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Tropocoronands as Binucleating Ligands. Synthesis, Structure, and Properties of a (μ-Acetato)(μ-methoxo)dicopper(II) Derivative

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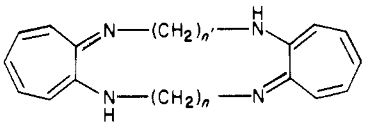
The reaction of copper(II) acetate in methanol with the tropocoronand ligand H_2(TC-6,6), one member of a new class of metal-complexing macrocycles comprised of two aminotropone imines linked by two hexamethylene chains, yields the derivative [Cu_2(OMe)(OAc)(TC-6,6)]. In this complex, the structure of which was determined by X-ray crystallography, two copper(II) ions are coordinated to the two bidentate aminotropone iminate portions of the macrocycle (average Cu–N distance 1.92 Å and N–Cu–N angle 82.7°) and bridged by both a methoxide (Cu–O = 1.95 Å, Cu–O–Cu′ = 105.7°) and a bidentate acetate (Cu–O = 1.98 Å) ligand. The resulting four-coordinate stereochemistry of copper is tetrahedrally distorted with a twist angle of 31.4 (5)°. The Cu···Cu distance is 3.100 (3) Å. Temperature-dependent magnetic susceptibility studies of solid [Cu_2(OMe)(OAc)(TC-6,6)] with a SQUID type susceptometer revealed antiferromagnetic behavior with a spin exchange coupling constant J of −35.4 (1) cm^{-1}. Exchange coupling was also evident in the frozen-solution electron spin resonance spectrum, demonstrating that the bridged binuclear structure persists in solution. Crystal data for $C_{29}H_{40}N_4O_3Cu_2$: orthorhombic, space group $Cmc2_1$, a = 18.352 (3) Å, b = 15.841 (3) Å, c = 9.912 (2) Å; V = 2881.7 Å^3; Z = 4. The structure was refined to R = 0.049 on the basis of 987 data having $F_o > 4\sigma(F_o)$.

Introduction

While investigating the chemistry of mononuclear copper(II) tropocoronand complexes, [Cu(TC-n,n')], where n,n' = 3,3; 4,4; 4,5; 5,5; 6,6, we discovered that the ligand could become binucleating.[1] As the number of methylene groups in the linker chains connecting the two aminotropone imine poles of the macrocycle increases from 3 to 6, mononuclear copper(II)[1] and nickel(II)[2] complexes distort from planar toward tetrahedral geometries. Molecular mechanics calculations[1,2] reveal, however, that even this distortion is insufficient to relieve the steric strain built up within the linker chains across the series. Thus the attempt to prepare mononuclear [Cu(TC-6,6)] resulted instead in the formation of the interesting new molecule [Cu_2(OMe)(OAc)(TC-6,6)], in which the tropocoronand-6,6 ligand is binucleating. Coordination of the aminotropone iminate chelate rings to two metals stretches out the hexamethylene linker chains, providing additional relaxation of the internal steric constraints.[2]



(TC-n,n')H_2
n, n' = 3,3; 4,4; 4,5; 5,5; 6,6

The chemistry of copper(II) in binucleating macrocycles is a topic of considerable current interest. Compounds with bridging imidazolate, hydroxide, azide, and related ligands have been extensively studied as models for the physical and chemical properties of binuclear copper centers in biology.[3] The focus of much of this work has been on magnetic exchange interactions between the two copper(II) ions, which can be diagnostic for the nature and geometry of the ligand-bridged binuclear center.[4]

Table I. Experimental Details of the X-ray Diffraction Study of [Cu_2(OMe)(OAc)(TC-6,6)]

(A) Crystal Parameters[a]

a, Å	18.352 (3)	Z	4
b, Å	15.841 (3)	ρ(calcd), g cm^{-3}	1.428
c, Å	9.912 (2)	ρ(obsd),[b] g cm^{-3}	1.421 (5)
V, Å^3	2881.7	fw	619.74
space group	$Cmc2_1$		

