Scheme IV. Electrode Mechanism for (TPP)Fe

$$[(TPP)Fe^{III}]^+ + e^- \underset{}{\overset{+0.18\ V}{\rightleftharpoons}} (TPP)Fe^{II}$$

$$(TPP)Fe^{II} + e^- \underset{}{\overset{-1.32\ V}{\longleftarrow}} [(TPP)Fe^I]^-$$

$$[(TPP)Fe^I]^- + e^- \underset{}{\overset{-1.70\ V}{\rightleftharpoons}} [(TPP)Fe^I]^{2-}$$
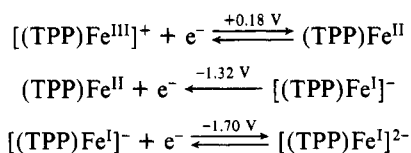
[(TPP)Fe]$_2$N has previously been given the unusual assignment of III$^1/_2$ based upon the results from Mössbauer,[1,5] ESCA,[3b] and EPR[4] experiments. As [(Pc)Fe]$_2$N yields comparable EPR[9] and electrochemical activity, the formal valences of the Fe atoms are similarly assigned. The oxidation of the two μ-nitrido dimers yields diamagnetic complexes with two equivalent Fe(IV) centers. This assignment has been clearly established by Mössbauer and NMR experiments.[3c,5c,9]

For all four electron transfers, the reduction of the phthalocyanine complex occurs at more positive potentials as compared to the reduction of the TPP complex. This is in accord with expectations; the more basic the macrocycle, the more negative the reduction potential. For both dimers, only the first reduction process is free from the complicating effects of dimer decomposition. We have assigned these electroreductions as metal-centered electron-transfer reactions in accordance with the MO diagram put forth for these complexes.[6] The HOMO in these dimers is an A$_1$ orbital comprised of the in-phase and out-of-phase combinations of the N 2s and Fe d$_{z^2}$ atomic orbitals. The LUMO is an e$_1$ orbital derived from the N 2p and Fe d$_{xz}$ and d$_{yz}$ atomic orbitals. The first electroreduction pairs the electron residing in the A$_1$ orbital, producing two Fe(III) centers. The expected change in the electronic spectrum for a metal-centered reduction is a red shifting in the Soret and visible bands with an increase in the intensity of the Soret band. This is indeed observed.

Subsequent reductions populate the antibonding e$_1$ orbital and destabilize the dimeric linkage. We have assigned the dianion for both dimers as an Fe$^{II\ 1/2}$–N–Fe$^{II\ 1/2}$ species. This assignment assumes that the extent of electron delocalization present in the neutral complex does not significantly differ from that present in the dianion. The ultimate reduction products (the monomers) are designated in accordance with the findings of Reed[12] for the porphyrin complex and of Lever[13] for the phthalocyanine complex.

For both μ-nitrido complexes, decomposition of the dimeric structure frees an N^{3-} species. This species is probably hydrolyzed by adventitious water present in the supporting electrolyte to form NH$_3$ or NH$_2^-$. Experiments are presently under way to determine the fate of the bridging moiety after multielectron transfer.

Contribution from the Departments of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and Columbia University, New York, New York 10027

Copper(II) Tropocoronands: Synthesis, Structure, and Properties of Mononuclear Complexes

WILLIAM M. DAVIS,[†] ARIE ZASK,[‡] KOJI NAKANISHI,[‡] and STEPHEN J. LIPPARD[*†]

The synthesis of four mononuclear copper(II) tropocoronands, [Cu(TC-*n,n′*)] (*n,n′* = 3,3; 4,4; 4,5; 5,5), is described. Tropocoronands are a new class of metal-complexing macrocycles derived from two aminotropone imine moieties connected by two polymethylene linker chains of lengths *n* and *n′*. The complexes [Cu(TC-3,3)], [Cu(TC-4,4)], and [Cu(TC-5,5)] have been structurally characterized by X-ray crystallography. The geometry at the copper center smoothly distorts from planar (tetrahedral twist angle θ = 0°) toward tetrahedral (twist angles θ = 36.6 and 61.3°, respectively) along this series. Molecular mechanics calculations reveal the tetrahedral twist to result from relief of unfavorable steric interactions within the polymethylene linker chains as *n* increases. The smooth variation in θ with *n* for copper(II) tropocoronands contrasts with previous results for the corresponding nickel(II) complexes where the transition was discontinuous owing to an additional electronic barrier to the conversion from planar, *S* = 0, to tetrahedral, *S* = 1, stereochemistry. No such change in spin state can occur for copper(II). The variation in electronic structures of all four copper(II) tropocoronand complexes in solution is manifest by striking, if predictable, changes in electron spin resonance spectral parameters and optical spectroscopic (d–d) absorption bands. The solid-state magnetic susceptibilities of the four [Cu(TC *n,n′*)] complexes, measured by SQUID susceptometry down to 5–10 K, are reported. [Cu(TC-3,3)], CuC$_{20}$H$_{22}$N$_4$, crystallizes in the monoclinic system, space group *P*2$_1$/*n*, *a* = 9.933 (1) Å, *b* = 5.798 (1) Å, *c* = 14.520 (2) Å, *β* = 91.82 (1)°, and *Z* = 2; [Cu(TC-4,4)], CuC$_{22}$H$_{26}$N$_4$, crystallizes in the monoclinic system, space group *P*2$_1$/*c*, *a* = 11.178 (2) Å, *b* = 8.636 (1) Å, *c* = 20.188 (8) Å, *β* = 90.39 (2)°, and *Z* = 4; [Cu(TC-5,5)], CuC$_{24}$H$_{30}$N$_4$, crystallizes in the hexagonal system, space group *P*6$_5$22, *a* = *b* = 11.044 (2) Å, *c* = 30.390 (3) Å, and *Z* = 6.

Introduction

Recently we have been exploring the coordination chemistry of the tropocoronands H$_2$(TC-*n,n′*), a new class of ligands derived from aminotropone imines.[1,2] In the case of [Ni(TC-*n,n′*)]

H$_2$(TC-*n,n′*)
n,n′ =3,3; 4,4; 4,5; 5,5; 6,6
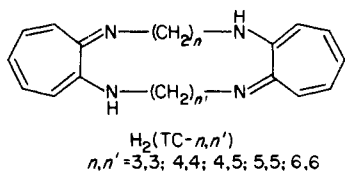
complexes, increasing the numbers of methylene groups (*n,n′*) in the two linker chains resulted in distortion of the stereochemistry at the metal center from planar, twist angle θ = 0°, toward tetrahedral, θ = 90°. For Ni(II) the planar-to-tetrahedral transition is accompanied by a change in electronic spin state from *S* = 0 to *S* = 1. As a consequence, the distortion of the nickel(II) tropocoronands from planar to tetrahedral is discontinuous, with the changeover occurring between [Ni(TC-4,5)] (*S* = 0, θ =

[†] Massachusetts Institute of Technology.
[‡] Columbia University.

(1) (a) Imajo, S.; Nakanishi, K.; Roberts, M.; Lippard, S. J.; Nozoe, T. *J. Am. Chem. Soc.* **1983**, *105*, 2071. (b) Zask, A.; Gonnella, N.; Nakanishi, K.; Turner, C. J.; Imajo, S.; Nozoe, T., to be submitted for publication.
(2) Davis, W. M.; Roberts, M. M.; Zask, A.; Nakanishi, K.; Nozoe, T.; Lippard, S. J. *J. Am. Chem. Soc.* **1985**, *107*, 3864.

