spectrum should present a shoulder around 4966 eV, which is observed in all samples of an octahedral coordination. We did not see it, even in the second derivative of the spectrum.

X-ray absorption results seem to be in agreement with structure I: three equivalent Ti sites in 5-fold coordination. In such a model, titanium atoms are surrounded by three short Ti–O bonds and two long Ti–O bonds. This is in agreement with the ratio betwen short and long distances (3.4 at 1.82 Å, 1.8 at 2.05 Å) given by our EXAFS results. So, structure I appears to be more realistic for describing the $Ti(OEt)_4$ structure, but it is certainly not the only one. XANES and EXAFS results for $Ti(OBu^n)_4$ are similar to those concerning $Ti(OEt)_4$. The same structural model might then be proposed.

Acknowledgment. We wish to thank A. Michalowicz for the use of his EXAFS analysis programs and R. Cortes and B. Poumellec for help in programming.

Registry No. $Ti(OAm^t)_4$, 10585-26-9; $Ti(OPr^i)_4$, 546-68-9; $Ti(OEt)_4$, 3087-36-3; $Ti(OBu^n)_4$, 5593-70-4.

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Doping of Copper(II) into the Macrocyclic Amine tet a: Structural and Spectroscopic Studies

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The synthesis, X-ray structure, and electronic and EPR spectra of the Cu(II)-doped dihydroperchlorate of tet a (*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) are presented. Pale pink crystals of $(H_{1.86}Cu_{0.07}C_{16}H_{36}N_4)(ClO_4)_2 \cdot 2(CH_3)_2SO$ are monoclinic, space group $P2_1/n$, with $a = 12.330$ (4) Å, $b = 15.119$ (12) Å, $c = 8.808$ (2) Å, $\beta = 104.07$ (2)°, $Z = 2$, and R_F (R_{wF}) = 0.057 (0.078) for 2426 reflections. The structure contains Cu-doped diprotonated tet a cations $[Cu_{0.07}H_{1.86}(\text{tet a})]^{2+}$ with site symmetry C_i separated by perchlorate anions and dimethyl sulfoxide solvate molecules. As determined crystallographically, 7% of the Cu sites are occupied; 93% of the cations are diprotonated amines whose structure compares favorably with that reported for the diperchlorate salt of the $H_2(\text{cyclam})^{2+}$ cation. *Apparent* Cu–N distances are 2.117 (2) and 2.015 (2) Å for the quaternary and ternary amines, respectively. The shortest possible apical bonding distance from the center of symmetry (the Cu(II) site) involves a perchlorate O atom (Cu···O = 2.905 (2) Å). This distance is ca. 0.3 Å longer than those reported for related diperchlorate salts of Cu(II)–macrocyclic amine complexes. The observed blue shift of the doped Cu(II) species absorbance (λ_{max} = 485 (1) nm) relative to that of the reference neat Cu(tet a)$(ClO_4)_2$ (λ_{max} = 506 (1) nm) is attributed to the increased ligand field associated with the unusually weak apical bonding in the doped species. Consistent with the apparent lack of crystallographic disorder, the EPR spectra of the doped material are those of a single tetragonal Cu(II) species having $g_{\parallel} = 2.185$, $g_{\perp}$ = ca. 2.05, and $A_{\parallel}^{Cu} = 203 \times 10^{-4}$ cm^{-1}.

In the course of preparing stable Cu(II) aliphatic thiolates, we found it useful to displace macrocyclic ligands such as tet a[1] or tet b from Cu(II) with N_2S_2 ligands.[2,3] For example, the reaction of Cu(tet a)$(ClO_4)_2$ with *N,N'*-ethylenebis(L-cysteine) dimethyl ester yields the stable CuN_2S_2 complex and displaced tet a·$2HClO_4$. When a DMSO/water cosolvent was used, the ligand salt crystallized and occasionally exhibited a faint pink coloration. Subsequent studies yielded crystallographically identical pink crystals from solutions of tet a·$2HClO_4$ and Cu(tet a)$(ClO_4)_2$. EPR studies revealed the presence of magnetically dilute tetragonal Cu(II) ions, and electronic spectral studies suggested that the Cu(II) ions experienced a ligand field (LF) significantly greater than that of neat Cu(tet a)$(ClO_4)_2$. We have been interested in the structural, spectroscopic, and magnetic properties of Cu(II) complexes that readily dope into the structurally similar lattices of protonated amino acid ligands.[4-6] In order to determine the structural basis for the spectroscopic features of the doped Cu(II)/tet a·$2HClO_4$ system, this present study was undertaken.