(B) Measurement and Treatment of Intensity Data

instrument: Enraf-Nonius CAD-4F κ-geometry diffractometer
radiation: Mo Kα (λ_α = 0.71073 Å) graphite monochromatized
temp: 26 °C
stds: ($\bar{4}$20), ($\bar{1}$31), (53$\bar{1}$)
no. of reflcns collected: 1904, $3° \leq 2\theta \leq 25°$ ($+h,+k,\pm l$); $25° \leq 2\theta \leq 50°$ ($+h,+k,+l$)

(C) Treatment of Intensity Data[d]

linear abs coeff, cm^{-1}	15.1	no. of reflcns after averaging	1549
transmission coeff	[e]	obsd unique data [$F_o > 4\sigma(F_o)$]	987
av R_{av}	0.023		

[a] From a least-squares fit to the setting angles of 25 reflections having $2\theta > 24°$. [b] By neutral buoyancy in aqueous KI. [c] Monitored every 3600 s of exposure time for intensity and after every 250 reflections for orientation control. [d] See ref 9. [e] Owing to the small crystal size, no absorption correction was applied.

In this article we report the synthesis, structure, magnetic properties, and electron spin resonance spectrum of [Cu_2(OMe)(OAc)(TC-6,6)], the first binuclear tropocoronand complex.

Experimental Section

The synthesis of the H_2(TC-6,6) ligand, the source of the chemicals, and the instrumentation used to obtain electronic, infrared, electron spin resonance, and magnetic susceptibility data have been described previously.[1]

Synthesis of [Cu_2(OMe)(OAc)(TC-6,6)]. A heterogeneous mixture of $Cu(OAc)_2 \cdot H_2O$ (125 mg, 0.625 mmol) and H_2(TC-6,6) (125 mg, 0.31 mmol) was stirred in 50 mL of methanol for 3 h and then filtered. The solid thus obtained was recrystallized from toluene/MeOH to give 83 mg (0.133 mmol, 43% yield) of [Cu_2(OMe)(OAc)(TC-6,6)]. Anal. Calcd for $C_{29}H_{40}N_4O_3Cu_2$: C, 56.20; H, 6.51; N, 9.04. Found: C, 56.36; H, 6.61; N, 9.05. Electronic spectrum (λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 850 (325), 560 (sh), 455 (20000), 430 (16000), 380 (25000). Infrared spectrum (KBr pellet, cm^{-1}): 2910 (w), 2850 (w), 2700 (w), 1590 (m), 1560 (s), 1505 (s), 1465 (m), 1430 (s), 1395 (s), 1340 (s), 1235 (s), 1220 (s), 1045 (m), 1010 (w), 1000 (w), 900 (m), 745 (s), 685 (s).

Magnetic Susceptibility Measurements. Variable-temperature (8–300 K) measurements were made on a 11.32-mg sample of [Cu_2(OMe)(OAc)(TC-6,6)] by using a SQUID susceptometer operating at 25 kG. Molar magnetic susceptibilities were corrected for underlying diamag-

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netism[5] with ligand constitutive effects applied for acetate[6] and the tropocoronand-6,6 dianion.[1]

Electron Spin Resonance Spectra. Measurements were obtained on a 5 mM frozen solution in 1:1 toluene/methylene chloride at 77 K in a 5-mm quartz tube. Spectra were calibrated with the Mn^{2+} impurity in strontium oxide.[7]

