Synthesis, Structure and Properties of Five-Coordinate Copper(II) Complexes of Pentadentate Ligands with Pyridyl Pendant Arms

Grant A. McLachlan, Gary D. Fallon, Raymond L. Martin, and Leone Spiccia*

Department of Chemistry, Monash University, Clayton, Victoria, 3168, Australia

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The syntheses and characterization of five-coordinate Cu(II) complexes of the pentadentate ligands trenimpy (4-[4-(2-pyridyl)-3-aza-3-butenyl]-1,4,7-triazaheptane), trenpy (4-[4-(2-pyridyl)-3-azabutyl]-1,4,7-triazaheptane) and dmptacn (1,4-bis(2-pyridylmethyl)-1,4,7-triazacyclononane) are described. X-ray diffraction studies have established the structures of [Cu(trenimpy)](ClO_4)$_2$ and [Cu(trenpy)](ClO_4)$_2$. [Cu(trenimpy)](ClO_4)$_2$ crystallizes in the monoclinic space group $P2_1/n$, with $a = 12.940(5)$Å, $b = 15.418(2)$ Å, $c = 9.853(3)$ Å, $\beta = 96.59(2)°$, and $Z = 4$. Refinement gave final R and R_w values of 0.066 and 0.070, respectively, for 2170 observed reflections. [Cu(trenpy)](ClO_4)$_2$ crystallizes in the monoclinic space group $P2_1$, with $a = 16.367(2)$ Å, $b = 15.191(1)$ Å, $c = 8.132(1)$ Å, $\beta = 96.21(2)°$, and $Z = 4$. Refinement gave final R and R_w values of 0.065 and 0.063, respectively, for 2796 observed reflections. Two slightly different cations were present in the unit cell. The geometry of Cu(II) in the [Cu(trenimpy)]$^{2+}$ cation is close to square pyramidal while that of Cu(II) in [Cu(trenpy)]$^{2+}$ is intermediate between square pyramidal (SP) and trigonal bipyramidal (TBP). Visible spectra recorded in Nujol mulls were consistent with these geometries but the spectra recorded in various solvents indicated a shift in stereochemistry toward TBP for both complexes. This was not apparent in the case of [Cu(dmptacn)](ClO_4)$_2$ where the mull and solution spectra were very similar and indicated a geometry close to SP. Frozen solution ESR spectra indicate that the geometry is close to SP for all three complexes. Significant changes in stereochemistry are induced by changes in the environment around the cations. Cyclic voltammetry of the complexes in acetonitrile solution revealed a quasi-reversible redox wave, corresponding to the Cu(II)–Cu(I) couple, at −0.80, −0.94, and −0.81 V for [Cu(trenimpy)]$^{2+}$, [Cu(trenpy)]$^{2+}$, and [Cu(dmptacn)]$^{2+}$, respectively. Thus, some stabilization of the Cu(I) state results from the greater ability of trenimpy and dmptacn (cf. trenpy) to accept electron density from Cu(I).

Introduction

Investigations of the coordination chemistry of copper(II) continue to be stimulated by interest in developing models for copper proteins and in understanding the factors which give rise to the seemingly infinite variety of distortions from regular stereochemistry observed in Cu(II) complexes.[1] Five-coordinate Cu(II) complexes are quite common, but relatively few of these complexes have pentadentate ligands coordinated to Cu(II). However, the number of such complexes has grown considerably in recent years.[2–12] The stereochemistry adopted by these complexes ranges between square pyramidal (SP) and trigonal bipyramidal (TBP). Very few Cu(II) complexes with regular SP or TBP geometry are known with most adopting geometries that are intermediate between these extremes.[2]

This paper reports the structures and physicochemical properties of Cu(II) complexes of trenimpy (**1**, 4-[4-(2-pyridyl)-3-aza-3-butenyl]-1,4,7-triazaheptane), trenpy (**2**, 4-[4-(2-pyridyl)-3-azabutyl]-1,4,7-triazaheptane) and dmptacn (**3**, 1,4-bis(2-pyridylmethyl)-1,4,7-triazacyclononane), for which variations in stereochemistry are apparent in going from the solid state to solution. The trenimpy and trenpy ligands are bifurcated pentaaza ligands derived from tren and are closely related to trenen (**4**). Thus, the Cu(II) trenimpy and trenpy complexes might be anticipated to adopt a similar structure to [Cu(trenen)]Br_2[5] which shows the Cu(II) center to be five-coordinate, with distorted TBP geometry. Recently, the structures of Cu(II) complexes of dmptdacn (**5**)[8] and daptacn (**6**)[11] have been reported, both of which contain two pendant arm pentadentate ligands that are closely related to dmptacn. For both complexes, the geometry around the Cu(II) centers is close to regular SP with the two pendant-arm donors and the two tertiary amines forming the basal plane of the square pyramids.

Experimental Section

Materials and Reagents. All materials were of reagent grade unless indicated otherwise. Trenimpy, trenpy, and dmptacn were prepared according to published methods.[13]

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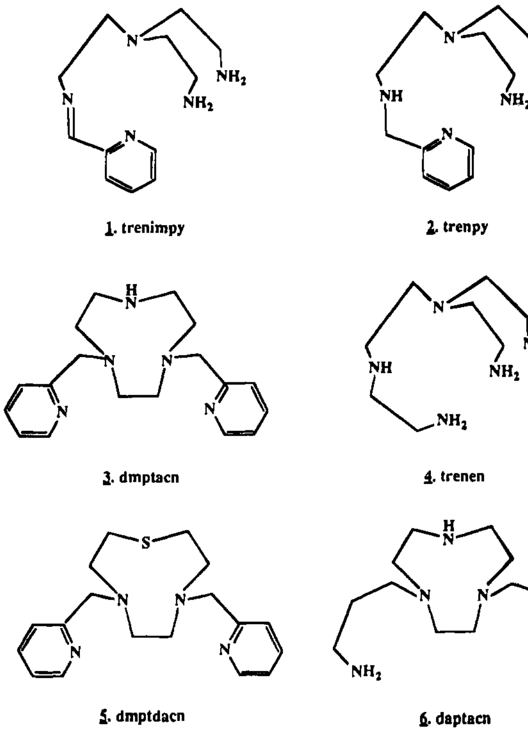
Scheme 1



1. trenimpy

2. trenpy

3. dmptacn

4. trenen

5. dmptdacn

6. daptacn

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 1600 FTIR spectrophotometer as KBr pellets. Electronic spectra were recorded on a Hitachi 150-20 or a Cary 3 spectrophotometer. Electron microprobe analyses were made with a Joel JSM-1 scanning electron microscope through an NEC X-ray detector and pulse processing system connected to a Packard multichannel analyzer. Solid samples were mounted on an aluminum planchette and covered with a very thin film of carbon by using a Balzer Union CED 010 carbon sputterer. Microanalysis were performed by Chemical and Micro-Analytical Services (CMAS) Melbourne, Australia.

Caution! *Although no problems were encountered in this work, transition metal perchlorates are potentially explosive. They should be prepared in small quantities and handled with care.*

Synthesis of [Cu(trenimpy)](ClO₄)₂ (1). To a solution of trenimpy (0.74 g, 3.16 mmol) in water (25 mL) was added $Cu(ClO_4)_2{\cdot}6H_2O$ (1.21 g, 3.16 mmol). Sodium perchlorate (2.0 g) was then added and the solution was stored overnight at 4 °C. A dark dark green precipitate was collected by filtration and washed with ethanol and ether (yield 1.49 g, 85%). Crystals suitable for single crystal X-ray analysis were grown by slow evaporation of an aqueous solution of the compound.