27.1°) and [Ni(TC-5,5)] ($S = 1$, $\theta = 70.1°$).[2] Since no such change in ground-state spin multiplicity can occur for related copper(II) complexes, we were interested to synthesize and study the analogous series of copper(II) tropocoronands, where the effect of steric factors alone on the geometry and electronic properties of the metal ion could be clearly delineated.[3] The results of these investigations are presented and discussed in this paper.

An additional incentive for preparing and characterizing mononuclear copper(II) tropocoronands derives from the current interest in tetraaza macrocyclic ligands among both coordination and bioinorganic chemists.[4] The tropocoronands afford an especially nice opportunity to tune the stereochemistry at the metal center without changing the number, identity, or electronic properties of the donor atoms. The resulting effects particularly on the optical and ESR spectroscopic properties of the copper ion provide useful models for the kinds of steric constraints often encountered in crystals and proteins containing isolated cupric centers.

Experimental Section

Crystalline samples of the $H_2(TC-n,n')$ ligands were prepared as reported elsewhere.[1b] Copper(II) acetate monohydrate (Fisher) was recrystallized from a 1:1 mixture of ethanol and acetic acid. Electronic spectra were recorded by using methylene chloride solutions on a Cary 118C spectrophotometer in the UV–vis region and a Perkin-Elmer 330 instrument in the near-infrared region. A Beckman Acculab 10 instrument was used to obtain infrared spectra on samples pressed into KBr pellets.

Synthetic Work. [Cu(TC-3,3)]. $Cu(OAc)_2 \cdot H_2O$ (25 mg, 0.125 mmol) dissolved in 3 mL of EtOH was added to a 10-mL CH_2Cl_2 solution containing 40 mg (0.125 mmol) of $H_2(TC-3,3)$. The resulting dark brown solution was heated gently on a steam bath. Accompanying the evaporation of CH_2Cl_2 was the deposition of brown needlelike crystals. The crystalline material was collected and recrystallized from $CH_2Cl_2/EtOH$ to give a 92% yield (44 mg) of [Cu(TC-3,3)]. Anal. Calcd for $C_{20}H_{22}N_4Cu$: C, 62.89; H, 5.81; N, 14.67. Found: C, 62.71; H, 5.86; N, 14.67. Electronic spectra, λ_{max} (nm) (ϵ (M^{-1} cm^{-1})): 674 (278), 564 (sh), 436 (18450), 407 (31000). Infrared (cm^{-1}): 2920 (m), 2900 (m), 2830 (m), 1580 (s), 1500 (s), 1455 (m), 1430 (s), 1400 (s), 1350 (m), 1265 (m), 1230 (m), 1185 (m), 1100 (m), 710 (s).

[Cu(TC-4,4)]. A 25-mg sample of $H_2(TC-4,4)$, 0.072 mmol, was dissolved in 10 mL of CH_2Cl_2. To this yellow solution was added 3 mL of EtOH containing 15 mg of $Cu(OAc)_2 \cdot H_2O$ (0.075 mmol). Upon addition of the metal salt the yellow solution developed a deep brown color. Removal of the $CH_2Cl_2/EtOH$ yielded 15 mg (50%) of [Cu(TC-4,4)]. Anal. Calcd for $C_{22}H_{26}N_4Cu$: C, 64.45; H, 6.39; N, 13.66. Found: C, 64.21; H, 6.40; N, 13.56. Electronic spectra, λ_{max} (nm) (ϵ (M^{-1} cm^{-1})): 912 (1220), 600 (sh), 462 (sh), 451 (16900), 404 (19700). Infrared (cm^{-1}): 2930 (w), 2900 (w), 2880 (w), 2850 (w), 2830 (w), 1590 (s), 1505 (s), 1470 (m), 1435 (s), 1395 (s), 1340 (m), 1270 (s), 1230 (s), 1085 (m), 990 (m), 970 (m), 940 (m), 920 (m), 890 (m), 860 (m), 725 (s).

[Cu(TC-4,5)]. A 3-mL ethanolic solution of 14 mg (0.069 mmol) of $Cu(OAc)_2 \cdot H_2O$ was added to a yellow solution of 25 mg of $H_2(TC-4,5)$ (0.070 mmol) dissolved in 10 mL of CH_2Cl_2. The resulting brown solution was warmed to remove the methylene chloride, yielding flakes with a metallic luster. Recrystallization from $CH_2Cl_2/EtOH$ produced 13 mg (44%) of [Cu(TC-4,5)]. Anal. Calcd for $C_{23}H_{28}N_4Cu$: C, 65.15; H, 6.66; N, 13.21. Found: C, 64.96; H, 6.69; N, 13.21. Electronic spectra, λ_{max} (nm) (ϵ (M^{-1} cm^{-1})): 1215 (460), 960 (330), 625 (770), 463 (24000), 445 (22700), 395 (35000). Infrared (cm^{-1}): 2920 (m), 2860 (m), 1590 (s), 1505 (s), 1470 (s), 1445 (s), 1420 (s), 1395 (s), 1375 (m), 1342 (m), 1280 (s), 1240 (s), 730 (s).

[Cu(TC-5,5)]. To a 10-mL CH_2Cl_2 solution of 25 mg (0.066 mmol) of $H_2(TC-5,5)$ was added 13 mg (0.065 mmol) of $Cu(OAc)_2 \cdot H_2O$ in 3 mL of EtOH. A dark brown microcrystalline solid was recovered following the removal of solvents at reduced pressure. [Cu(TC-5,5)] was recrystallized from CH_2Cl_2/n-heptane to yield 10 mg (35%). Owing to the small amounts of material handled in this synthesis, elemental analyses could not be performed. The composition was established by X-ray crystallography (vide infra). Electronic spectra, λ_{max} (nm) (ϵ (M^{-1} cm^{-1})): 1715 (br), 750 (sh), 613 (1150), 480 (18000), 450 (sh), 390

(25000). Infrared (cm^{-1}): 2920 (m), 2910 (m), 2900 (m), 2860 (m), 1590 (s), 1505 (s), 1435 (s), 1415 (s), 1400 (m), 1275 (s), 1235 (s), 1110 (m), 730 (s).

