue
cryst habit	prismatic
cryst size, mm	$0.60 \times 0.25 \times 0.20$
d_{exptl}, kg·m^{-3}	1.694×10^3
μ(Mo Kα), cm^{-1}	18.2
cryst syst	monoclinic
space group	*P*2/*c*
a, Å	5.726 (1)
b, Å	8.806 (2)
c, Å	12.866 (4)
β, deg	101.12 (1)
V, Å^3	636.58
Z	2
diffractometer	Philips PW1100
monochromator	graphite
radiation (λ, Å)	Mo Kα (0.710 70)
temp, °C	21
scan type	θ–2θ
2θ range, deg	6–60
scan speed, deg·s^{-1}	0.03
bkgd	half of scan time, in two parts, before and after every scan, in fixed position
no. of std. reflcns	3, measd every 2 h
reflcns measd, $+h$, $\pm k$, $\pm l$	$0 \rightarrow 8, 12, 15$
no. of reflcns collcd	3940
no. of indep reflcns merged	1799
R_i	6.1 (2924 reflcns)
no. of reflcns kept for refinement	1404 [$I > 3\sigma(I)$]

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(1) (a) Department of General and Inorganic Chemistry, University of Thessaloniki. (b) Department of Physics, University of Thessaloniki. (c) University of Wroclaw.

(2) Bakalbassis, E. G.; Mrozinski, J.; Tsipis, C. A. *Inorg. Chem.* **1985**, *24*, 4231.

(3) Bakalbassis, E. G.; Mrozinski, J.; Tsipis, C. A. *Inorg. Chem.* **1986**, *25*, 3684.

0020-1669/88/1327-0529$01.50/0

Table II. Structure Refinements

computing program	XRAY72[a]
minimized function	$R_w = \sum_i w_i(F_o - F_c)^2$
secondary extinction	none obsd
abs cor	not applied
weighting scheme	$w = (A/F_o)^2$, $A = 80$
av shift/esd (last cycle)	0.03
$N_{\text{reflcns}}/N_{\text{variable}}$	16.1
final residuals: R, R_w	0.041, 0.049

[a] Stewart, J. M.; Kruger, G. J.; Ammon, H. L.; Dickinson, C.; Hall, S. R. "XRAY System"; Technical Report TR-192; Computer Science Center, University of Maryland: College Park, MD, 1972.

Table III. Atomic Parameters[a] for the Non-Hydrogen Atoms and Their Equivalent Isotropic Temperature Factors

atom	x/a	y/b	z/c	B, Å^2
Cu	0.50000	0.45689 (7)	0.25000	2.23
O1	0.2908 (6)	0.2995 (4)	0.1749 (2)	3.86
O2	0.4642 (5)	0.2937 (4)	0.0355 (2)	4.07
O(W)	0.1672 (5)	0.4808 (4)	0.3659 (2)	3.94
N	0.6661 (6)	0.6251 (4)	0.3407 (3)	2.85
C1	0.6276 (8)	0.7675 (5)	0.2800 (3)	3.91
C2	0.3168 (6)	0.2479 (4)	0.0860 (3)	2.21
C3	0.1507 (6)	0.1202 (4)	0.0417 (3)	2.07
C4	0.1922 (6)	0.0385 (4)	−0.0463 (3)	2.45
C5	−0.0433 (6)	0.0804 (4)	0.0880 (3)	2.38

[a] Standard deviations of the last significant figures are given in parentheses.

Crystal Structure Determination and Refinement. The structure of the complex was solved by direct methods. Systematic absences indicated $P2/c$ and Pc as probable space groups, of which the former gave a plausible structure with $R = 0.041$. Cell dimensions were obtained by least squares from the setting angles of 60 reflections. No absorption correction was applied. General crystallographic information is given in Tables I and II.