Characterization. Anal. Calcd for $[Cu(C_{12}N_5H_{21})](ClO_4)_2$: C, 28.9; H, 4.2; N, 14.1. Found: C, 28.9; H, 4.35; N, 14.2. *Electron microprobe*: Cu:Cl ratio 1:2. *IR spectrum* (KBr, cm^{-1}): 3369 s, 3326 m, 3280 m, 3205 s, 3121 m (NH's), 1668 m (C=N, imine), 1606 s, 1475 m, 1462 (pyridine ring), 1086 s, 625 s (ClO_4^-). *UV–visible spectrum*: Nujol mull, λ_{max}, 610 nm; solution, λ_{max}, nm (ϵ_{max}, $M^{-1}\ cm^{-1}$) H_2O 650 (149); CH_3CN 647 (162); DMF 653 (152). *Magnetic moment*: μ_{eff} (295 K) = 1.91 μ_B.

Table 1. Crystal Data for [Cu(trenimpy)]$(ClO_4)_2$ and [Cu(trenpy)]$(ClO_4)_2$[a]

	[Cu(trenimpy)]$(ClO_4)_2$	[Cu(trenpy)]$(ClO_4)_2$
color, habit	aqua, prismatic	royal blue, tabular
formula	$C_{12}H_{21}Cl_2CuN_5O_8$	$C_{12}H_{23}Cl_2CuN_5O_8$
M	497.8	499.8
a, Å	12.940(5)	16.367(2)
b, Å	15.418(2)	15.191(1)
c, Å	9.853(3)	8.132(1)
β, deg	96.59(2)	96.21(2)
V, Å^3	1953(1)	2010.0(4)
Z	4	4
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1$ (by successful refinement)
radiation, Å	1.5418 (Cu Kα)	0.7107 (Mo Kα)
$F(000)$	1020	1028
D_{meas}, g cm^{-3}	1.69(1)	1.66(1)
D_{calc}, g cm^{-3}	1.71	1.65
μ, cm^{-1}	46.1	14.0
R	0.066	0.065
R_w	0.070	0.063
ϱ, eÅ^{-3}	0.99	0.84

[a] Cell parameters were determined from 24 accurately centered reflections and were calculated by a standard Philips program. $R_w = \Sigma(|F_o - F_c|\omega^{1/2}/\Sigma|F_o|\omega^{1/2}$ and $\omega = [\sigma^2(F_o)]^{-1}$.

Synthesis of [Cu(trenpy)](ClO₄)₂ (2). To a solution of trenpy (0.75 g, 3.16 mmol) in methanol (25 mL) was added $Cu(ClO_4)_2{\cdot}6H_2O$ (1.21 g, 3.16 mmol) and the pH was adjusted to 7. The dark blue solution was diluted and adsorbed onto a cation exchange column (Dowex 50X-2). The compound was eluted with 1 M $NaClO_4$. The eluate was concentrated to half-volume and left standing overnight. The dark blue microcrystalline precipitate that had formed was collected and washed with ethanol (yield 0.90 g, 57%). Crystals suitable for single crystal X-ray analysis were grown from a DMF solution of the compound.

Characterization. *Anal.* Calcd for $[Cu(C_{12}N_5H_{23})](ClO_4)_2$: C, 28.8; H, 4.6; N, 14.0. Found: C, 29.0; H, 4.8; N, 13.8. *Electron microprobe*: Cu:Cl ratio 1:2. *IR spectrum* (KBr, cm^{-1}): 3368 s, 3296 m, 3231 s, 3126 s (NH's), 1611 m, 1477 m, 1447 m (pyridine ring), 1083 vs, 626 s (ClO_4^-). *UV–visible* spectrum; Nujol mull, λ_{max}, 648 nm; solution, λ_{max}, nm (ϵ_{max}, $M^{-1}\ cm^{-1}$) H_2O 723 (151); CH_3CN 724 (168); DMF 724 (145). *Magnetic moment*: μ_{eff} (295 K) = 1.88 μ_B.

Synthesis of [Cu(dmptacn)](ClO₄)₂ (3). A solution of dmptacn (0.83 g, 2.66 mmol) in methanol (40 mL) was added to a solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (1.02 g, 2.66 mmol) in methanol (20 mL) and the solution was stirred for 1 h. Sodium perchlorate (3 g) was then added and the solution was stored overnight at 4 °C. The blue precipitate that formed was filtered and washed with ethanol and ether (yield 1.17 g, 75%).

Characterization. *Anal.* Calcd for $[Cu(C_{18}H_{25}N_5)](ClO_4)_2$: C, 37.7; H, 4.4; N, 12.2. Found: C, 37.6; H, 4.7; N, 12.2. *Electron microprobe*: Cu:Cl ratio 1:2. *IR spectrum* (KBr, cm^{-1}): 3336 m (NH), 1612 m, 1489 m, 1447 m (pyridine ring), 1090 vs, 624 s (ClO_4^-). *UV–visible spectrum*: Nujol mull, λ_{max}, 600 nm; solution, λ_{max}, nm (ϵ_{max}, $M^{-1}\ cm^{-1}$) H_2O 610 (210); CH_3CN 613 (176); DMF 608 (182). *Magnetic moment*: μ_{eff} (295 K) = 1.86 μ_B.

Crystal Structure Determinations. Crystal data and refinement parameters for [Cu(trenimpy)]$(ClO_4)_2$ and [Cu(trenpy)]$(ClO_4)_2$ are given in Table 1. A representative aqua prismatic crystal of [Cu(trenimpy)]$(ClO_4)_2$ (**1**) (dimensions 0.16 × 0.21 × 0.28 mm) and royal blue tabular crystal of [Cu(trenpy)]$(ClO_4)_2$ (**2**) (dimensions 0.31 × 0.28 × 0.14 mm) were used for data collection. Intensity measurements were made on a Philips PW1100 diffractometer with graphite-monochromated Cu Kα radiation for **1** (with 6° < $2\theta \le 130°$, operating in a ω

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scan mode with a symmetric scan range of $\pm(0.75 \pm 0.10 \tan \theta)°$ in ω from the calculated Bragg scattering angle at a scan rate of 0.05 ° s^{-1}) and Mo Kα radiation for **2** (with $6° < 2\theta \leq 60°$, operating in a ω scan mode with a symmetric scan range of $\pm(0.90 \pm 0.15 \tan \theta)°$ in ω from the calculated Bragg scattering angle at a scan rate of 0.03° s^{-1}). A total of 3324 unique data were collected for **1** and 6067 unique data for **2** ($\pm h,+k,+l$). Of these 2170 (**1**) and 2796 (**2**) data were considered to be observed [$I \geq 3\sigma(I)$]. For both complexes, three standard reflections monitored every 4 h showed no significant variation in intensity over the collection period. Intensity data were corrected for Lorentz and polarization effects and were processed as described previously.[14] A face indexed numerical absorption correction was applied.[15] For **1**, the maximum and minimum transmission factors were, respectively 0.576 and 0.433 while the corresponding values for **2** were 0.811 and 0.678. The atomic scattering factors for neutral atoms were taken from ref 16 and were corrected for anomalous dispersion by using values from ref 16. The program used for least squares refinement was that due to Sheldrick.[15] The structures were solved by direct methods. Final refinement for **1** was by full-matrix least-squares employing anisotropic thermal parameters for all non-hydrogen atoms, and a single isotropic thermal parameter for hydrogen which refined to 0.075(7) Å^2—positioned in geometrically idealized positions: C−H 0.96 Å, N−H 0.90 Å. Final refinement for **2** was by full-matrix least-squares employing anisotropic thermal parameter for hydrogen—fixed at 0.08 Å^2—positioned in geometrically idealized positions. For **1**, final atomic parameters, and selected bond lengths and bond angles are given in Tables 2 and 3. Figure 1 shows the molecular structure of the cation and atomic labeling scheme. For **2**, final atomic parameters, bond lengths and bond angles are given in Tables 4 and 5. Figure 2 shows the molecular structure of both cations and atomic labeling scheme.