Electron Spin Resonance Spectroscopy. ESR spectra were recorded at 77 K and at room temperature on a Varian E-line spectrometer operating between 9.1 and 9.6 GHz. Frozen-solution spectra of all four complexes were recorded in 1:1 CH_2Cl_2/toluene glasses and were calibrated by using the naturally occurring Mn^{2+} impurity in SrO.[5] The spectra of the symmetric complexes [Cu(TC-n,n')], $n = n' = 3, 4$, or 5, were axially symmetric whereas that of [Cu(TC-4,5)] exhibited significant rhombic character. The hyperfine coupling constants $A_{\parallel}$ (A_z) were measured directly from glass spectra. Values for $A_{\perp}$ were obtained by using eq 1, where A_0 is the copper hyperfine coupling constant in the

$$A_0 = \frac{1}{3}A_{\parallel} + \frac{2}{3}A_{\perp} \tag{1}$$

isotropic spectrum, obtained in fluid solution at room temperature, and the parallel and perpendicular components are denoted as $A_{\parallel}$ and $A_{\perp}$, respectively. The $g_{\parallel}$ values were calculated from the resonant field frequencies of the absorbances in the parallel region by using eq 2 and 3, where $H_{\parallel}$ is the value of the magnetic field at $g_{\parallel}$, H_I is the value of

$$H_{\parallel} = H_I - A_{\parallel}(m_I) \tag{2}$$

$$g_{\parallel} = \frac{h\nu}{\beta H_{\parallel}} \tag{3}$$

the resonant field for a given m_I component, $\pm^1/_2$ and $\pm^3/_2$. The remaining terms in eq 3 are β, the Bohr magneton, h, Planck's constant, and ν, the microwave frequency. Values for $g_{\perp}$ of the axial spectra were obtained in a manner analogous to that used for the $A_{\perp}$ components. The g values in the perpendicular region of the [Cu(TC-4,5)] spectrum were obtained from the fitting procedure outlined below. We emphasize the ambiguity in assigning the x and y components of the [Cu(TC-4,5)] spectrum owing to the lack of single-crystal data.

The validity of these assignments was verified by spectral simulations carried out on a VAX 11/780 computer using the Fortran program POWDER.[6] In these calculations, g and A parameters were varied to optimize agreement between the observed and calculated resonant field positions. Line broadening was also accounted for in the simulation by employing Gaussian line shapes. Contributions from ligand superhyperfine interactions were not included.

Magnetic Susceptibility Measurements. Magnetic measurements were recorded on crystalline samples of each complex. Weights of the samples ranged from 3 to 7 mg. An SHE Corp. SQUID variable-temperature susceptometer was used to obtain the data. All measurements were made between 8 and 300 K at a magnetic field strength of 25 kG in an Al–Si alloy bucket. Diamagnetic corrections for the ligands were obtained by measuring the susceptibility of $H_2(TC-6,6)$, -253×10^{-6} cgsu mol^{-1}, and subtracting the appropriate values of Pascal's constants[7] for hydrogen atoms and methylene groups. Molar susceptibilities were fit by least-squares methods[2] to the Curie–Weiss law (4).

$$\chi_M = \frac{C}{T - \theta} + N\alpha \tag{4}$$

X-ray Structural Work. Table I summarizes the details of data collection, reduction, and refinement; typical procedures in our laboratory are further described in ref 8. All data were collected on an Enraf-Nonius CAD-4F diffractometer by using monochromatized Mo Kα (λ 0.7107 Å) radiation and $\theta/2\theta$ scans. Unit cell parameters were refined by using the setting angles of 25 reflections having $2\theta > 25°$. Standard reflections monitored showed no crystal decay.

[Cu(TC-3,3)]. Single crystals were obtained by slow evaporation of a $CH_2Cl_2/EtOH$ solution. A dark brown needle bounded by (100) and ($\bar{1}$00), 0.075 mm apart, (010) and (0$\bar{1}$0), 0.33 mm apart, and (001) and (00$\bar{1}$), 0.075 mm apart was chosen for the diffraction study. Open-counter ω-scans of low-angle reflections revealed broad ($\Delta\omega_{1/2} = 0.36°$), structureless profiles. From the systematic absences the space group was chosen to be $P2_1/n$ (C_{2h}^5, No. 14).[9a] The structure was solved by

(3) (a) Gerlach, D. H.; Holm, R. H. *Inorg. Chem.* **1970**, *9*, 588. (b) Holm, R. H.; O'Connor, M. J. *Prog. Inorg. Chem.* **1971**, *14*, 241.

(4) For recent reviews, cf.: (a) Henrick, K.; Tasker, P. A.; Lindoy, L. F. *Prog. Inorg. Chem.* **1985**, *33*, 1. (b) Meade, T. J.; Busch, D. H. *Prog. Inorg. Chem.* **1985**, *33*, 59.

(5) Bolton, J. R.; Borg, D. C.; Swartz, H. M. In "Biological Applications of Electron Spin Resonance"; Swartz, H. M., Bolton, J. R., Borg, D. C., Eds.; Wiley-Interscience: New York, 1972; p 100.

(6) David, C.; Schläpfer, C. W.; Mohos, B.; Ammeter, J.; Gamp, E. *Comput. Phys. Commun.* **1981**, *21*, 385.

(7) Sellwood, P. W. "Magnetochemistry", 2nd revised ed.; Interscience: New York, 1956; p 93.

(8) Silverman, L. D.; Dewan, J. C.; Giandomenico, C.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 3379.

(9) "International Tables for Crystallography"; D. Reidel: Dordecht, Holland; 1983; Vol. A: (a) p 177; (b) p 176; (c) pp 560–1.

Table I. Experimental Details of the X-ray Diffraction Studies

	[Cu(TC-3,3)]	[Cu(TC-4,4)]	[Cu(TC-5,5)]
formula	$CuC_{20}H_{22}N_4$	$CuC_{22}H_{26}N_4$	$CuC_{24}H_{30}N_4$
fw	381.96	410.02	438.07
space group	$P2_1/n$	$P2_1/c$	$P6_522$
a, Å	9.933 (1)	11.178 (2)	11.044 (2)
b, Å	5.798 (1)	8.636 (1)	
c, Å	14.520 (2)	20.188 (8)	30.390 (3)
β, deg	91.82 (1)	90.39 (2)	
V, Å^3	835.8	1948.8	3210.1
Z	2	4	6
d_{calcd}, g/cm^3	1.518	1.397	1.359
d_{obsd},^{a} g/cm^3	1.49 (1)	1.395 (5)	1.363 (5)
temp, °C	25	25	26
no. of reflcns collcd	2035	5316	2089
data collcn range, deg	$3 \leqslant 2\theta \leqslant 55$ ($\pm h$,+k,+l)	$3 \leqslant 2\theta \leqslant 55$ ($\pm h$,+k,+l)	$3 \leqslant 2\theta \leqslant 50$ ($-h$,+k,+l; $k > |h|$)
no. of unique data	1470	4464	1560
no. of obsd data	1170	2657	766
μ(Mo Kα), cm^{-1}	13.2	11.3	10.4
trans coeff^b	0.79–0.84	0.83–0.89	
R_1^{c}	0.036	0.035	0.045
R_2^{d}	0.050	0.043	0.055
largest shift/esd, final cycle	0.001	0.001	0.003
largest peak, e/Å^3	0.6	0.33	0.35

^{a} By suspension in aqueous CsCl. ^{b} Applied by using the Wehe–Busing–Levy ORABS program. $^c R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $^d R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table II. Final Positional Parameters for [Cu(TC-3,3)]^a

atom	x	y	z
Cu	0.0000	0.0000	0.0000
N1	−0.0014 (2)	0.2514 (4)	0.08865 (15)
N2	0.1849 (2)	0.0993 (5)	−0.00980 (17)
C11	0.1114 (3)	0.3710 (5)	0.0974 (2)
C12	0.1206 (3)	0.5880 (6)	0.1418 (2)
C13	0.2300 (3)	0.7229 (6)	0.1678 (2)
C14	0.3666 (3)	0.6807 (6)	0.1594 (2)
C15	0.4229 (4)	0.4944 (6)	0.1176 (3)
C16	0.3623 (3)	0.3143 (6)	0.0692 (2)
C17	0.2246 (3)	0.2616 (5)	0.0491 (2)
C1	−0.1215 (3)	0.3227 (5)	0.1359 (2)
C2	−0.2154 (3)	0.1207 (6)	0.1527 (2)
C3	−0.2824 (3)	0.0176 (7)	0.0673 (3)