The phases of 160 strong reflections were determined by direct phase determination with the MULTAN 77 system.[4] On the resulting E map it was possible to locate all the non-hydrogen atoms of the asymmetric unit. Successive least-squares refinements led to $R = 0.106$ with isotropic thermal parameters and to 0.048 with anisotropic thermal parameters for all atoms other than hydrogens. The hydrogen atoms were added in calculated fixed positions and included in further refinement with fixed isotropic temperature factors (equal to those of the corresponding C and O atoms to which they are bonded) assigned to them. At this stage a systematic weight analysis was carried out which led to the following weighting scheme: $w = (80/F_o)^2$. Convergence was reached at $R = 0.041$ ($R_w = 0.049$). The final difference Fourier map was virtually featureless. Atomic and thermal parameters are shown in Tables III and SI,[5] respectively, and main distances and bond angles in Tables IV and V.

Atomic scattering factors and anomalous dispersion corrections for Cu are from ref 6.

Optical Measurements. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer (4000–250 cm^{-1}) using KBr pellets. Reflectance spectra have been measured in the range 200–800 nm on a Hitachi 356 spectrometer by using Nujol films. Sr_2ZnTeO_6 and freshly sintered MgO were used as standards.

Magnetic Measurements. These were carried out on a Faraday type magnetometer using a sensitive Cahn RG-HV electrobalance in the temperature range of 4.2–295 K. The magnetic field applied was 6.25 kG. Diamagnetic corrections were estimated as -153×10^{-6} cm^3·mol^{-1}.

EPR spectra were recorded on a JEOL JES-ME X-band ($\nu = 9.30$ GHz) spectrometer using a nuclear magnetometer (MJ 110 R) and a microwave frequency meter (JES-SH-30X), and EPR standards were used at both room temperature and 173 K.

Results and Discussion

Description of the Structure. Each unit cell contains two formula units. The Cu(en) moieties are bridged sequentially by terephthalato dianions, coordinated in a bis-unidentate fashion through the oxygen atoms of their carboxylate groups. Thus, infinite zigzag chains along the b axis and parallel to $(\bar{1}02)$ are formed. Neighboring chains are interconnected by hydrogen bonds from the amine groups to O atoms. The copper(II) ions are in 4 + 2 surroundings. Each basal plane includes the two nitrogen atoms of the en ligand and two oxygen atoms of two different terephthalato bridges. The apical positions are occupied by oxygen donor atoms of two water molecules. Hence, the local geometry around each paramagnetic center is approximately distorted-elongated octahedral.

A normal projection of the complex is shown in Figure 1. The terephthalato group possesses a center of symmetry, and the Cu(II) atoms lie on 2-fold axes. Therefore, two successive terephthalato dianions in the zigzag chain are symmetrically equivalent, and this is also the case with the two water molecules of each magnetic center.

In the octahedral chromophores the Cu–N bond distance of 2.008 (3) Å is comparable with the distances found in other copper(II) amine complexes.[7,8] The Cu–O1 "short" distance of 1.961 (3) Å is also comparable with the 1.931 and 1.971 Å ones found in (μ-terephthalato)copper(II) dimers.[9] The "long" Cu–O(W) bond distance of 2.644 (3) Å is also in line with the corresponding ones given in the above references. All angles of the

Table IV. Main Interatomic Distances (Å)[a,b]

Cu–Cu			
intermolecular	11.1673 (6)	shortest intermolecular	5.7263 (1)
Cu Surroundings			
Cu–O1	1.961 (3)	Cu–N	2.008 (3)
Cu–O(W)	2.644 (3)	Cu–O2	3.083 (3)
Bridging Terephthalato Ligand			
C2–O1	1.266 (5)	C3–C4	1.399 (5)
C2–O2	1.228 (5)	C3–C5	1.403 (5)
C2–C3	1.512 (5)	C4–C(5)^{i}	1.390 (5)
Ethylenediamine Ligand			
C1–C(1)^{i}	1.515 (6)	N–C1	1.471 (6)
Hydrogen Bonds			
N···O(2)^{iii}	3.041 (5)	H1(N)···O(2)^{iii}	2.04
N···O(W)^{iv}	3.098 (4)	H2(N)···O(W)^{iv}	2.13

[a] Standard deviations of the last significant figures are given in parentheses. [b] Symmetry Codes: (i) $1 - x, y, {}^1/_2 - z$; (ii) $-x, y, -z$; (iii) $x, 1 - y, {}^1/_2 + z$; (iv) $1 + x, y, z$.