Results and Discussion

Synthesis of Copper(II) Complexes. The preparation of [Cu(trenimpy)]$(ClO_4)_2$, [Cu(trenpy)]$(ClO_4)_2$, and [Cu(dmptacn)]$(ClO_4)_2$ has been achieved by reacting the free ligand with Cu$(ClO_4)_2 \cdot 6H_2O$:

$$\mathrm{Cu(ClO_4)_2{\cdot}6H_2O + L \rightarrow [CuL](ClO_4)_2}$$

$$\mathrm{L = trenimpy,\ trenpy,\ dmptacn}$$

Elemental analyses of the three compounds were consistent with the composition [CuL]$(ClO_4)_2$. In each case, electron microprobe gave a Cu:Cl ratio of 1:2. The infrared spectrum of the complexes showed bands due to skeletal vibrations of the pyridine ring in the 1400−1600 cm^{-1} region. The [Cu(trenimpy)]$(ClO_4)_2$ complex also exhibits a band at 1668 cm^{-1}, characteristic of the imine C=N stretch, which is not present in the other complexes. The trenimpy and trenpy complexes show more bands in the 3000−3500 cm^{-1} region due to NH vibrations than the dmptacn complex which has one such band at 3360 cm^{-1}. The crystal structures of the trenimpy and trenpy complexes are discussed below. Despite several attempts, crystals of [Cu(dmptacn)]$(ClO_4)_2$ suitable for single-crystal X-ray diffraction could not be obtained.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for [Cu(trenimpy)]$(ClO_4)_2$

atom	*x*	*y*	*z*	*U*(eq) (Å^2)[a]
Cu	0.03513(8)	0.24377(7)	0.22921(10)	0.0413(4)
Cl(1)	−0.2380(2)	0.4401(2)	0.3540(2)	0.0673(9)
Cl(2)	0.3539(2)	0.2903(1)	0.3005(2)	0.0533(7)
C(1)	−0.1582(8)	0.1891(7)	0.3190(11)	0.075(4)
C(2)	−0.0869(8)	0.1219(7)	0.3704(10)	0.075(4)
C(3)	0.0858(10)	0.0744(6)	0.3222(12)	0.087(5)
C(4)	0.0716(10)	0.0682(6)	0.1700(12)	0.091(5)
C(5)	0.0692(8)	0.1817(7)	0.5042(9)	0.072(4)
C(6)	0.0399(8)	0.2760(7)	0.5213(8)	0.074(4)
C(7)	0.0791(7)	0.3959(6)	0.3747(9)	0.060(4)
C(8)	0.0925(6)	0.4208(5)	0.2348(9)	0.052(3)
C(9)	0.1215(7)	0.5023(6)	0.1969(11)	0.065(4)
C(10)	0.1380(7)	0.5166(7)	0.0647(12)	0.073(4)
C(11)	0.1238(7)	0.4506(7)	−0.0292(11)	0.070(4)
C(12)	0.0937(6)	0.3699(6)	0.0142(9)	0.057(3)
N(1)	−0.1321(5)	0.2252(5)	0.1897(7)	0.063(3)
N(2)	0.0236(6)	0.1458(5)	0.3695(7)	0.057(3)
N(3)	0.0890(6)	0.1537(4)	0.1095(7)	0.061(3)
N(4)	0.0508(5)	0.3175(5)	0.3916(6)	0.053(3)
N(5)	0.0766(5)	0.3552(4)	0.1436(6)	0.046(2)
O(1)	−0.1969(8)	0.3980(7)	0.4754(8)	0.133(4)
O(2)	−0.2141(12)	0.4064(7)	0.2344(9)	0.192(8)
O(3)	−0.1990(15)	0.5249(8)	0.3508(11)	0.252(9)
O(4)	−0.3351(11)	0.4555(14)	0.3640(16)	0.300(12)
O(5)	0.3255(7)	0.3206(9)	0.1700(7)	0.174(6)
O(6)	0.4586(7)	0.2720(10)	0.3241(10)	0.180(7)
O(7)	0.3273(10)	0.3542(6)	0.3916(9)	0.163(6)
O(8)	0.2919(11)	0.2249(8)	0.3297(18)	0.230(9)

[a] The equivalent isotropic thermal parameter is defined as one-third of the orthogonalized **U** tensor (Å^2).

Table 3. Selected Bond Distance (Å) and Bond Angles (deg) in [Cu(trenimpy)]$(ClO_4)_2$

Cu−N(1)	2.174(7)	N(2)−C(2)	1.48(1)
Cu−N(2)	2.065(7)	N(2)−C(3)	1.47(1)
Cu−N(3)	1.998(7)	N(2)−C(5)	1.50(1)
Cu−N(4)	1.954(7)	N(3)−C(4)	1.48(1)
Cu−N(5)	2.013(7)	N(4)−C(6)	1.45(1)
N(1)−C(1)	1.46(1)	N(4)−C(7)	1.28(1)
N(1)−Cu−N(2)	82.9(3)	Cu−N(2)−C(2)	109.3(5)
N(1)−Cu−N(3)	102.1(3)	Cu−N(2)−C(3)	104.5(6)
N(1)−Cu−N(4)	103.4(3)	Cu−N(2)−C(5)	105.8(6)
N(1)−Cu−N(5)	110.2(3)	C(2)−N(2)−C(3)	112.3(8)
N(2)−Cu−N(3)	86.8(3)	C(2)−N(2)−C(5)	111.8(7)
N(2)−Cu−N(4)	83.5(3)	C(3)−N(2)−C(3)	112.6(7)
N(2)−Cu−N(5)	161.4(3)	Cu−N(3)−C(6)	107.7(6)
N(3)−Cu−N(4)	151.3(3)	Cu−N(4)−C(7)	117.0(6)
N(3)−Cu−N(5)	102.6(3)	Cu−N(4)−C(7)	116.6(6)
N(4)−Cu−N(5)	80.7(3)	C(6)−N(4)−C(7)	126.1(7)
Cu−N(1)−C(1)	102.6(5)		

Crystal Structure of [Cu(trenimpy)]$(ClO_4)_2$. The molecular structure of [Cu(trenimpy)]$(ClO_4)_2$ (Figure 1) consists of discrete five-coordinate [Cu(trenimpy)]$^{2+}$ cations and two perchlorate anions. The coordination geometry about the central Cu(II) atom is best described as slightly distorted square pyramidal (SP). Four nitrogens from the pyridyl N(5), imine N(4), tertiary amine N(2), and one primary amine N(3) groups form the base of a square pyramid with the other primary amine N(1) occupying the apical position. The Cu−N(2) and Cu−N(3) bond lengths (Table 3) are in the normal range for Cu−amine distances (1.99−2.08 Å). The apical Cu−N(1) bond is slightly longer, 2.174(7) Å, as is typical for SP Cu(II) geometries. The Cu−N(4) distance of 1.954(7) Å and C(7)−N(4) distance of 1.28(1) Å are typical of Cu−N(imine) and C=N bonds, respectively. Inclusion of the pyridyl group within a rigid five-membered pyridyl-α-imine chelate ring results in a short Cu−N(5) distance, 2.013(7) Å, compared with typical Cu−N(py) distances (average 2.070(3) Å). In fact, the bond lengths and angles within the pyridyl-α-imine arm of the ligand are very similar to those found in pyridyl Schiff base Cu(II)