^{a} Numbers in parentheses are errors in the last significant digit(s).

standard Patterson and difference Fourier maps and refined by least-squares methods using SHELX-76.[10] Hydrogen atoms were fixed in calculated positions (C–H = 0.95 Å) and allowed to ride on the carbon atoms to which they were attached except for the hydrogen atoms bonded to the carbon atoms at the ends of the linker chain where the hydrogen atoms were allowed to refine. These hydrogen atoms refined to an average C–H distance of 0.94 (4) Å with a common thermal parameter of $U = 0.04$ (1) Å^2. Each group of hydrogen atoms was given a common isotropic temperature factor, which converged at $U = 0.052$ (5) Å^2 for the tropone ring hydrogen atoms and $U = 0.045$ (5) Å^2 for the methylene protons. Non-hydrogen atoms were refined anisotropically. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1.3116/[(\sigma^2(F_o) + 0.000625(F_o)^2]$. For groups of data sectioned according to parity group, $(\sin\theta)/\lambda$, $|F_o/F_{max}|^{1/2}$, $|h|$, $|k|$, and $|l|$, the average values of $w(|F_o| - |F_c|)^2$ showed good consistency, thus confirming the validity of the weighting scheme. Scattering factors for neutral atoms and corrections for anomalous dispersion were taken from ref 11. Hydrogen atom scattering factors were those of Stewart et al.[12] Final coordinates for the non-hydrogen atoms are given in Table II. Listings of anisotropic thermal parameters, hydrogen atom positional and thermal parameters, all bond lengths and angles, torsional angles of the polymethylene chain, and observed and calculated structure factors are available as supplementary material (Tables S1–S5).

[Cu(TC-4,4)]. Dark brown needles of [Cu(TC-4,4)] were grown at 4 °C from CH_2Cl_2/EtOH. The crystal selected for the diffraction ex-

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

(11) "International Tables for X-ray-Crystallography"; Kynock Press: Birmingham, England, 1974; Vol. IV, pp 99, 149.

(12) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

Table III. Final Positional Parameters for [Cu(TC-4,4)]^a

atom	x	y	z
Cu	0.14039 (4)	0.22464 (5)	0.19863 (2)
N11	0.0907 (3)	0.2125 (3)	0.10634 (13)
N12	−0.0298 (2)	0.1928 (3)	0.21328 (12)
N21	0.2129 (2)	0.1584 (3)	0.28078 (12)
N22	0.2864 (2)	0.3445 (3)	0.19494 (13)
C11	−0.0272 (3)	0.2019 (4)	0.09688 (16)
C12	−0.0820 (4)	0.2253 (5)	0.03429 (18)
C13	−0.2000 (4)	0.2137 (6)	0.0134 (2)
C14	−0.3007 (4)	0.1688 (6)	0.0467 (2)
C15	−0.3055 (4)	0.1258 (5)	0.1124 (2)
C16	−0.2156 (3)	0.1286 (4)	0.16029 (18)
C17	−0.0944 (3)	0.1747 (4)	0.15879 (16)
C21	0.3142 (3)	0.2243 (4)	0.29821 (15)
C22	0.3679 (3)	0.2052 (4)	0.36141 (17)
C23	0.4769 (3)	0.2542 (4)	0.38705 (19)
C24	0.5666 (3)	0.3377 (5)	0.3584 (2)
C25	0.5668 (3)	0.3952 (5)	0.2943 (2)
C26	0.4794 (3)	0.3897 (4)	0.2453 (2)
C27	0.3639 (3)	0.3246 (4)	0.24425 (16)
C1	0.1677 (3)	0.2264 (5)	0.04736 (16)
C2	0.2997 (4)	0.2041 (5)	0.06348 (18)
C3	0.3681 (3)	0.3507 (5)	0.08166 (19)
C4	0.3115 (3)	0.4418 (4)	0.13773 (17)
C1A	0.1460 (3)	0.0578 (4)	0.32579 (16)
C2A	0.0644 (3)	0.1497 (5)	0.37080 (16)
C3A	−0.0185 (3)	0.2611 (4)	0.33281 (16)
C4A	−0.0909 (3)	0.1890 (4)	0.27765 (16)

^{a} See footnote a, Table II.

periment was bounded by (101) and ($\bar{1}0\bar{1}$), 0.14 mm apart, (001) and (00$\bar{1}$), 0.10 mm apart, and (010) and (0$\bar{1}$0), 0.52 mm apart. Crystal quality was checked by open-counter ω-scans of several strong low-angle reflections. The average width at half-height, $\Delta\bar{\omega}_{1/2}$, was 0.25°, and no unusual structure was observed in any of the traces. The structure was solved by introducing the copper atom at the known coordinate positions of nickel in the structure of the isomorphous [Ni(TC-4,4)] complex, space group $P2_1/c$ (C_{2h}^5, No. 14),[9b] for phasing and locating the other non-hydrogen atoms by difference Fourier techniques. Aromatic and aliphatic hydrogen atoms were treated in the same manner as those in [Cu(TC-3,3)] (vide supra) with thermal parameters converging at $U = 0.054$ (3) Å^2 for the aromatic protons and $U = 0.050$ (3) Å^2 for the methylene hydrogens. Anisotropic temperature factors were used for all non-hydrogen atoms. Other details of the structure factor calculation and least-squares refinement were identical with those mentioned above, with $w = 1.0/[\sigma^2(F_o) + 0.000625(F_o)^2]$. Table III lists the positional parameters for all non-hydrogen atoms. Their temperature factors, hydrogen atom positional and thermal parameters, interatomic distances and angles, linker chain torsional angles, and observed and calculated

Table IV. Final Positional Parameters for [Cu(TC-5,5)][a]

atom	x	y	z
Cu	0.58849 (8)	1.17699 (17)	0.7500
N1	0.5527 (8)	0.3325 (9)	0.7574 (2)
N2	0.4380 (7)	0.0224 (9)	0.7169 (2)
C11	0.6662 (10)	0.4599 (11)	0.7570 (3)
C12	0.6637 (12)	0.5818 (14)	0.7703 (3)
C13	0.7580 (13)	0.7193 (13)	0.7688 (3)
C14	0.8906 (9)	1.7811 (18)	0.7500
C21	0.4133 (9)	0.8998 (12)	0.7294 (3)
C22	0.3320 (9)	0.7758 (11)	0.7041 (3)
C23	0.2795 (10)	0.6353 (12)	0.7127 (4)
C24	0.2849 (9)	0.5698 (18)	0.7500
C1	0.4193 (11)	0.3201 (12)	0.7684 (3)
C2	0.2903 (11)	0.1784 (12)	0.7567 (4)
C3	0.2552 (11)	0.1676 (12)	0.7082 (5)
C4	0.3580 (11)	0.1652 (12)	0.6763 (3)
C5	0.3716 (10)	0.0382 (10)	0.6775 (3)