Collection and Reduction of X-ray Data. Dark brown parallelepipeds of $[Cu_2(OMe)(OAc)(TC\text{-}6,6)]$ were obtained by liquid–liquid diffusion of methanol into a toluene solution of the complex at 4 °C. Preliminary examination on the Weissenberg camera indicated an orthorhombic system with systematic absences consistent with space groups *Cmcm* (D_{2h}^{17}, No. 63), *Cmc*2_1 (C_{2v}^{12}, No. 36), or *C*2*cm* (C_{2v}^{16}, a nonstandard setting of No. 40).[8] A crystal bounded by $(\bar{1}10)$ and $(1\bar{1}0)$, 0.10 mm apart, (110) and $(\bar{1}\bar{1}0)$, 0.10 mm apart, and (001) and $(00\bar{1})$, 0.20 mm apart, was examined by using an automated diffractometer with Mo K$\bar{\alpha}$, (λ = 0.7107 Å) radiation. Open-counter ω scans of several strong, low-angle reflections showed somewhat broad ($\Delta\bar{\omega}_{1/2}$ = 0.36°) but structureless peaks. The crystal was deemed acceptable for data collection, details for which are reported in Table I (see ref 9 for typical procedures used in our laboratory).

Solution and Refinement of the Structure. The structure was solved by conventional heavy-atom methods in *Cmc*2_1. From difference Fourier maps it was apparent that the carbon atoms of the hexamethylene chain were disordered about the crystallographic mirror plane containing the bridging methoxide ligand and two carbon atoms of the bridging acetate group. After several trials to account for this disorder, none of which was completely satisfactory, the following model was employed in which the carbon atoms closest to the mirror plane (*m*), CC3A, CC3B, CC6A, and CC6B, were given half-occupancy and the distances CC3A–CC3B and CC6A–CC6B were fixed at 1.05 (1) Å. This latter value results from using the mean geometry (C–C bond lengths 1.516 Å, C–C–C angles 113.6°) from several known structures[1,2] involving the tropocoronand ring system. The two disordered units CC2, CC3A, CC3B and CC5, CC6A, CC6B were then treated as rigid groups pivoting upon atoms CC1 and CC4. Calculations were performed by using SHELX-76,[10] with neutral-atom scattering factors and anomalous dispersion corrections for the non-hydrogen atoms obtained from ref 11 and hydrogen atom scattering factors from ref 12. All non-hydrogen atoms were refined anisotropically except for carbon atoms of type CC3 and CC6, which were assigned isotropic temperature factors. Hydrogen atoms of the aminotropone imine rings were allowed to ride on their respective carbon atoms at a fixed C–H distance of 0.95 Å. A common isotropic temperature factor assigned to these hydrogen atoms was refined to a value of U = 0.093 Å^2. Least-squares refinement, minimizing the function $\sum w(|F_o| - |F_c|)^2$, in this manner with 162 variable parameters and unit weights converged at R_1 = 0.049 and R_2 = 0.053.[13] Toward the end of the refinement the choice of enantiomer for the polar space group was confirmed by inspection of the observed and calculated structure factor amplitudes for strong Friedel pairs of reflections. The largest peak on the final difference Fourier map was ~1 e Å^{-3}, located near the region of the disordered methylene groups in the linker chains.