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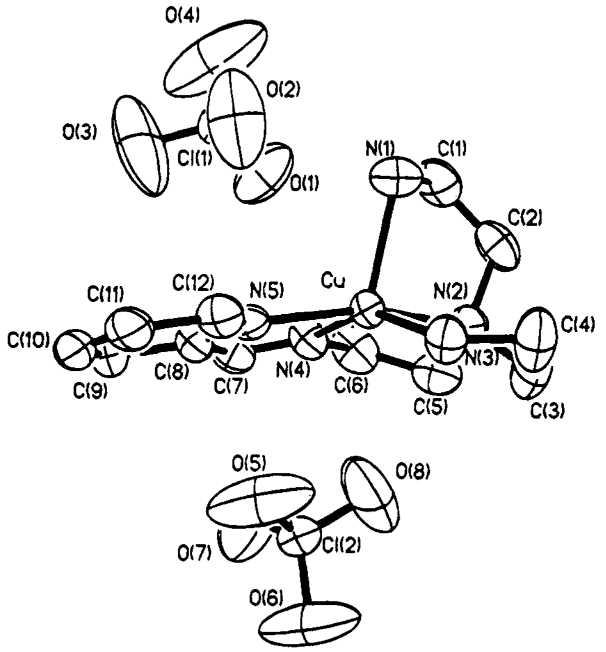

Figure 1. Molecular structure and atomic labeling scheme for [Cu(trenimpy)]$^{2+}$.

compounds.[17] For example, the N(4)−Cu−N(5) bite angle of 80.5° is typical of pyridyl-α-imine complexes.[17] The distance between one of the perchlorate oxygens (O(2)) and N(2) of 3.04(1) Å is indicative of a weak hydrogen bonding contact. The shortest O··Cu contact is 3.37(1) Å and thus no coordination of perchlorate to Cu(II) is apparent.

The Cu atom lies 0.36 Å above the basal plane toward the apical nitrogen N(1) (*i.e.* $\varrho = 0.36$). An inverse correlation has been shown to exist between ϱ and the Cu−(apical) distance in SP Cu(II) complexes,[2] viz. as the apical distance increases, ϱ decreases and the structure tends toward SP geometry. The value of ϱ (0.36) for [Cu(trenimpy)]$^{2+}$ is slightly larger than expected from the relatively small lengthening the Cu−N(1) probably because N(1) is situated 0.51 Å off the perpendicular axis passing through basal plane at the Cu(II) center. The angle between the *trans* basal nitrogens N(2)−Cu−N(5) ($\theta = 161.4°$), although less than the expected 180°, is in the range for SP Cu(II) complexes (160−170°) in which the Cu(II) center lies slightly above the basal plane. For example, in [Cu(NH$_3$)$_5$]$^{2+}$, in which there are no angular strains imposed by chelate rings, the angles between the *trans* amines are 164.0 and 165.4°.[18] In [Cu(trenimpy)]$^{2+}$, the slightly smaller angle between the other *trans* basal nitrogens (151.3°) is indicative of some distortion toward TBP geometry (see later).

Description of the Crystal Structure of [Cu(trenpy)](ClO$_4$)$_2$. The unit cell of [Cu(trenpy)](ClO$_4$)$_2$ contains two slightly different five-coordinate Cu(trenpy)$^{2+}$ cations (Figure 2). The geometries about both Cu(II) centers are nearly identical with the tren portion of trenpy coordinating in a tripodal arrangement and the extended pyridyl arm meridionally. The slight differences are due to hydrogen bonding and crystal packing effects. While the ORTEP view emphasizes the TBP aspect of the [Cu(trenpy)]$^{2+}$ cations, more detailed analysis (see below) reveals that the geometry of both [Cu(trenpy)]$^{2+}$ cations in the unit cell is intermediate between SP and TBP geometries.

Table 4. Atomic Coordinates and Isotropic Displacement Parameters (Å^2) for [Cu(trenpy)](ClO$_4$)$_2$

atom	x	y	z	U(iso) (Å^2)
Cu(1)	0.1288(1)	0.5667	0.0172(2)	0.0344(5)
Cu(2)	0.6556(1)	0.5274(1)	0.4454(2)	0.0414(5)
Cl(1)	−0.0263(2)	0.3954(2)	0.4663(4)	0.049(1)
Cl(2)	0.7142(3)	0.0805(3)	0.5133(5)	0.068(2)
Cl(3)	0.8037(3)	0.5132(3)	−0.0345(6)	0.069(2)
Cl(4)	0.4892(3)	0.7254(3)	0.1053(6)	0.071(2)
O(1)	0.0201(9)	0.3881(8)	0.3282(16)	0.108(6)
O(2)	0.0279(7)	0.3821(8)	0.6198(16)	0.086(5)
O(3)	−0.0894(6)	0.3316(7)	0.4572(14)	0.071(4)
O(4)	−0.0590(7)	0.4812(6)	0.4710(13)	0.069(4)
O(5)	0.6625(9)	0.1311(12)	0.4015(17)	0.129(7)
O(6)	0.7401(9)	0.1403(11)	0.6473(20)	0.126(7)
O(7)	0.7875(9)	0.0513(13)	0.4472(15)	0.123(7)
O(8)	0.6756(11)	0.0118(10)	0.5835(30)	0.164(10)
O(9)	0.7732(12)	0.4610(11)	0.0813(31)	0.178(10)
O(10)	0.7408(10)	0.5649(14)	−0.1050(23)	0.165(9)
O(11)	0.8401(11)	0.4621(13)	−0.1445(21)	0.153(9)
O(12)	0.8605(9)	0.5734(13)	0.0441(21)	0.140(8)
O(13)	0.5488(12)	0.7654(15)	0.2104(27)	0.195(11)
O(14)	0.4560(9)	0.6650(10)	0.2021(24)	0.144(8)
O(15)	0.4351(13)	0.7918(13)	0.0646(22)	0.163(9)
O(16)	0.5199(23)	0.6855(19)	−0.0165(30)	0.268(17)
C(11)	0.1529(10)	0.3754(10)	0.0508(19)	0.062(4)
C(21)	0.1998(10)	0.2974(12)	0.0408(21)	0.072(5)
C(31)	0.2761(10)	0.3020(11)	−0.0010(20)	0.068(4)
C(41)	0.3121(9)	0.3806(10)	−0.0276(18)	0.062(4)
C(51)	0.2660(8)	0.4593(9)	−0.0082(17)	0.045(3)
C(61)	0.2969(8)	0.5463(9)	−0.0244(18)	0.057(4)
C(71)	0.2402(10)	0.7025(11)	−0.0444(22)	0.074(5)
C(81)	0.1597(8)	0.7474(10)	−0.0753(19)	0.053(4)
C(91)	0.0849(9)	0.7264(11)	0.1697(20)	0.070(4)
C(101)	0.0418(9)	0.6571(9)	0.2560(19)	0.059(4)
C(111)	0.0141(9)	0.7018(11)	−0.1142(19)	0.068(4)
C(121)	0.0135(11)	0.6314(11)	−0.2416(22)	0.078(5)
C(12)	0.7858(9)	0.6598(10)	0.3990(19)	0.064(4)
C(22)	0.8223(10)	0.7421(11)	0.4055(22)	0.076(5)
C(32)	0.7814(10)	0.8105(12)	0.4797(20)	0.073(5)
C(42)	0.7130(10)	0.7940(11)	0.5459(21)	0.067(5)
C(52)	0.6782(9)	0.7071(10)	0.5354(19)	0.057(4)
C(62)	0.6012(10)	0.6816(11)	0.6112(21)	0.072(5)
C(72)	0.5294(11)	0.5405(12)	0.6522(23)	0.088(5)
C(82)	0.5213(11)	0.4478(13)	0.5841(23)	0.092(6)
C(92)	0.6418(14)	0.3584(17)	0.5672(32)	0.119(8)
C(102)	0.7180(14)	0.3574(14)	0.5237(29)	0.101(7)
C(112)	0.5389(21)	0.4161(28)	0.3102(41)	0.206(15)
C(122)	0.5430(12)	0.4609(15)	0.1835(27)	0.099(7)
N(11)	0.1881(6)	0.4531(7)	0.0309(14)	0.043(3)
N(21)	0.2315(7)	0.6082(8)	−0.0825(16)	0.058(3)
N(31)	0.0940(7)	0.6964(7)	−0.0049(14)	0.050(3)
N(41)	0.0791(6)	0.5697(8)	0.2393(12)	0.053(3)
N(51)	0.0274(7)	0.5450(8)	−0.1703(15)	0.065(3)
N(12)	0.7155(6)	0.6428(8)	0.4548(14)	0.047(3)
N(22)	0.5760(11)	0.5942(12)	0.5698(24)	0.121(6)
N(32)	0.5804(8)	0.4253(8)	0.4744(16)	0.065(3)
N(42)	0.7495(7)	0.4433(8)	0.4947(16)	0.063(3)
N(52)	0.6083(8)	0.5193(10)	0.1939(17)	0.085(4)