[a] See footnote a, Table II.
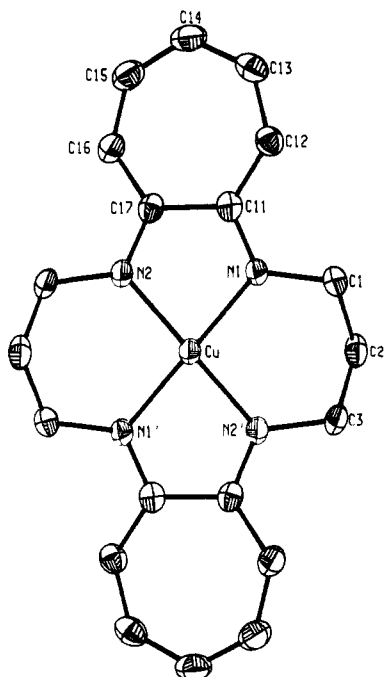
Figure 1. Structure of [Cu(TC-3,3)] showing the atom-labeling scheme and 40% probability thermal ellipsoids. Primed and unprimed atoms are related by a crystallographically required inversion center. Hydrogen atoms are omitted.
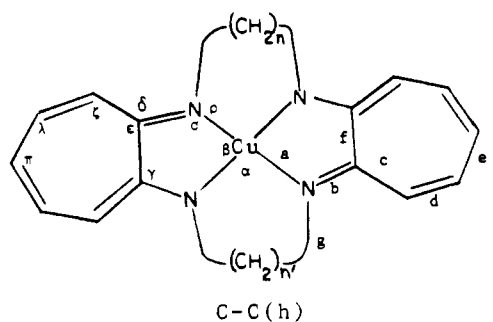

Figure 2. Structure of [Cu(TC-4,4)] showing the atom-labeling scheme and 40% probability thermal ellipsoids, but omitting hydrogens.

Figure 3. Structure of [Cu(TC-5,5)] showing the atom labels and 40% probability thermal ellipsoids and omitting hydrogen atoms. Primed atoms are generated by a crystallographically required C_2 axis.

structure factors are listed in Tables S6–S10, respectively, in the supplementary material.

[Cu(TC-5,5)]. Hexagonal rods of this complex were harvested from CH_2Cl_2/heptane solutions, and a fragment of dimensions 0.35 mm × 0.25 mm × 0.25 mm was chosen for data collection. Open-counter ω-scans revealed sharp peaks with $\Delta\bar{\omega}_{1/2} \sim 0.18°$. The structure of [Cu(TC-5,5)] proved to be enantiomorphous to that of the nickel(II) analogue, crystallizing in space group $P6_522$ (D_6^3, No. 179).[9c] Initial phasing was accomplished in the same manner as for [Cu(TC-4,4)]. The positions of the remaining non-hydrogen atoms were taken from subsequent structure factor calculations and difference Fourier maps. Refinement, however, was not performed until the positions of non-hydrogen atoms were located, and these were refined anisotropically.[10] Hydrogen atoms in general positions were allowed to ride upon their respective carbon atoms at a fixed C–H distance of 0.95 Å. Two of the tropone hydrogen atoms, on the outermost carbons of each ring, lie on a crystallographic 2-fold axis. These atoms were placed at special positions x, $2x$, $^3/_4$ as required by space group symmetry and fixed at 0.95 Å from their respective carbon atoms. These atoms were refined in this configuration while their isotropic temperature factors converged at $U = 0.05$ (4) Å². The thermal parameters of the remaining hydrogen atoms of the tropone ring settled at $U = 0.13$ (2) Å² while the methylene hydrogen atoms converged with $U = 0.09$ (1) Å². Weights were assigned the function $w = 1.660/[\sigma^2(F_o) + 0.000625(F_o)^2]$. Refining the structure in $P6_122$ gave an R_1 value of 0.050, confirming the original choice of

space group enantiomorph (cf. Table I). Table IV reports non-hydrogen atomic coordinates. Tables S11–S15 (supplementary material) list, respectively, anisotropic thermal parameters, hydrogen atom parameters, interatomic distances and angles, torsional angles for the pentamethylene linker chains, and observed and calculated structure factors.

Results

Description of the Structures. The molecular structures of [Cu(TC-3,3)], [Cu(TC-4,4)], and [Cu(TC-5,5)] are depicted in Figures 1–3, respectively. Crystallographic symmetry constrains [Cu(TC-3,3)] to have a planar coordination environment, giving rise to a dihedral angle (θ) between the two CuN_2 planes of the 5-membered chelate rings of exactly 0°. As the number of atoms in the linker chains increases to 4 and 5, θ also enlarges to 36.6 and 61.3°, respectively (Table V). This increase reflects a progressive distortion from planar toward pseudotetrahedral symmetry. A crystallographically required 2-fold symmetry axis passes through atoms C14, Cu, and C24 of [Cu(TC-5,5)], relating the halves of the molecule. Table V summarizes average structural parameters for all three compounds. No close nonbonded contacts were observed in any of the three crystal structures.

Electron Spin Resonance Spectra. Figure 4 displays the observed and simulated frozen-solution ESR spectra of [Cu(TC-3,3)], [Cu(TC-4,4)], [Cu(TC-4,5)], and [Cu(TC-5,5)]. Table VI lists the spectral parameters derived from the simulations. Inspection of these values reveals that, as the tetrahedral distortion

Table V. Summary of Structural Information for the Copper(II) Tropocoronands[a]

C–C(h)

	[Cu(TC-3,3)]	[Cu(TC-4,4)]	[Cu(TC-5,5)]
θ[b]	0	36.6	61.3
a	1.939 (6)	1.938 (7)	1.96 (1)
b	1.323 (2)	1.324 (8)	1.32 (2)
c	1.419 (4)	1.413 (3)	1.425 (5)
d	1.384 (2)	1.387 (2)	1.365 (15)
e	1.378 (11)	1.379 (10)	1.375 (15)
f	1.486 (4)	1.491 (10)	1.48 (1)
g	1.460 (5)	1.469 (8)	1.455 (5)
h	1.517 (5)	1.521 (9)	1.51 (2)
σ	115.6 (2)	115.8 (1.2)	114.6 (8)
α	98.5 (1)	103.3 (1)	111.5 (4)
ρ	123.3 (1)	123.5 (3.4)[c]	125.4 (4)
β	81.5 (1)	81.6 (7)	81.7 (6)
γ	112.9 (4)	112.9 (8)	113.9 (6)
δ	123.5 (1)	123.0 (5)	123.1 (1)
ϵ	123.6 (3)	124.1 (3)	123.0 (8)
ζ	131.8 (1)	132.0 (4)	133.5 (5)
λ	129.9 (2)	130.2 (6)	128.5 (1.5)
π	126.4 (3)	126.0 (1)	128 (3)

[a] Bond lengths are in angstroms and interbond angles are in degrees. Standard deviations are computed as $[(\sum x^2 - n\bar{x}^2)/n]^{1/2}$. [b] Dihedral angles between two CuN_2 planes as defined in the text. [c] Mean value of two disparate sets.