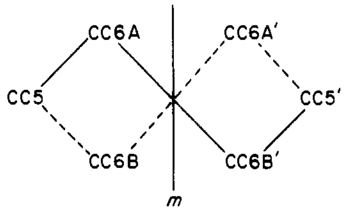

Table II. Final Positional Parameters for $[Cu_2(OMe)(OAc)(TC\text{-}6,6)]^a$

ATOM	X	Y	Z
Cu1	0.08446 (7)	0.25072 (11)	0.2500
O1	0.0603 (4)	0.1302 (5)	0.2259 (12)
O2	0.0000	0.2631 (9)	0.3669 (13)
N1	0.1482 (6)	0.2546 (8)	0.0966 (12)
N2	0.1428 (6)	0.3447 (7)	0.3080 (12)
C1	0.0000	0.0922 (12)	0.227 (2)
C2	0.0000	-0.0049 (11)	0.235 (4)
C3	0.0000	0.2134 (14)	0.492 (2)
C11	0.1977 (8)	0.3164 (9)	0.0997 (15)
C12	0.2522 (11)	0.3279 (9)	-0.009 (2)
C13	0.3069 (9)	0.3850 (12)	-0.0189 (19)
C14	0.3236 (9)	0.4532 (13)	0.051 (2)
C15	0.2935 (10)	0.4788 (12)	0.1685 (18)
C16	0.2369 (7)	0.4450 (9)	0.238 (2)
C17	0.1926 (7)	0.3703 (8)	0.2209 (17)
CC1	0.1280 (8)	0.3911 (10)	0.4363 (14)
CC2	0.0828 (8)	0.4702 (10)	0.4181 (14)
CC3A	0.0143 (8)	0.4700 (10)	0.5032 (14)
CC3B	0.0546 (8)	0.5061 (10)	0.5518 (14)
CC4	0.1424 (8)	0.1975 (10)	-0.0233 (18)
CC5	0.0983 (8)	0.2345 (10)	-0.1395 (18)
CC6A	0.0277 (8)	0.2738 (10)	-0.0928 (18)
CC6B	0.0189 (8)	0.2123 (10)	-0.1314 (18)

[a] Numbers in parentheses are errors in the last significant digit(s). See Figure 1 for atom-labeling scheme.

Table III. Interatomic Distances (Å) and Angles (deg) for $[Cu_2(OMe)(OAc)(TC\text{-}6,6)]^a$

	Distances		
	Coordination Sphere		
Cu1–N1	1.92 (1)	Cu1–N2	1.92 (1)
Cu1–O2	1.945 (8)	Cu1–O1	1.975 (8)
Cu···Cu′	3.100 (3)		
	Ligand		
O1–C1	1.26 (1)	O2–C3	1.47 (3)
N1–C11	1.34 (2)	N1–CC4	1.50 (2)
N2–C17	1.32 (2)	N2–CC1	1.49 (2)
C1–C2	1.54 (3)	C11–C17	1.48 (2)
C11–C12	1.48 (3)	C12–C13	1.35 (3)
C13–C14	1.32 (3)	C14–C15	1.35 (3)
C15–C16	1.36 (2)	C16–C17	1.45 (2)
CC1–CC2	1.51 (2)	CC2–CC3A	1.51 (2)
CC2–CC3B	1.53 (2)	CC3A–CC3B′	1.47 (2)
CC4–CC5	1.53 (2)	CC5–CC6B	1.50 (2)
CC5–CC6A	1.51 (2)	CC6A–CC6B′	1.35 (2)
	Angles		
	Coordination Sphere		
N1–Cu1–N2	82.7 (5)	N1–Cu1–O2	162.6 (5)
N1–Cu1–O1	94.1 (5)	N2–Cu1–O2	100.8 (5)
N2–Cu1–O1	155.6 (4)	O2–Cu1–O1	89.4 (5)
Cu–O2′–Cu	105.6 (5)		
	Ligand		
C1–O1–Cu1	131.2 (9)	C3–O2–Cu1	116.7 (6)
C3–O2–Cu1	116.7 (6)	Cu1–O2–Cu1′	105.7 (6)
C11–N1–CC4	121 (1)	C11–N1–Cu1	115 (1)
CC4–N1–Cu1	124.5 (9)	C17–N2–CC1	122 (1)
C17–N2–Cu1	115 (1)	CC1–N2–Cu1	122.4 (9)
O1–C1–O1′	123 (2)	O1–C1–C2	118.5 (8)
O1–C1–C2	118.5 (8)	N1–C11–C17	114 (1)
N1–C11–C12	112 (1)	C17–C11–C12	124 (1)
C13–C12–C11	129 (2)	C14–C13–C12	133 (2)
C13–C14–C15	127 (2)	C14–C15–C16	129 (2)
C15–C16–C17	134 (2)	N2–C17–C16	124 (1)
N2–C17–C11	113 (1)	C16–C17–C11	122 (1)
N2–CC1–CC2	114 (1)	CC3A–CC2–CC1	113 (1)
CC1–CC2–CC3B	113 (1)	CC3B′–CC3A–CC2	154 (1)
CC2′–CC3B′–CC3A	82 (1)	CC5′–CC6B′–CC6A	117 (1)
N1–CC4–CC5	114 (1)	CC6B–CC5–CC4	113 (1)
CC6A–CC5–CC4	112 (1)	CC6B′–CC6A–CC5	99 (1)