[a] The equivalent isotropic thermal parameter for Cu, Cl, and O is defined as one-third of the orthogonalized **U** tensor (Å^2).

The Cu−N(2), −N(3) and −N(4) distances (Table 5, average 2.047(3) Å) are in the normal range for Cu−N(amine) distances. However, the Cu−N(5) distances in both molecules are much longer than these Cu−N(amine) distances (average 2.162(14) Å) while the Cu−N(1) distances (*ca.* 2.00 Å) are slightly shorter than normal for five-coordinate Cu(II)−pyridine complexes (average 2.070(3) Å).[19] Weak H-bonding interactions between the perchlorate oxygens and the amine hydrogens are indicated by the O1−N(41) and O2−N(51) distances of 3.04(2) and 3.01-

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(18) (a) Duggan, M.; Ray, N.; Hathaway, B. J.; Tomlinson, G.; Brint, P.; Pelin, K. *J. Chem. Soc., Dalton Trans.* **1980**, 1342. (b) Nagle, P.; Hathaway, B. J.; O'Sullivan, E.; Muller, E. *J. Chem. Soc., Dalton Trans.* **1990**, 3399.

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Table 5. Selected Bond Distances (Å) and Bond Angles (deg) in $[Cu(trenpy)](ClO_4)_2$

Cu(1)–N(11)	1.98(1)	Cu(2)–N(12)	2.01(1)
Cu(1)–N(21)	2.04(1)	Cu(2)–N(22)	2.01(1)
Cu(1)–N(31)	2.05(1)	Cu(2)–N(32)	2.01(1)
Cu(1)–N(41)	2.06(1)	Cu(2)–N(42)	2.00(1)
Cu(1)–N(51)	2.15(1)	Cu(2)–N(52)	2.11(1)
C(51)–C(61)	1.43(2)	C(52)–C(62)	1.51(2)
C(61)–N(21)	1.46(2)	C(62)–N(22)	1.42(2)
N(11)–Cu(1)–N(21)	82.6(5)	N(12)–Cu(2)–N(22)	83.1(6)
N(11)–Cu(1)–N(31)	166.5(4)	N(12)–Cu(2)–N(32)	166.5(5)
N(11)–Cu(1)–N(41)	102.0(5)	N(12)–Cu(2)–N(42)	100.9(5)
N(11)–Cu(1)–N(51)	104.0(4)	N(12)–Cu(2)–N(52)	102.4(5)
N(21)–Cu(1)–N(31)	84.4(5)	N(22)–Cu(2)–N(32)	83.8(6)
N(21)–Cu(1)–N(41)	139.5(4)	N(22)–Cu(2)–N(42)	138.2(7)
N(21)–Cu(1)–N(51)	111.7(5)	N(22)–Cu(2)–N(52)	109.1(6)
N(31)–Cu(1)–N(41)	85.6(5)	N(32)–Cu(2)–N(42)	87.2(5)
N(31)–Cu(1)–N(51)	84.2(4)	N(32)–Cu(2)–N(52)	84.4(5)
N(41)–Cu(1)–N(51)	106.1(4)	N(42)–Cu(2)–N(52)	110.5(5)

(2) Å, respectively. The shortest Cu···O contact is 3.47(2) Å and indicates that ClO_4^- is not coordinated to Cu(II). In both cations, the angles around the tripodal nitrogens, N(3)–Cu–N(*i*), *i* = 2, 4, and 5, are acute (average 84.9(9)°). Consequently, the Cu(II) centers lie *ca.* 0.18 Å below the plane defined by N(2), N(4) and N(5) toward the pyridyl nitrogen N(1). These values are comparable to those found in the related complexes $[Cu(trenen)]Br_2$[5] and $[Cu(tren)(NH_3)](ClO_4)_2$.[18] The angles spanning the axial positions in two cations, N(1)–Cu–N(3) (average 166.4°) are less than 180° expected for ideal TBP geometry but they are close to the value of 169.6° reported for $[Cu(trenen)]Br_2$.

The arrangement of the tren portion of trenpy around Cu(II) is similar to that found in other $[Cu(tren)X]^{n+}$ complexes (X = NH_3,[18a] 2-MeIm,[20] SCN^- [21]) in which the tren ligand confers (distorted) TBP geometry on the Cu(II) ion. The cations in $[Cu(trenpy)]^{2+}$ show considerable deviation from the C_{3v} symmetry. The trigonal angles (between N(2), N(4), and N(5)) are inequivalent, two being less and one larger than 120°, and the Cu–N(5) axial bond is longer than the others (Table 6). Similar geometric features have been observed in [Cu(tren)(NCS)](NCS), and in both cases the distortion in $[Cu(trenpy)]^{2+}$ appears to be along the Berry pathway (Figure 3). In contrast, in complexes with close to regular TBP geometry (e.g. $[Cu(tren)(NH_3)](ClO_4)_2$, C_{3v} symmetry[18]) the trigonal angles and Cu–N(eq) bond lengths are equivalent.