Table VI. ESR Spectral Parameters for the Copper(II) Tropocoronands[a]

complex	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$, cm^{-1} × 10^4	g_o	A_o, G
[Cu(TC-3,3)]	2.147	2.075	217.5	2.082	115.4
[Cu(TC-4,4)]	2.155	2.083	188	2.092	92.1
[Cu(TC-4,5)][b]	2.185	2.058	159	2.093	77.0
		2.038			
[Cu(TC-5,5)]	2.219	2.062	142	2.114	59.8

[a] Recorded at 77 K in toluene/methylene chloride (50:50). [b] Displays a rhombic spectrum. The two values reported for g are unassigned g_x and g_y components.

parameter θ increases (vide supra), $g_{\parallel}$ increases and $A_{\parallel}$ decreases. Both of these trends are monotonic and are correlated with the increase in length of the alkyl linker chains of the tropocoronand ligand system. Ligand superhyperfine coupling is observed in all the experimental spectra, decreasing with increasing θ.

Magnetic Susceptibility Results. All four copper(II) tropocoronands studied here obey the Curie–Weiss law, eq 4. Least-squares fitting of the molar magnetic susceptibilities over the temperature range $5 \leqslant T \leqslant 300$ K resulted in excellent agreement between the observed and calculated values. From the Curie constants the effective magnetic moments were computed and found to lie in the range 1.77–1.80 μ_B. Tables S16–S19 (supplementary material) list the observed and calculated χ values for [Cu(TC-n,n')] complexes, n,n' = 3,3, 4,4, 4,5, and 5,5, respectively.

Discussion

Synthesis. The synthetic procedures employed here provide excellent to satisfactory yields of mononuclear copper(II) tropocoronands. As the length of the linker chain increases, the yields decrease. One possible explanation is that binuclear copper(II) tropocoronands, such as the known[13] compound [Cu$_2$(O$_2$C-
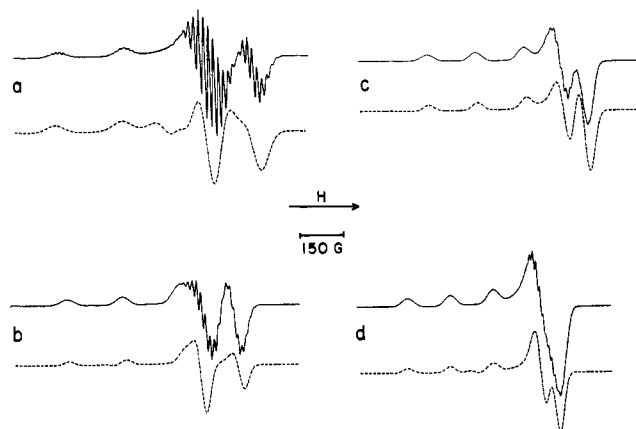
Figure 4. Observed (solid lines) and calculated (dashed lines) frozen-solution (77 K, methylene chloride/toluene) ESR spectra: (a) [Cu(TC-3,3)]; (b) [Cu(TC-4,4)]; (c) [Cu(TC-4,5)]; (d) [Cu(TC-5,5)]. Instrument settings: microwave frequency, 9.180 GHz; modulation frequency, 100 kHz; receiver gain, 2000; modulation amplitude, 8 G.
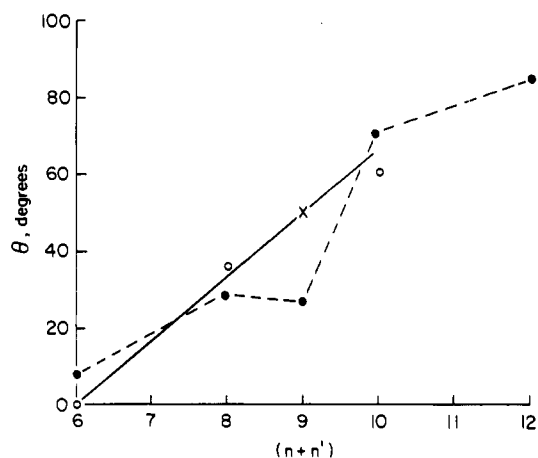
Figure 5. Plot showing the variation of the twist angle θ (see text) with the total number ($n + n'$) of methylene groups in the linker chains of the [M(TC-n,n')] complexes: M = Cu(open circles, solid line); M = Ni (closed circles, dashed line). The symbol × denotes the predicted θ value for [Cu(TC-4,5)].

CH$_3$)(OCH$_3$)(TC-6,6)], form and diminish the amount of mononuclear products obtained. The use of solvents and cupric salts that would not provide good bridging ligands might circumvent this problem, but we have not yet investigated these alternatives.

Stereochemistry of Mononuclear Copper(II) Tropocoronands. The crystal structure of [Cu(TC-3,3)] provides a good starting point for discussion since the copper and four nitrogen atoms are crystallographically constrained to be planar. The angle θ between the two N–Cu–N planes of the 5-membered chelate rings is therefore rigorously 0°. As shown in Figure 5, θ increases almost linearly as a function of ($n + n'$) for the [Cu(TC-n,n')] complexes. This result contrasts strikingly with corresponding data (Figure 5) for the nickel(II) tropocoronands, where a change in spin state from $S = 0$ to $S = 1$ accompanies the planar-to-tetrahedral transition.[2] Mononuclear copper(II) complexes have the same spin state ($S = {}^1/_2$) irrespective of geometry, and therefore the distortion observed in the copper(II) tropocoronands must be steric in origin. Unfortunately, the asymmetric [Cu(TC-4,5)] complex crystallizes as very thin flakes, and X-ray quality crystals were not obtained. Its geometry is expected to be intermediate between those of [Cu(TC-4,4)] and [Cu(TC-5,5)], and from Figure 5 we estimate its θ value to be $\sim$50°.

The steric effect of the tropocoronands upon the geometry of the copper(II) center results from packing an increasing number

(13) (a) Davis, W. M.; Lippard, S. J. *Inorg. Chem.* **1985**, *24*, 3688. (b) Villacorta, G. M.; Gibson, D.; Williams, I. D.; Lippard, S. J. *J. Am. Chem. Soc.*, in press.

of methylene groups between the (α, ω) methylene carbon atoms attached to the iminato nitrogen atoms. In [Cu(TC-3,3)], the distance between these carbon atoms (C1 and C3; Figure 1) is 2.60 Å, increasing to 3.056 Å (average of two values) and 4.00 Å, respectively, in [Cu(TC-4,4)] and [Cu(TC-5,5)]. The increase observed for the latter two compounds is the result primarily of the planar-to-tetrahedral conversion, since the Cu–N bond lengths (parameter a in Table V) remain relatively constant. Molecular mechanics calculations using MM-2[14,15] were previously used to demonstrate that the sources of steric strain during the planar-to-tetrahedral conversion are the H–H van der Waals, bending, and torsional forces between adjacent methylene groups in the linker chains as n increases from 3 to 6.[2] Similar results were obtained for the copper(II) tropocoronands. Energy minimizations were performed by fixing the α,ω-end carbon atoms at the crystallographically determined distances for [Cu(TC-4,4)] and [Cu(TC-5,5)] and then comparing the results for identical calculations in which the distances were fixed at 2.6 Å, the value for an idealized planar molecule (θ = 0°), as observed for [Cu(TC-3,3)]. In both cases the former calculations converged nicely and gave C–C–C–C torsion angles in excellent agreement with the crystallographic values. For [Cu(TC-4,4)] the observed and calculated angles were 53.9 and 54.7°, respectively, and for [Cu(TC-5,5)] the angles were 66.4 and 68.3°, observed, and 69.0 and 68.9°, calculated. The calculations in which the α,ω-carbon pair was fixed at 2.6 Å did not converge and gave significantly higher energies. As with the nickel complexes, the van der Waals, bending, and torsional interactions were most severe.