Table V. Main Bond Angles (deg)[a]

Cu Surroundings			
O(W)–Cu–O1	84.0 (1)	O1–Cu–O(1)^{i}	90.0 (1)
O(W)–Cu–N	85.7 (1)	O1–Cu–N	169.7 (1)
O(W)–Cu–O(1)^{i}	102.5 (1)	O1–Cu–N^{i}	93.4 (1)
O(W)–Cu–N^{i}	87.5 (1)	N–Cu–N^{i}	84.9 (1)
O(W)–Cu–O(W)^{i}	170.9 (1)		
Bridging Terephthalato Ligand			
Cu–O–C2	122.1 (3)	C2–C3–C4	119.7 (3)
O1–C2–O2	124.9 (3)	C2–C3–C5	121.2 (3)
O1–C2–C3	115.6 (3)	C4–C3–C5	119.1 (3)
O2–C2–C3	119.4 (3)	C3–C4–C(5)^{ii}	120.8 (3)
		C3–C5–C(4)^{ii}	120.0 (3)
Ethylenediamine Ligand			
Cu–N–C1	108.3 (2)	N–C1–C(1)^{i}	107.5 (3)
Hydrogen Bonds			
N–H(1)N···O(2)^{iii}	166.4	N–H2(N)···O(W)^{iv}	157.8

[a] Standard deviations for the last significant figures are given in parentheses. For i–iv, see Table IV, footnote *b*.

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(4) Main, P.; Lessinger, L.; Woolfson, M. M.; Germain, G.; Declercq, J.-P. "MULTAN 77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data"; University of York, England, and University of Louvain, Belgium, 1977.

(5) Supplementary material.

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(9) Verdaguer, M.; Gouteron, J.; Jeannin, S.; Jeannin, Y.; Kahn, O. *Inorg. Chem.* **1984**, *23*, 4291.

Table VI. Computed Magnetic Parameters of the Complex

temp range, K	Weiss const Θ, K	Curie const *C*, cm^3·mol^{-1}·K	model of magnetic interacn	*J*, cm^{-1}	*zJ'*, cm^{-1}	error
4.2–20	−11.5	0.733				5.73×10^{-4}
25–290	−0.2	0.430				6.43×10^{-7}
8–293			Fisher	3.9	−6.9	1.35×10^{-6}
8–293			1D Ising	4.1	−7.2	1.31×10^{-6}
25–290			Fisher	4.4	−6.9	7.59×10^{-8}
25–290			1D Ising	4.5	−7.0	7.63×10^{-8}