Degree of Distortion in $[Cu(trenimpy)](ClO_4)_2$ and $[Cu(trenpy)](ClO_4)_2$. Since many five-coordinate structures with geometries intermediate between regular SP and TBP stereochemistries lie on the Berry pathway (Figure 3), methods have been developed which attempt to quantify the degree of distortion and thus provide a more precise description of the structure. Two of these methods have been applied in the case of $[Cu(trenimpy)]^{2+}$ and $[Cu(trenpy)]^{2+}$. The simplest method, applicable to complexes in which one bond is longer than the others and can be identified as the apical bond, as is the case for $[Cu(trenimpy)]^{2+}$ and $[Cu(trenpy)]^{2+}$, utilizes the angles between the donor atoms that would form the basal plane in a SP structure. The ratio of the two basal angles, τ, defined[22] as $\tau = [(\theta - \phi)/60] \times 100$, represents the percentage trigonal distortion from square pyramidal geometry. For an ideal square pyramid, τ is 0 while for an ideal trigonal bipyramid τ is 100. The relevant angles in $[Cu(trenimpy)]^{2+}$, $\theta = 161.4°$ and $\phi = 151.3°$, yield a τ value of 17% which indicates a geometry close to SP while those for the cations in $[Cu(trenpy)](ClO_4)_2$, θ = 166.6 and 166.5° and ϕ = 138.9 and 139.5°, yield τ values of 45 and 43% and indicate a geometry intermediate between SP and TBP. The variation in θ is small, due to the similar coordination of the extended arms of trenimpy and trenpy, and cannot account for the changes in geometry. A comparison of the trigonal angles in the two complexes indicates that the main difference is due to changes in the coordination of the two primary amines. The trigonal angles in $[Cu(trenimpy)]^{2+}$ of 102.1, 103.4, and 151.4° are closer to those found in SP complexes (ca. 102, 102, and 160°) than in TBP complexes (120°) while the corresponding angles in the $[Cu(trenpy)]^{2+}$ cations (108.3, 110.4, and 138.9°) are intermediate between the SP and TBP values.

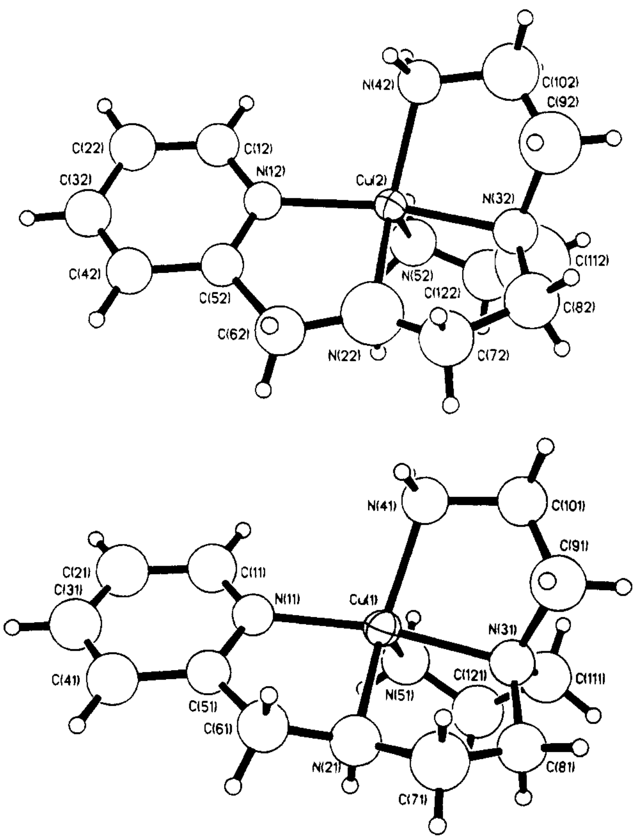

Figure 2. Molecular structure and atomic labeling scheme of the two cations in $[Cu(trenpy)]^{2+}$.

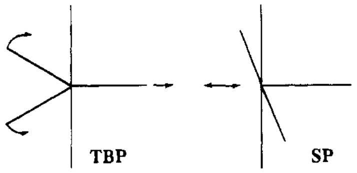

Figure 3. Berry mechanism for transition between square pyramidal and trigonal bipyramidal geometry.

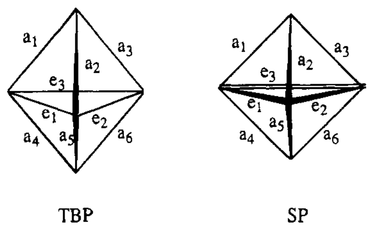

Figure 4. Definition of dihedral angles in five-coordinate geometries.[23]

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(20) Su, C.-C.; Lu, W.-S.; Hui, T.-Y.; Chang, T.-Y.; Wang, S.-L.; Liao, F.-L. *Polyhedron* **1993**, *12*, 2249.

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Table 6. Trigonal Bond Angles and Distances in Cu(II) Complexes of Tren and Tren Derived Ligands

compound	small trigonal angles (°)	large trigonal angle (°)	Cu−N(short) (Å)	Cu−N(long) (Å)
$[Cu(tren)(NH_3)](ClO_4)_2$[a]	119.2, 119.2	119.2	2.082, 2.082	2.082
$[Cu(trenpy)](ClO_4)_2$[b]	109.1, 110.5	138.2	2.01, 2.00	2.11
$[Cu_2(tren)_2(CN)_2](BPh_4)_2$[c]	112.5, 120.4	122.6	2.083, 2.090	2.119
$[Cu(tren)(NCS)](NCS)$[d]	114.3, 112.9	129.5	2.055, 2.055	2.144
$[Cu(trenpy)](ClO_4)_2]$[b]	106.1, 111.7	139.5	2.04, 2.06	2.15
$[Cu(trenimpy)](ClO_4)_2$[a]	102.1, 103.4	151.3	1.954, 1.998	2.174

[a] Reference 18. [b] This work. [c] Duggan, D. M.; Hendrickson, D. N. *Inorg. Chem.* **1974**, *13*, 1911. [d] Reference 21.

Table 7. Dihedral Angles (deg) in $[Cu(trenimpy)](ClO_4)_2$, $[Cu(trenpy)](ClO_4)_2$ and Other Five-Coordinate Compounds

angle	TBP	L = trenimpy	L = trenpy	L = trenpy	$[Ni(CN)_5]^{3-}$ [a]	$[Cu(paphy)Br_2]$[b]	SP
δa_1	101.5	109.7	106.3	104.4	106.3	112.2	121.8
δa_3	101.5	108.2	102.8	103.7	106.4	115.7	121.8
δa_4	101.5	121.6	115.6	113.5	108.3	113.7	121.8
δa_6	101.5	117.3	107.5	109.0	110.3	116.4	121.8
δa_2	101.5	84.9	88.4	88.5	87.4	89.9	73.9
δa_5	101.5	80.9	88.7	90.3	88.2	78.4	73.9
δe_1	53.1	62.9	57.5	57.6	62.7	77.4	73.9
δe_2	53.1	77.3	73.0	69.8	68.6	67.8	73.9
δe_3	53.1	13.7	31.3	32.7	32.2	5.6	0.0
Δ[d]	0.0	0.73	0.38	0.38	0.50	0.73	1.0
τ	1.0	0.17	0.45	0.43	0.53[c]	0.13	0.0

[a] Raymond, K. N.; Corfield, P. W. R.; Ibers, J. A. *Inorg. Chem.* **1968**, *7*, 1362. [b] Mesa, J. L.; Arriortua, M. I.; Lezama, L.; Pizarro, J. L.; Rojo, T.; Beltran, I. *Polyhedron* **1988**, *7*, 1383. paphy = pyridine-2-carboxaldehyde 2-pyridylhydrazone. [c] The θ and ϕ values are 172.83 and 141.17°, respectively, for $Ni(CN)_5^{3-}$. [d] Δ is the average of the distortion from TBP and from SP, defined as $\Delta = 0.5\sum_i(|\delta_i(SP) - \delta_i(M)|/|\delta_i(SP) - \delta_i(TBP)|) + 0.5\sum_i(|\delta_i(TBP) - \delta_i(M)|/|\delta_i(SP) - \delta_i(TBP)|)$.