[a] Primed atoms are at $-x$, y, z. See footnote *a* of Table II.

Final non-hydrogen atom positional parameters are reported in Table II. Interatomic distances and angles are given in Table III. Listings of thermal parameters for the non-hydrogen atoms, hydrogen atom positional and thermal parameters, and observed and calculated structure

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(10) SHELX-76: a package of crystallographic programs written by G. M. Sheldrick. All computations were performed on a DEC VAX-11/780 computer.

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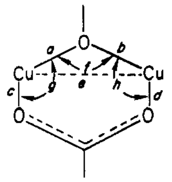
(13) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table IV. Comparison of Structural and Magnetic Parameters for Asymmetrically Bridged Dicopper(II) Complexes[a]



	$[Cu_2(OMe)(OAc)(TC\text{-}6,6)]$	$[Cu_2(apaca)(OAc)]\cdot H_2O$	$[Cu_2(apaca)(OAc)]$	$[Cu_2(L\text{-}Et)(OAc)]^{2+}$
a, Å	1.945 (8)	1.913 (6)	1.924 (4)	1.89 (1)
b, Å	1.945 (8)	1.902 (6)	1.929 (4)	1.92 (1)
c, Å	1.975 (8)	1.930 (6)	1.946 (4)	1.93 (1)
d, Å	1.975 (8)	1.946 (1)	1.943 (4)	1.91 (1)
e, Å	3.100 (3)	3.502 (2)	3.237 (1)	3.459 (2)
f, deg	105.7 (6)	133.3 (3)	114.3 (2)	130.6 (5)
g, deg	89.4 (5)	95.1 (3)	92.0 (4)	95.2 (4)
h, deg	89.4 (5)	94.2 (3)	91.9 (2)	95.7 (4)
$\sum$(angles), deg[b]	338.8	N/A[c]	335.5	N/A
J, cm^{-1}	−35.4	−82.5	+18.9	+12
ref	this work	15	16	4b

[a] Standard deviations are given in parentheses. [b] Sum of angles about the bridging oxygen atom of the RO^- ligand. [c] N/A = not available.

factor amplitudes are given in supplementary Tables S1–S3, respectively.

Results and Discussion

Synthesis. As described previously,[1] mononuclear copper(II) complexes of the troporoconands [Cu(TC-*n*,*n'*)], where *n*,*n'* = 3,3; 4,4; 4,5; 5,5, form in moderate to good yields when the protonated form of the ligand reacts with cupric acetate in methanol. Initial work with the H_2(TC-6,6) ligand immediately indicated different behavior, however. ESR spectra of the reaction mixture revealed the presence of a binuclear species, based upon the occurrence of half-field $\Delta M = \pm 2$ transitions (vide infra). Because the yield of the reaction is only 43%, it is unlikely that all of the ligand reacts to form the binuclear complex. The only byproduct of the reaction was an insoluble, brown-black material. One explanation for the occurrence of this intractable decomposition product is that the putative mononuclear [Cu(TC-6,6)] complex, expected to be tetrahedral by analogy to the known nickel(II) complex,[2] might have a high enough redox potential to oxidize the ligand irreversibly. Electrochemical studies of H_2(TC-3,3) and H_2(TC-4,4) reveal a relatively accessible ($E_{1/2} \approx 0.6$ V vs. SCE), irreversible oxidation.[14] No free ligand was isolated from the reaction mixture.