In all three Cu(II) tropocoronand complexes the C–N–C–C torsion angles to the linker chain carbon atoms have values close to those expected[16] for atoms connected by sp²–sp³ bonds, 30, 90, or 150°. The methylene linker chain torsion angles also adopt nearly ideal geometry with N–C–C–C and C–C–C–C values lying near the potential energy minimum for saturated alkanes, ~60°. Since, unlike the nickel(II) tropocoronands, the copper(II) complexes relieve the steric constraint mainly by increasing θ, the ligands can assume their preferred geometry. In a related study[17] of tetrahedral distortions produced by steric constraints of tetraaza macrocyclic ligands on copper(II), the tetrahedral angle θ was found to vary from 11.5 to 36.6° as a result of the placement of N=C bonds (cis vs. trans) in the 18-membered ring. Other examples of tetrahedrally distorted cupric complexes are discussed in that report.

Other geometric features of the copper(II) tropocoronands are summarized in Table V. The internal ligand geometry agrees well with that reported previously for the nickel(II) analogues.[2] As in the series of nickel(II) complexes, increasing the number of atoms in the linker chains expands not only θ but also α, the N–Cu–N angle, and leads to a small expansion in the Cu–N bond lengths (parameter a, Table V).

Electronic Spectroscopy. All four complexes exhibit intense brown colors in aprotic solvents. These colors are the result of highly probable ($\epsilon \sim 10^4$ M^{-1} cm^{-1}) transitions in the 400–450-nm range, which we tentatively assign as charge-transfer bands since they are absent in the spectra of the free ligands and their alkali metal salts. Bands approximately 2 orders of magnitude weaker are observed at longer wavelengths. These absorptions are assigned as Cu(II) d–d transitions. A strong correlation exists between the position of the lowest energy d–d band and the parameter θ for the series of complexes.[18] In particular, there is a steady decrease in energy with increasing tetrahedral distortion, [Cu(TC-3,3)] (θ = 0°, λ_{max} = 674 nm) > [Cu(TC-4,4)] (θ = 36.6°, λ_{max} = 912 nm) > [Cu(TC-4,5)] ($\theta_{est} \sim 50°$, λ_{max} = 1215 nm)

Table VII. Electronic Spectral Properties of the Copper(II) Tropocoronands[a]

[Cu(TC-3,3)]	[Cu(TC-4,4)]	[Cu(TC-4,5)]	[Cu(TC-5,5)]	assgnt[b]
407 (31 000)	404 (19 700)	395 (35 000)	390 (25 000)	CT
436 (18 450)	451 (16 900)	445 (22 700)	450 (sh)	CT
	462 (sh)	463 (24 000)	480 (18 000)	CT
564 (sh)	600 (sh)	625 (770)	613 (1150)	d–d
674 (278)	912 (1220)	960 (330)	750 (sh)	d–d
		1215 (460)	1715 (br)	d–d

[a] Absorption maxima are given in nm. Numbers in parentheses are molar extinction coefficients, M^{-1} cm^{-1}. [b] Key: CT, charge transfer; d–d, metal d-orbital internal transitions. For discussion, see text.

> [Cu(TC-5,5)] (θ = 61.3°, λ_{max} = 1712 nm). The occurrence of this trend indicates that the structures of these complexes in solution closely resemble those found in the solid state. Also apparent from the spectra is the resolution of more d–d transitions as the tetrahedral distortion increases (Table VII). A definitive assignment of these bands requires single-crystal polarized spectra. It is likely, however, that the assignments will parallel those made for analogous tetrahedrally distorted Cu^{II}N$_4$ chromophores.[19] Thus, for [Cu(TC-5,5)], the low-energy band would be $^2B_2 \rightarrow {}^2E$, the 750-nm band would be $^2B_2 \rightarrow {}^2B_1$, and the 613-nm band would be $^2B_2 \rightarrow {}^2A_1$.

Electron Spin Resonance Spectroscopy. The ESR spectra of copper(II) (d^9) complexes are characterized by two major features: first, $g_{\parallel} > g_{\perp}$, and second, the Cu ($I$ = $^3/_2$) hyperfine splitting in the parallel region is much greater than its perpendicular counterpart, the latter being unobservable in most cases. The present study is consistent with these expectations. Axially symmetric spectra are observed for three out of four of the Cu(II) tropocoronands, with [Cu(TC-4,5)] displaying significant rhombic character. The rhombicity of this, the most asymmetric, complex reflects the overall environment about the metal ion. The most notable feature in the ESR spectra of these complexes is the effect of tetrahedral distortion upon $A_{\parallel}$. A change of 66 cm^{-1} in $A_{\parallel}$ accompanies the increase in θ of 61.6° in moving from [Cu(TC-3,3)] to [Cu(TC-5,5)]. This phenomenon has its origins in orbital mixing. In D_{2d} symmetry the ground-state d$_{xy}$ orbital belongs to the same irreducible representation (B$_2$) as the p$_z$ orbital. The latter can therefore mix with the d$_{xy}$ orbital, attenuating $A_{\parallel}$.[20] A semiquantitative analysis of the isotropic spectra of these complexes reveals a relationship between the Fermi contact parameter and the attenuation of $A_{\parallel}$. Expressions 5 and 6 are

$$A_{\parallel} = P\left[-\kappa - \frac{4\alpha^2}{7} + (g_{\parallel} - 2.0023) + \frac{3(g_{\perp} - 2.0023)}{7}\right] \quad (5)$$

$$A_{\perp} = P\left[-\kappa + \frac{2\alpha^2}{7} + \frac{11(g_{\perp} - 2.0023)}{14}\right] \quad (6)$$

simplified theoretical equations that describe the parallel and perpendicular nuclear hyperfine coupling in Cu(II) complexes where the unpaired electron resides in the d$_{x^2-y^2}$ orbital.[21] In these equations, P is the nephelauxetic parameter, κ is the Fermi contact term, and α^2 describes the dipole–dipole interaction between the unpaired electron and the Cu nucleus. Combination of these expressions leads to a simple equation (eq 7) containing only the

$$\kappa = g_o - (A_o/P) - 2.0023 \quad (7)$$

isotropic ESR parameters, g_o and A_o, the Fermi contact parameter, κ, and the nephelauxetic term, P. The value for P was chosen from the literature[22] for Cu(II) complexes of ligands in which all

(14) Molecular mechanics calculations were performed on a VAX 11/780 computer using the program MODEL by W. C. Still, Columbia University. This program employs MM-2, a conformational analysis program by Allinger.[15]
(15) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.
(16) Bailey, M. F.; Maxwell, I. E. *J. Chem. Soc., Dalton Trans.* **1972**, 938.
(17) Timmons, J. H.; Rudolf, P.; Martell, A. E.; Martin, J. W. L.; Clearfield, A. *Inorg. Chem.* **1980**, *19*, 2331.
(18) Gouge, E. M.; Geldard, J. F.; Sinn, E. *Inorg. Chem.* **1980**, *19*, 3356.