Table 8. ESR Data for a Selection of Five-Coordinate Cu(II) Complexes

complex	$g_\parallel$	$A_\parallel$[a]	$g_\perp$	$A_\perp$[a]	g_{iso}
$[Cu(trenimpy)](ClO_4)_2$[a]	2.20	155	2.0		2.089
$[Cu(trenpy)](ClO_4)_2$[a,c]	2.19	125	2.043		2.081
$[Cu(tmptacn)](ClO_4)_2$[a,c]	2.21	175	2.046		2.066
$[Cu(daptacn)](ClO_4)_2$[d]	2.238	179	2.061	*ca.* 38	
$[Cu(dtma)(\mu\text{-}im)Zn(dtma)](ClO_4)_2$[e]	2.224	178			
$[Cu(tren)(2\text{-}MeIm)](ClO_4)_2$[b,f]	2.000	52	2.181	122	
$[Cu(tren)(py)](ClO_4)_2$[b,f]	2.001	51	2.178	130	
$[Cu(tren)(NH_3)](ClO_4)_2$[b,f]	2.029	84	2.176	110	2.132
$K[Cu(NH_3)_5](PF_6)_3$[g]	2.240		2.053		

[a] *A* values are $\times 10^4$ cm^{-1}. [b] Recorded in 1:1 $MeOH:H_2O$ glass at 77 K. [c] This work. [d] Reference 11. [e] Reference 25. [f] Reference 20. [g] Reference 18a.

Table 9. Visible Spectral Data for a Selection of Five-Coordinate Cu(II) Complexes

compound	solution	λ_{max}, nm (ϵ_{max})[a]
$[Cu(trenimpy)](ClO_4)_2$[b]	mull	610
	H_2O	650 (149)
	CH_3CN	647 (162)
	DMF	653 (152)
$[Cu(trenpy)](ClO_4)_2$[b]	mull	648
	H_2O	723 (151)
	CH_3CN	724 (168)
	DMF	724 (145)
$[Cu(dmptacn)](ClO_4)_2$[b]	mull	600
	H_2O	610 (210)
	CH_3CN	613 (176)
	DMF	608 (182)
$K[Cu(NH_3)_5](PF_6)_3$[d]	dr[c]	650, 910 (sh)
$[Cu(tren)(NH_3)](ClO_4)_2$[d]	dr[c]	880, 660 (sh)
$[Cu(tren)(2\text{-}MeIm)](ClO_4)_2$[e]	dr[c]	795, 650 sh
	CH_3CN	790 (178), 660 (sh)
$[Cu(tren)(py)](ClO_4)_2$[e]	CH_3CN	800 (160), 660 (sh)
$[Cu(daptacn)](ClO_4)_2$[f]	H_2O	578 (106), 865 (39)

[a] ϵ_{max} in units of M^{-1} cm^{-1}. [b] This work. [c] Diffuse reflectance spectrum. [d] Reference 18a. [e] Reference 20. [f] Reference 11.

The method of Muetterties and Guggenberger[23] can also be used to calculate the degree of distortion from regular geometry in $[Cu(trenimpy)](ClO_4)_2$ and $[Cu(trenpy)](ClO_4)_2$. In this analysis, the dihedral angles (defined in Figure 4) about the coordination polyhedra are compared to those expected for regular TBP and SP geometries. The relevant angles for $[Cu(trenimpy)]^{2+}$, $[Cu(trenpy)]^{2+}$ and a number of other five-coordinate Cu(II) complexes are gathered in Table 7. The sums of the differences between the dihedral angles in a compound, $\delta(M)$, and those expected for regular SP and TBP geometries, suggested by Sheldrick,[24] gives a measure of the distortion of complexes along the Berry pathway (Figure 3). The formula

$$\sum_i\left(\frac{|\delta_i(SP) - \delta_i(M)|}{|\delta_i(SP) - \delta_i(TBP)|}\right) \times 100\%$$

gives the percentage distortion from SP, while the formula

$$\sum_i\left(\frac{|\delta_i(TBP) - \delta_i(M)|}{|\delta_i(SP) - \delta_i(TBP)|}\right) \times 100\%$$

gives the percentage distortion from TBP. The values for $[Cu(trenimpy)](ClO_4)_2$ are 28% from SP and 74% from TBP, which gives an average distortion of 73% from TBP toward SP geometry. The values for $[Cu(trenpy)](ClO_4)_2$ are 65% from SP and 41% from TBP for both cations, which gives an average distortion of 38% from ideal TBP toward SP geometry. Although this method gives slightly lower distortions from TBP than the τ analysis, the results are in broad agreement. A constraint of the Berry mechanism is that each point on the surface must have at least a 2-fold symmetry axis (C_{2v}), and thus pairing of some dihedral angles should be observed, i.e., $\delta e_1 = \delta e_2$, $\delta a_2 = \delta a_5$ while $\delta a_1 = \delta a_3 = \delta a_4 = \delta a_6$, and the sum of the percentage distortion from SP and TBP should equal 100%. Pairing of the dihedral angles (see Table 7), especially δe_1 and δe_2, is not strictly observed in $[Cu(trenimpy)]^{2+}$ and $[Cu(trenpy)]^{2+}$, i.e. these complexes do not strictly follow the

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Table 10. Cyclic Voltammetric Data for a Selection of Cu(II) Complexes

				E_{pC} (V)	
compound	$E_{1/2}$ Cu(II)−Cu(I) (V)	ΔE (mV)	i_{pa}/i_{pc}	Cu(II)−Cu(I)	Cu(II)−Cu(I)
[Cu(trenimpy)](ClO$_4$)$_2$[a]	−0.80	68	1.0	−0.82	−1.93
[Cu(trenpy)](ClO$_4$)$_2$[a]	−0.94	79	0.65	−0.96	
[Cu(dmptacn)](ClO$_4$)$_2$[a]	−0.81	71	0.88	−0.86	−1.58
[Cu(N$_5$-[15]ane)](ClO$_4$)$_2$[b]	−0.73[c]			−1.12	−1.35[c]
[Cu(N$_5$-[16]ane)](ClO$_4$)$_2$[b]	−0.78[c]			−1.10	−1.45[c]
[Cu(*trans*-[14]diene)]$^{2+}$ [d]	−0.90[e]			−1.023[c]	−2.0[e]
[Cu(teta)]$^{2+}$ [f]	−1.08[e]			−1.16[e]	−2.2[e]

[a] This work, relative to the Fc$^+$/Fc couple. [b] Reference 28. [c] Relative to SCE. [d] Reference 30, *trans*-[14]diene = 5,12-methyl-7,14-dimethyl-1,4,8,11-tetraazacyclotetradecan-4,8-diene. [e] Relative to Ag/AgNO$_3$. [f] Reference 30, teta = 5,12-methyl-7,14-dimethyl-1,4,8,11-tetraazacyclotetradecane.

Berry pathway. Thus, this method of analysis can only give an approximate measure of distortion.