The incorporation of two copper ions into the $(TC\text{-}6,6)^{2-}$ ligand further relieves the steric constraints produced in mononuclear [M(TC-*n*,*n'*)] complexes as *n* and *n'* increase. Molecular mechanics calculations[1,2] indicate that the planar-to-tetrahedral distortion that occurs to relieve van der Waals, torsional, and bending forces in the mononuclear tropocoronands is insufficient to compensate for all the steric strain in [M(TC-6,6)]. Formation of the binuclear bridged complex permits the two linker chains to adopt a more favorable, stretched-out conformation. We anticipate that bridging ligands that extend the chains even more than acetate and alkoxide could be accommodated by the $(TC\text{-}6,6)^{2-}$ binucleating ligand.

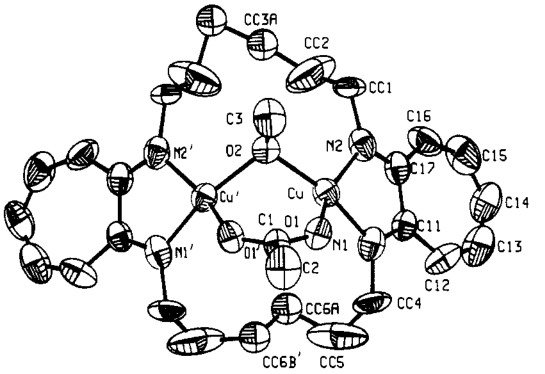


Figure 1. Structure of $[Cu_2(OMe)(OAc)(TC\text{-}6,6)]$ showing the atom-labeling scheme and 40% probability thermal ellipsoids. Primed and unprimed atoms are related by a crystallographically required mirror plane. Only one set of disordered (see text) methylene carbon atoms (CC3A, CC3B', CC6A, CC6B') is depicted. Hydrogen atoms are omitted for clarity.

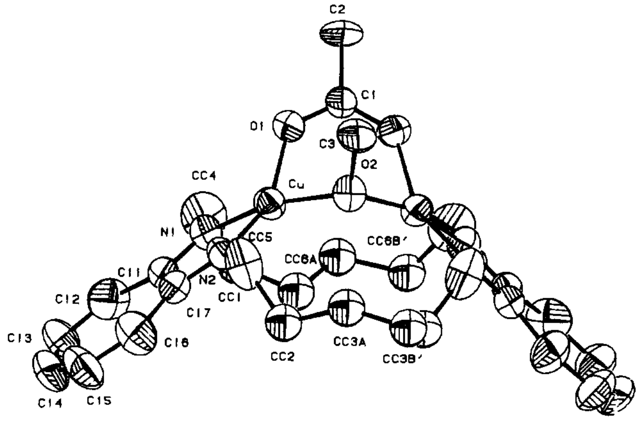


Figure 2. Alternate view of the $[Cu_2(OMe)(OAc)(TC\text{-}6,6)]$ structure (see caption to Figure 1). Disordered carbon atoms (CC2–CC6) of the linker chains were arbitrarily assigned an isotropic *B* value of 5 Å^2.