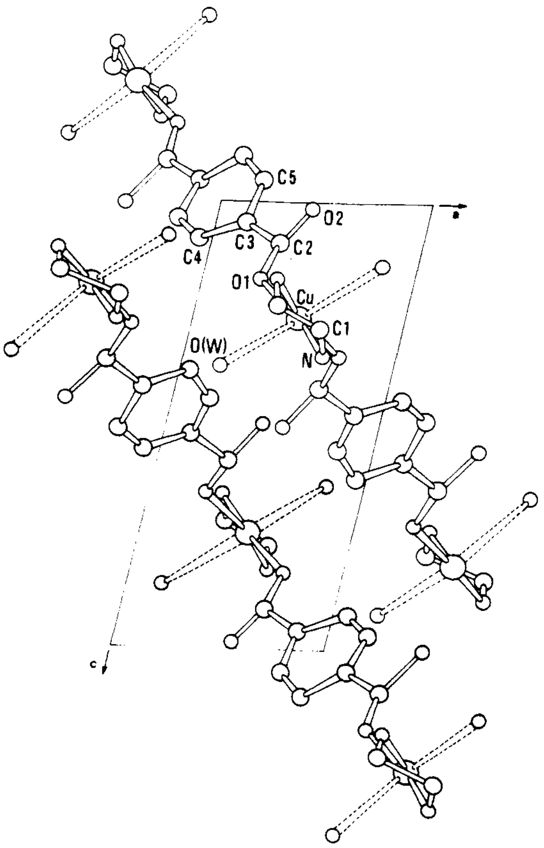

Figure 1. Normal projection of the complex on (010).

octahedron are normal, ranging from 84 to 102.5°.

The intramolecular Cu–Cu separation is 11.1673 (6) Å, quite close to those reported by Verdaguer et al.[9] for two (μ-terephthalato)copper(II) dimers. The shortest intermolecular Cu–Cu distance is 5.7263 (1) Å.

The atoms of the benzene ring do not deviate more than 0.001 Å from the respective mean plane. This plane is perpendicular (dihedral angle of 91.50 (1) Å) to the basal plane of the octahedral chromophore. The dihedral angle of 10.6 (2)° between the carboxylate group and the benzene ring is also in accordance with the angle (10.4°) found[9] in the [Cu(pmedien)$(H_2O)_2$tp$(ClO_4)_2$] dimer.

Finally, the noncoordinated oxygen atom (Cu–O2 distance = 3.083 (3) Å) of the carboxylate group forms an intermolecular hydrogen bond to one of the amine H atoms; this is also the case between the other amine H atom and the O atom of the water molecule (see also Tables IV and V).

Spectroscopic Characterization. The most salient feature of the IR spectrum of the compound was the existence of two strong and broad bands in the 1700–1200-cm^{-1} region, attributed to the $\nu_{as}(CO_2)$ (1587 cm^{-1}) and $\nu_s(CO_2)$ (1372 cm^{-1}) stretching vibrations of the coordinated carboxylato groups. These two bands were separated by ca. 215 cm^{-1}, suggesting[10] an amphimonodentate end-to-end bonding mode for the terephthalato bridging ligand. Moreover, the characteristic bands due to the ν(O–H) and $\nu(NH_2)$ stretchings of the coordinated water molecules (3410 cm^{-1}) and the ethylenediamine ligand (3305, 3258, and 3165 cm^{-1}) were also seen.

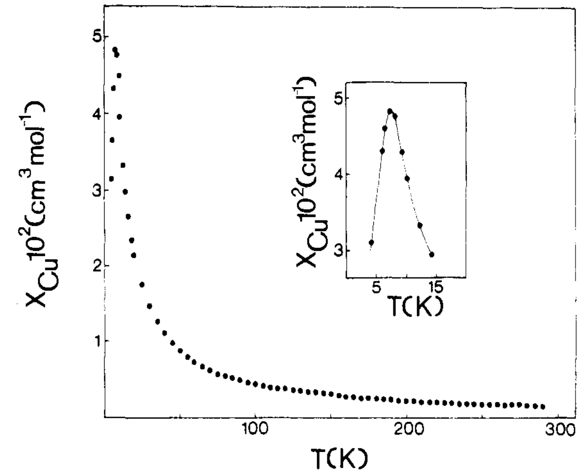

Figure 2. Temperature dependence of χ_M.