(19) (a) Solomon, E. I.; Hare, J. W.; Dooley, D. M.; Dawson, J. H.; Stephens, P. J.; Gray, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 168. (b) Gonteron, J.; Jeannin, S.; Jeannin, Y.; Livage, J.; Sanchez, C. *Inorg. Chem.* **1984**, *23*, 3387 and references cited therein.
(20) Bates, C. A.; Moore, W. S.; Standley, K. J.; Stevens, W. J. *Proc. Phys. Soc., London* **1962**, *79*, 73.
(21) Reference 5, pp 416–419.

donors are imine nitrogens and was held constant at 0.0388 cm^{-1} for each complex. This assumption is based upon crystallographic evidence that the bond lengths remain relatively constant throughout the series. Thus, taking the sign of the hyperfine coupling constant to be negative,[21] the calculated Fermi contact parameters are as follows: [Cu(TC-3,3)], 0.369; [Cu(TC-4,4)], 0.322; [Cu(TC-4,5)], 0.285; [Cu(TC-5,5)], 0.264. From these values α^2 was calculated by eq 5 to be ~0.6. It is therefore apparent that the major factor involved in the attentuation of $A_{\parallel}$ in the Cu(II) tropocoronands is the Fermi contact interaction.

Ligand superhyperfine splitting is observed in the parallel and perpendicular region of the ESR spectrum of [Cu(TC-3,3)] and in the perpendicular region for the remaining complexes. In all cases, there are more than the expected nine (^{14}N ($I = 1$), 1), 2NI + 1) ligand superhyperfine lines on $g_{\perp}$, possibly due to rhombic character in the spectra or to superhyperfine coupling from the hydrogen nuclei of the tropocoronand ligands.[23] Nine lines are observed in the parallel region of the [Cu(TC-3,3)] spectrum. The values of the superhyperfine coupling constants in all of the spectra fall in the 10–15-G range consistent with literature values for copper(II)–nitrogen donor ligand interactions.

Magnetic Susceptibility Measurements. The effective magnetic moments of the Cu(II) tropocoronands are independent of the extent of tetrahedral distortion. Since tetrahedral, d^9 metal complexes have a $^2T_2$ ground state, spin–orbit coupling is expected to contribute to the magnetic susceptibilities of such complexes, raising the value of the effective magnetic moments. The observed magnetic moments of the Cu(II) tropocoronand complexes, however, display little deviation from the spin-only value of 1.732 μ_B. This observation indicates that, although θ is as large as 61.3°, the orbital contribution to the magnetic moments is efficiently quenched by the ligands.

Concluding Remarks. The synthesis and structural characterization of the four mononuclear copper(II) tropocoronands has sharpened our understanding of the steric forces transmitted to the metal center. By packing an increasing number of methylene groups into the linker chains, the ligands distort the Cu(II) coordination geometry from planar toward tetrahedral along a D_2 (vs. a D_{2d}) symmetry path,[24] considering only the CuN$_4$ atom set. Unlike the corresponding nickel(II) tropocoronands,[2] this geometric transition is a smooth one and produces a corresponding set of changes in the optical and ESR spectroscopic properties of the copper(II) complexes. When the number of linker chain atoms becomes 6 or larger, the tropocoronand ligands become binucleating. The synthesis and properties of these interesting binuclear tropocoronand complexes are the subjects of separate reports.[13]

Registry No. [Cu(TC-3,3)], 98394-04-8; [Cu(TC-4,4)], 98394-05-9; [Cu(TC-4,5)], 98394-06-0; [Cu(TC-5,5)], 98394-07-1.

Supplementary Material Available: Tables S1–S19, reporting heavy-atom thermal parameters, hydrogen atom positional and thermal parameters, bond lengths and angles, torsional angles, observed and calculated structure factors, and magnetic susceptibility data for the copper(II) tropocoronands (37 pages). Ordering information is given on any current masthead page.

(22) Maroney, M. J.; Norman, J. G., Jr.; Osborne, J. H. *Inorg. Chem.* **1984**, *23*, 2261.
(23) Nonaka, Y.; Jokii, J.; Kida, S. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 312.

(24) See discussion in: Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. "Orbital Interactions in Chemistry"; Wiley-Interscience: New York, 1985; p 304.

Contribution from the Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973, and Contribution No. 7144 from the Arthur Amos Noyes Laboratory, California Institute of Technology, Pasadena, California 91125

Kinetics and Mechanisms of Electron Transfer between Blue Copper Proteins and Electronically Excited Chromium and Ruthenium Polypyridine Complexes

BRUCE S. BRUNSCHWIG,[1] PATRICIA J. DeLAIVE,[2] ANN M. ENGLISH,[2,3] MICHEL GOLDBERG,[2] HARRY B. GRAY,*[2] STEPHEN L. MAYO,[2] and NORMAN SUTIN*[1]

The kinetics of the quenching of the long-lived excited states of CrL$_3^{3+}$ and RuL$_3^{2+}$ complexes (L is 1,10-phenanthroline and 2,2′-bipyridine or substituted derivatives) by the copper proteins plastocyanin, azurin, and stellacyanin have been studied in aqueous solution. The rate constants for quenching by the Cu(I) proteins approach a limiting value of ~10^6 s^{-1} at high protein concentration. The kinetic behavior for plastocyanin is discussed in terms of a model in which the metal complex binds at a remote site 10–12 Å from the copper center. The model allows for electron transfer both from this remote site and by attack of the metal complex adjacent to the copper center. The results show that at low protein concentration the adjacent pathway is about 10 times faster than the remote pathway. The rate constant for the intramolecular electron transfer from the remote site is consistent with the value expected on the basis of theoretical calculations.

Introduction

The use of inorganic complexes to study the electron-transfer reactions of metalloproteins has been exploited in a number of laboratories.[4–7] In recent years increasing use has been made

of electronically excited complexes.[8,9] The use of an oxidant (or reductant) that can be "instantaneously" generated by a laser pulse

(1) Brookhaven National Laboratory.
(2) California Institute of Technology.
(3) Present address: Department of Chemistry, Concordia University, Montreal, Quebec, Canada H3G 1M8.
(4) Sutin, N. *Nature (London)* **1961**, *190*, 438.

(5) (a) Wherland, S.; Gray, H. B. In "Biological Aspects of Inorganic Chemistry"; Addison, A. W., Cullen, W. R., Dolphin, D., James, B. R., Eds.; Wiley: New York, 1977; p 289, and references therein. (b) Cummins, D.; Gray, H. B. *J. Am. Chem. Soc.* **1977**, *99*, 5158. (c) McArdle, J. V.; Coyle, C. L.; Gray, H. B.; Yoneda, G. S.; Holwerda, R. A. *J. Am. Chem. Soc.* **1977**, *99*, 2483. (d) Holwerda, R. A.; Knaff, D. B.; Gray, H. B.; Clemmer, J. D.; Crowley, R.; Smith, J. M.; Mauk, A. G. *J. Am. Chem. Soc.* **1980**, *102*, 1142. (e) Mauk, A. G.; Scott, R. A.; Gray, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 4360.