Structure. Figures 1 and 2 display two different perspectives of the $[Cu_2(OMe)(OAc)(TC\text{-}6,6)]$ structure. The molecule crystallizes as discrete units having mirror symmetry. In the center are two tetrahedrally distorted (tetrahedral twist angle[2] $\theta = 31.4$ (5)°) copper(II) ions separated by 3.100 (3) Å. Each is bound to two nitrogen atoms of the tropocoronand ligand as well as to oxygen atoms from the bridging acetate and methoxide ligands. The geometry (Table III) within the tropocoronand chelate rings compares favorably with that reported previously for the mononuclear [Cu(TC-*n*,*n'*)] complexes, *n*,*n'* = 3,3; 4,4; 5,5, in which the average Cu–N bond length and N–Cu–N angles were 1.94 (1) Å and 81.6 (5)°, respectively.[1] The geometry within the $\{Cu_2(OCH_3)(O_2CCH_3)\}^{2+}$ moiety is summarized in Table IV together with, for comparison purposes, structural information about three related complexes that contain both bridging alkoxide and acetate ligands.[4b,15,16] In all four complexes the Cu–O(alkoxide) bonds are significantly shorter than the Cu–O(acetate) bonds. Both distances are slightly longer in $\{Cu_2(OMe)(OAc)(TC\text{-}6,6)\}$, possibly because of the tetrahedral distortion

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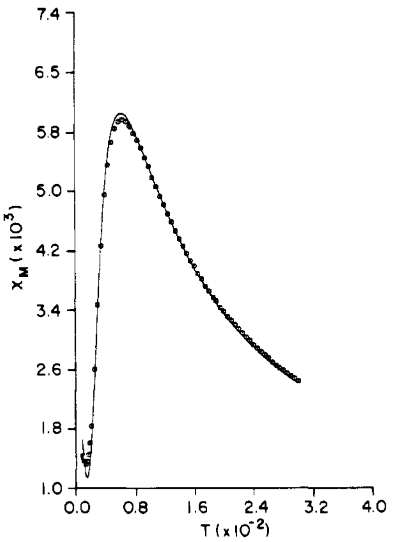
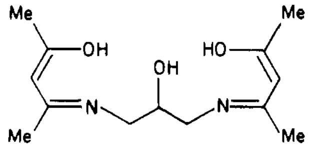


Figure 3. Plot of observed (symbols) and calculated (solid line) molar magnetic susceptibilities vs. temperature for $[Cu_2(OMe)(OAc)(TC\text{-}6,6)]$.

mentioned above, which tends to lengthen the copper(II)–ligand bonds.[1] From the sum of angles about the bridging oxygen atom O2 it is clear that it has pyramidal, rather than planar, geometry. As may be seen from Figure 2, the entire $\{Cu_2(OMe)(OAc)\}^{2+}$ core sits above the saddle-shaped tropocoronand ligand. The angle formed by the normals to the two seven-membered aminotropone iminate rings is 102 (1)°. Within these rings the bond lengths and interbond angles compare favorably with results for seven related structures.[1,2] Except for two chemically implausible angles, the linker chain geometry is reasonable, especially considering the disorder across the crystallographic mirror plane described above. A structurally more definitive description of the hexamethylene linker chains in two bridged binuclear copper(I) tropocoronand-6,6 complexes has been obtained and will be reported elsewhere.[17]

Magnetochemistry. A plot of observed and calculated molar susceptibilities as a function of temperature for $[Cu_2(OMe)(OAc)(TC\text{-}6,6)]$ is given in Figure 3. Numerical data are reported in Table S4 (supplementary material). The χ_M vs. T plot exhibits typical antiferromagnetic behavior, rising to a maximum at 65 K and diminishing at lower temperatures, where depopulation of the triplet becomes significant. At 10 K the only contribution to the magnetic susceptibility is a small amount of paramagnetic impurity. Least-squares fitting of the data to the Bleaney–Bowers equation[18] in the usual manner,[19] with the temperature-independent paramagnetism contribution held fixed at 120×10^{-6} cgsu, gave $J = -35.4$ (1) cm^{-1} and $g = 2.012$, where the spin-exchange Hamiltonian is defined as $H' = -2J\vec{S}_1\cdot\vec{S}_2$.