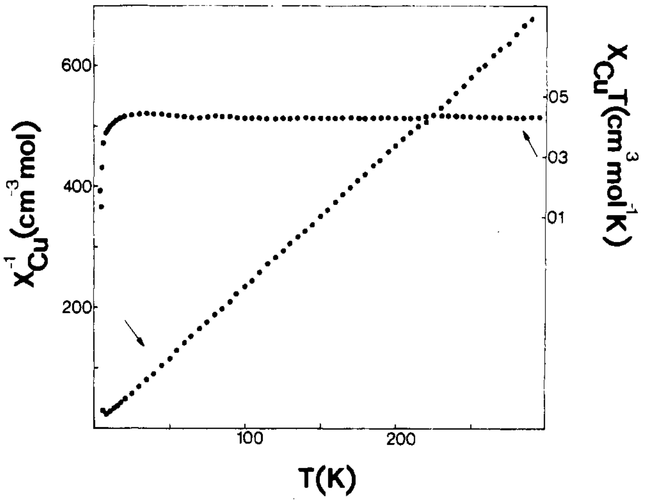

Figure 3. Temperature dependence of $\chi_M T$ and $1/\chi_M$.

The electronic reflectance spectrum of the compound exhibited a broad-band envelope with a maximum at ca. 14 925 cm^{-1} and a shoulder at ca. 17 857 cm^{-1}, along with a band envelope with a maximum at ca. 40 981 cm^{-1} and two shoulders at ca. 35 713 and 34 254 cm^{-1}. The broad-band envelope in the visible region covers the d–d transitions along with the MLCT and/or LMCT ones, in accordance with the results of EHMO calculations (Table SII[5]); still, the ultraviolet region of the spectrum was dominated by a number of symmetry-allowed MLCT, LMCT, and intraligand transitions.

Magnetic Data and Their Interpretation. Variable-temperature (4.2–295 K) magnetic susceptibility data (Tables SIII[5] and SIV[5]) were collected for a solid sample of the complex. Two models of magnetic interaction were used in an attempt to fit these data.

A least-squares fit to the experimental data to Fisher's classical Heisenberg model[11] for infinite linear chains with a molecular field correction[12] and to the one-dimensional Ising model[13] ($S = {}^1/_2$)

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[10] Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227.

[11] Fisher, M. E. *Am. J. Phys.* **1964**, *32*, 343.

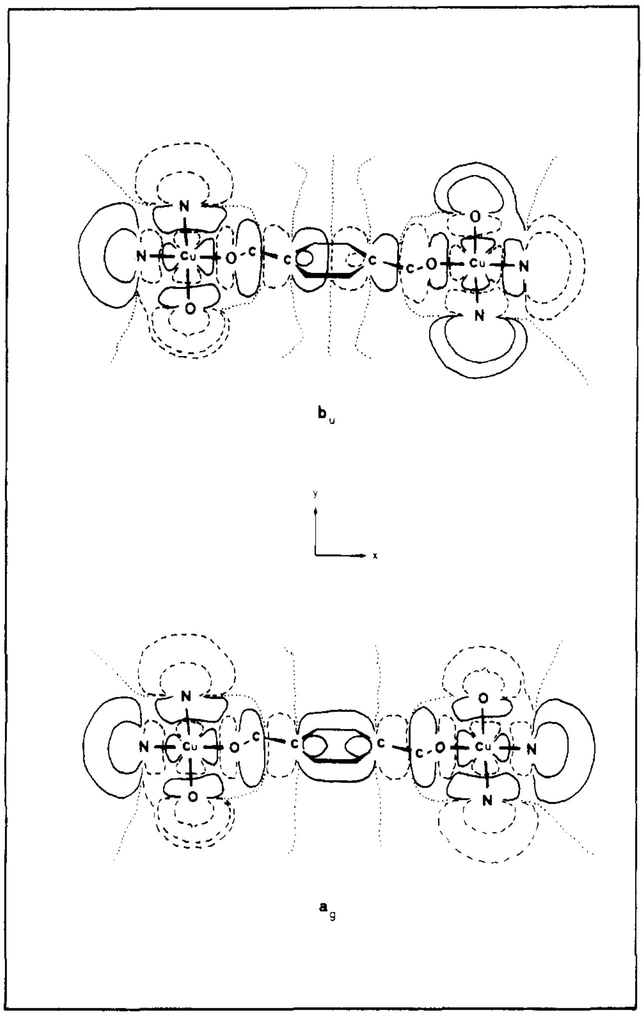

Figure 4. Contour maps plotted in the *xy* plane for the a_g and b_u SOMO's. Contour values used range from 0.0625 to 0.0002. The solid lines represent the positive isovalue curves, and the dashed lines, the negative ones. The dotted lines represent the nodal zones.