Electron Spin Resonance Spectra. The ESR spectra of [Cu(trenimpy)](ClO$_4$)$_2$, [Cu(trenpy)](ClO$_4$)$_2$, and [Cu(dmptacn)](ClO$_4$)$_2$ have been recorded as microcrystalline solids and in frozen DMF solutions, at −150 K. The data are summarized in Table 8, along with the g and A values of similar compounds. The frozen solution ESR spectrum of all three complexes is anisotropic, yielding the parameters ($g_{\parallel}$ = 2.19−2.21, $A_{\parallel}$ = (125−175) × 10^{-4} cm^{-1}, $g_{\perp}$ = 2.02−2.06) that are typical of SP Cu(II) complexes. For [Cu(trenimpy)](ClO$_4$)$_2$, the data are consistent with the geometry found in the crystal structure of the complex. The frozen solution ESR spectrum of [Cu(dmptacn)](ClO$_4$)$_2$ is very similar to that of the related complex, [Cu(daptacn)](ClO$_4$)$_2$.[11] The geometry of Cu(II) in these complexes is close to regular SP, and it is likely that the dmptacn complex adopts the same stereochemistry. The ESR data for [Cu(trenpy)](ClO$_4$)$_2$ indicate that it adopts a similar geometry in frozen solution despite the fact that in the solid state the Cu(II) geometry is considerably distorted from SP toward TBP. Presumably the energy difference between SP and TBP geometries is small for [Cu(trenpy)]$^{2+}$, and at low temperature there is a shift toward SP geometry. Similar changes in stereochemistry have been observed for other Cu(II) complexes. For example, the frozen solution ESR spectrum of [Cu(dtma)(μ-im)Zn(dtma)](ClO$_4$)$_3$,[25] (Table 8) is typical of SP geometry even though a dihedral angle analysis indicated that Cu(II) center has a distortion of 43% from TBP geometry in the solid state. For [Cu(trenpy)]$^{2+}$, significant changes in stereochemistry would only require a small shift in the coordination positions of the two primary amines N(4) and N(5). The reduced $A_{\parallel}$ values for [Cu(trenpy)](ClO$_4$)$_2$ compared with that for the dmptacn and trenimpy complexes could be reflecting some distortion in the geometry of a Cu(II) complex away from SP.[26,27] However, this would give rise to three g tensors and not two ($g_{\parallel}$ and $g_{\perp}$), as observed here.

Electronic Spectra. Visible spectral data for [Cu(dmptacn)](ClO$_4$)$_2$, [Cu(trenimpy)](ClO$_4$)$_2$ and [Cu(trenpy)](ClO$_4$)$_2$, recorded as solids and in various solvents, are summarized in Table 9 together with the data for a series of related compounds. The spectra of [Cu(trenimpy)](ClO$_4$)$_2$ and Cu(dmptacn)](ClO$_4$)$_2$, recorded as mulls show a broad band centered at 610 and 600 nm, respectively, and are typical of SP Cu(II) complexes with nitrogen donors which generally exhibit a single band between 555 and 665 nm (d_{xz}, d_{yz} → $d_{x^2-y^2}$). The structure of [Cu(trenimpy)](ClO$_4$)$_2$ supports this assignment. In contrast, trigonal bipyramidal Cu(II) complexes usually show a maximum at >800 nm, (d_{xy}, $d_{x^2-y^2}$ → d_{z^2}), with a higher energy shoulder (spin forbidden d_{xz}, d_{yz} → d_{z^2})^2. The fact that for both complexes the transition is observed at lower energy than reported for K[Cu(NH$_3$)$_5$](PF$_6$)$_3$, a complex with regular SP geometry, is a reflection of the higher ligand field strength trenimpy and dmptacn compared with the pentammine chromophore. The mull spectrum of [Cu(trenpy)](ClO$_4$)$_2$ consists of a broad band centered at 650 nm and indicates significant distortion toward TBP geometry. The solution visible spectrum of [Cu(dmptacn)](ClO$_4$)$_2$, recorded in various solvents, is similar to the mull spectrum, indicating little change in stereochemistry on dissolution. In contrast, the spectrum [Cu(trenimpy)](ClO$_4$)$_2$ in H$_2$O, CH$_3$CN and DMF exhibits a broad and unsymmetrical band at ca. 650 nm which is red-shifted by ca. 40 nm relative to the solid state spectrum. This indicates that in solution a geometry closer to TBP is adopted. A greater shift toward TBP geometry is indicated by the solution spectrum of [Cu(trenpy)](ClO$_4$)$_2$, which consists of a broad band at ca. 720 nm. This is in contrast to the ESR spectrum which indicates that SP geometry is adopted at liquid nitrogen temperatures.

Cyclic Voltammetry. Cyclic voltammetry measurements on [Cu(dmptacn)](ClO$_4$)$_2$, [Cu(trenimpy)](ClO$_4$)$_2$, and [Cu(trenpy)](ClO$_4$)$_2$ in CH$_3$CN and some comparable Cu(II) polyamine complexes are summarized in Table 10. In the potential range −2.0 to +1.5 V, only processes which could be ascribed to reduction of the metal center were observed, and no oxidation of either Cu(II) to Cu(III) or the ligands was apparent. For [Cu(dmptacn)](ClO$_4$)$_2$ and [Cu(trenimpy)](ClO$_4$)$_2$, two irreversible one electron reductions corresponding to reduction of Cu(II) to Cu(I) and then Cu(0) were observed on scanning to −2.0 V. Irreversible reduction to Cu(I) was also observed for [Cu(trenpy)](ClO$_4$)$_2$ but further reduction to Cu(0) was not apparent, presumably because this occurs at a more negative potential. Reversal of the potential scan just after the first reduction process, results in a quasi-reversible Cu(II)−Cu(I) couple, with $E_{1/2}$ values in the range −0.81 to −0.94 V for the three complexes. The anodic and cathodic peak potential differences (ΔE = 68−79 mV) are slightly larger than expected for a fully reversible one-electron process, as often found in nonaqueous solvents. Similar behavior has been reported for the Cu(II) complexes of saturated pentaaza macrocycles N$_5$-[15]ane, N$_5$-[16]ane, and N$_5$-[17]ane[28] (Table 10). These complexes also undergo two irreversible one-electron reductions to Cu(I) and Cu(0), the first of which becomes quasi-reversible if the potential scan is reversed just after traversing the peak. A comparison of the Cu(II)−Cu(I) potentials indicates that [Cu(dmptacn)]$^+$ and [Cu(trenimpy)]$^+$ complexes are more stable to reduction than [Cu(trenpy)]$^+$. This is in agreement with the observation that Cu(I) generally forms more stable complexes with polyaza ligands[29] with some degree of unsaturation. Although other

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factors, such as the rigidity of the ligand can be important, the variation in potentials of [Cu(trenimpy)](ClO_4)$_2$ and [Cu(trenpy)](ClO_4)$_2$ suggests that the π-acceptor capability of the trenimpy ligand stabilizes the Cu(I) state by ca. 140 mV. The presence of the imine π^* orbitals allows for some donation of electron density from the Cu(I) center to the ligand. The ligand *trans*-[14]diene affords a similar degree of stabilization of the Cu(I) state compared to its fully saturated analogue, teta[30] (Table 10). The degree of stabilization of the Cu(I) is similar to that observed for the cobalt complexes of trenimpy and trenpy, where the presence of the imine moiety stabilizes the Co(II) state by ca. 150 mV relative to the Co(III) state.[31]

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Supplementary Material Available: Tables of anisotropic thermal parameters, bond distances, bond angles, and H atom coordinates for [Cu(trenimpy)](ClO_4)$_2$ (Tables S1–S4) and [Cu(trenpy)](ClO_4)$_2$ (Tables S5–S8) (15 pages). Ordering information is given on any current masthead page.

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