At least three other dicopper(II) complexes having both a bridging acetate and a bridging alkoxide or aryloxide ligand have been both structurally and magnetically characterized. As shown in Table IV, the magnetic-exchange coupling constants in these complexes vary from $J = -82.5$ cm^{-1} for $[Cu_2(apaca)(OAc)]\cdot H_2O$[15] to $+18.9$ cm^{-1} for $[Cu_2(apaca)(OAc)]$.[16] No obvious relationship exists between the coupling constants and any one or combination of structural parameters, including Cu–O bond lengths, Cu–O–Cu angles, or deviations from planarity of the $\{Cu_2OR\}$ unit. The factors contributing to the magnitude and sign of the exchange coupling parameter J in these asymmetrically bridged dicopper(II) complexes are therefore much less well understood than for analogous $\{Cu_2(OH)_2\}^{2+}$ compounds.[20,21] Further study of these systems seems warranted.



H_3apaca

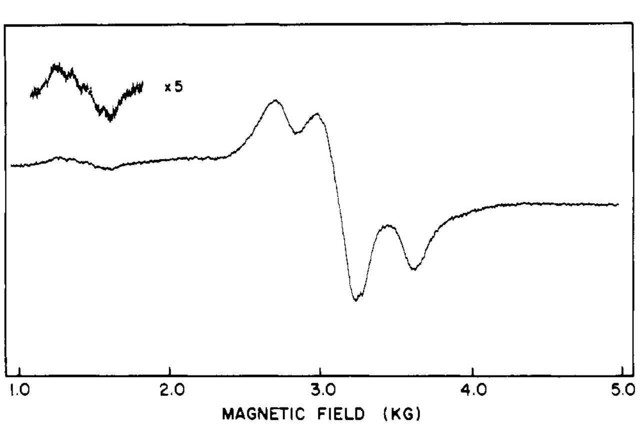


Figure 4. Frozen-solution (77 K, methylene chloride/toluene) ESR spectrum of $[Cu_2(OMe)(OAc)(TC\text{-}6,6)]$. Instrument settings: microwave frequency 9.132 GHz; modulation frequency 100 KHz; receiver gain 320; modulation amplitude 8 G; microwave power 20 mW.

Electron Spin Resonance Spectrum. Figure 4 displays the frozen-solution ESR spectrum of $[Cu_2(OMe)(OAc)(TC\text{-}6,6)]$, which is typical for a moderately antiferromagnetically coupled dicopper(II) species.[3a,4d] The low-field region of the spectrum reveals the $\Delta M = \pm 2$ transitions at ~1500 G, a feature characteristic of antiferromagnetically coupled, bridged binuclear copper(II) complexes. Between 2000 and 4000 G are the $\Delta M = \pm 1$ transitions, split into anisotropic components by the asymmetric ligand field. The feature at ~3600 G, due to the exchange contribution to the zero-field splitting,[4d] and the presence of the $\Delta M = \pm 2$ resonances clearly reveal that the bridged binuclear structure determined in the crystalline state persists in solution.

Concluding Remarks

The present study demonstrates the propensity of a tropocoronand ligand with six methylene carbon atoms in the linker chains to become binucleating. The resulting $[Cu_2(OMe)(OAc)(TC\text{-}6,6)]$ complex exhibits structural, magnetic, and ESR properties of interest in the context of bridged binuclear copper(II) systems studied extensively in both our laboratory and others. The versatility of the tropocoronand ligand system, which, through variation of the length of the linker chains, can tune the stereochemistry at a single metal center[1,2] or accommodate two metal atoms with bridging ligands,[17] provides an opportunity to explore new modes of chemical reactivity between metal centers held in close proximity. Studies directed toward this end are currently in progress.

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Registry No. $[Cu_2(OMe)(OAc)(TC\text{-}6,6)]$, 98088-58-5.

Supplementary Material Available: Tables S1–S4 reporting thermal parameters for non-hydrogen atoms, hydrogen atom positional parameters, observed and calculated structure factor amplitudes, and magnetic susceptibility data for $[Cu_2(OMe)(OAc)(TC\text{-}6,6)]$ (9 pages). Ordering information is given on any current masthead page.

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