with a molecular field correction led to the exchange parameters of Table VI. In this table a summary of the least-squares-fit exchange parameters J, zJ', Curie C, and Weiss Θ constants, determined from the magnetic susceptibility data of the complex, is presented. The results obtained from both models were essentially identical. In the least-squares fitting the experimental g_{av} value of the EPR spectrum of the complex (axial spectrum with $g_{\parallel} = 2.270$, $g_{\perp} = 2.066$, and $g_{av} = 2.136$ at 295 K; still, it did not exhibit any sign of exchange interaction or triplet ground state) was used. Moreover, the magnetic behavior of the complex in the form of both χ_M vs T and $\chi_M T$ vs T plots is depicted schematically in Figures 2 and 3.

The corrected molar magnetic susceptibility vs temperature plot (Figure 2) is indicative of antiferromagnetic exchange interaction, in line with the minus sign of the Weiss constant values. However, due to the sharp susceptibility maximum at ca. 7 K ($T_N = 7.5$ K), an intramolecular antiferromagnetic interaction should be excluded.[14] Moreover, the product $\chi_M T$ (Figure 3), T being the temperature, was constant and equal to about 0.430 $cm^3 \cdot mol^{-1} \cdot K$ down to ca. 20 K and then decreased below 20 K and reached 0.131 $cm^3 \cdot mol^{-1} \cdot K$ at 4.2 K. This latter value shows that a very weak intermolecular antiferromagnetic interaction occurs below 20 K. The dependence of $^1/\chi_M$ on T, shown also in Figure 3, was linear with only small anomalies at the liquid-helium temperature. However, the positive J parameter value of about 4 cm^{-1} implies intrachain ferromagnetic exchange interaction; still, the interchain effective exchange parameter zJ'value of about -7 cm^{-1} accounts for interchain antiferromagnetic exchange interaction.

Orbital Interpretation of the Exchange Mechanism. The mechanism of the AF coupling is now being considered. In this consideration the orbital model developed by Kahn et al.,[15] valid for chains of transition-metal ions without first-order angular momentum, will be used. In the complex under investigation each magnetic orbital is built from the $d_{x^2-y^2}$ metallic orbital pointing toward the two oxygen atoms bound to copper and the two nitrogen atoms of the en molecule. The magnitude of J_{AF} is related[15,16] to the energy gap (Δ_μ) between the a_g and b_u molecular orbitals (SOMO's) in the hypothetical binuclear entity. These SOMO's obtained by EHMO calculation are shown in Figure 4. The EHMO calculations, carried out with the parametrization already used,[3] led to a Δ_μ value of 0.010 29 eV, in line[17] with the weak AF interaction of the complex. Moreover, due to the nodal planes being in the bridging unit of the contour plots for these two SOMO's, a weak intramolecular F interaction seems probable. Therefore, the weak AF interchain interaction observed could be possibly due to (i) the weak interaction between the two magnetic orbitals of two nearest-neighbor copper ions of two neighboring chains (these orbitals are parallel to each other and on different planes[18]) and/or (ii) the weak interaction via the hydrogen bonds[19] of the complex.

Registry No. $Cu(en)(H_2O)_2(TA)$, 111905-45-4.

Supplementary Material Available: Table SI, listing anisotropic temperature coefficients U_{ij} for the non-hydrogen atoms, Table SII, listing electronic absorptions and assignments, Tables SIII and SIV, listing experimental and calculated magnetic susceptibility data, and tables of atomic parameters for the hydrogen atoms and O–H and C–H distances (7 pages); tables of calculated and observed structure factors (10 pages). Ordering information is given on any current masthead page.

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