Experimental Section

1. Direct Preparation of the Doped Complex (1). The meso macrocyclic amine tet a was synthesized as the dihydrate by following a published procedure[7] and separated from the *d,l* isomer tet b by fractional crystallization. The neat copper complex was prepared by dissolving 1 mmol (0.32 g) of tet a·$2H_2O$ and 1 mmol (0.38 g) of $Cu(H_2O)_6(ClO_4)_2$ in a mixture of 16 mL of methanol and 10 mL of H_2O. The mixture turned bluish purple when heated to boiling. The addition of trace amounts of NaOH resulted in rapid conversion to the stable red form. The hot solution was filtered through a fine frit and left to evaporate to dryness in air at approximately 30 °C. The product consisted exclusively of dark red six-sided plates (yield 0.462 g, 84.4%). *Caution*! Compound may explode if heated when dry.

The dihydroperchlorate salt of tet a was prepared by adding 3.2 mmol of $HClO_4$ (as a 70% aqueous solution) to a solution of 1.6 mmol of tet a·$2H_2O$ in 20 mL of methanol. The initially clear solution began to deposit a colorless crystalline solid after about 5 min. The solid was collected by filtration and dried in air (yield 0.8 g). *Caution*! Compound may explode if heated when dry.

The doped material was prepared by adding a solution of Cu(tet a)$(ClO_4)_2$ (5 mg, 0.0091 mmol) in 1 mL of DMSO to a solution of the above salt (0.8 g, 1.25 mmol) in 20 mL of warm H_2O. The resulting pale pink solution was filtered through a fine frit and concentrated by evaporation at room temperature in a desiccator containing concentrated H_2SO_4. After 5 days, the resulting pale pink crystals were collected by filtration and dried in air (yield 0.6 g). Crystals obtained from this preparation, nominally doped at the 0.7% level, were uniform in color to the eye and were used for EPR and electronic spectral studies. *Caution*! Compound may explode if heated when dry.

Serendipitous, Indirect Preparation of the Doped Complex (1). A filtered, deoxygenated solution containing 80 mg (0.30 mmol) of *N,N'*-ethylenebis(L-cysteine) dimethyl ester, $(-CH_2NHCH(CO_2CH_3)CH_2SH)_2$, in 5 mL of methanol was added to a deoxygenated solution of 120 mg (0.27 mmol) of Cu(tet a)$(ClO_4)_2$ in 10 mL of DMSO. The resulting solution, which turned dark red in about 5 min at room temperature, was placed in a freezer at −14 °C and allowed to stand for 1 week. Under

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(1) tet a and tet b, respectively, are the meso and rac forms of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane.

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Table I. Crystal and Refinement Data for **1**

formula	$Cu_{0.07}Cl_2S_2O_{10}N_4C_{20}H_{49.86}$
fw	645.969
a, Å	12.330 (4)
b, Å	15.119 (12)
c, Å	8.808 (2)
β, deg	104.07 (2)
V, Å^3	1592 (2)
space group	$P2_1/n$
Z	2
no. of reflcns used to detn cell consts	25 (17.69 < θ < 19.61°)
d_{calcd}, g/cm^3	1.348
d_{obsd}, g/cm^3	1.35 (1)
radiation used (λ)	graphite monochromated Mo Kα (0.71073 Å)
linear abs coeff, cm^{-1}	4.3
cryst dimens, mm	0.3 × 0.4 × 0.4
rel transmissn factor range	0.98–1.00
diffractometer	Enraf-Nonius CAD-4
data collecn method	θ–2θ
2θ range, deg	4–55
temp, K	299 (1)
scan rate	variable
scan range, deg	1.0 + 0.35 tan θ
weighting scheme^a	$w = 4(F_o)^2/[\sigma(F_o)^2]^2$
no. of std reflcns	3
% variation in std intens	±3
no. of unique data collcd	3647
no. of data used in refinement	2426
data:param ratio	8.8
final GOF	2.54
final R_F, R_{wF}	0.057, 0.078
syst absences obsd	$h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$
data collcd	$h,k,\pm l$
final largest shift/esd	0.05
highest peak in final diff map, e/Å^3	0.39

^{a} $[\sigma(F_o)^2]^2 = [S^2(C + R^2B) + (pF_o^2)^2]/(Lp)^2$, where S is the scan rate, C is the integrated peak count, R is the ratio of scan to background counting time, B is the total background count, and p is a factor used to downweight intense reflections. For this structure, p = 0.04.

these conditions, the expected *cis*-$Cu^{II}N_2S_2$ monomeric complex of the above ligand did not precipitate. Instead, pale pink crystals of **1** formed and were collected by filtration.

A crystal from this preparation was used for the structure determination and was shown to have the composition $Cu_{0.07}H_{1.86}$(tet a)$(ClO_4)_2 \cdot 2(CH_3)_2SO$. Both preparations gave homogeneously colored pink crystals having identical morphologies and equivalent unit cell parameters, suggesting comparable levels of doping in all crystals from the same batch.

2. X-ray Diffraction Studies. Crystalline, pale pink plates of **1** suitable for X-ray diffraction were obtained from the indirect synthetic procedure. Crystal data, data collection, and refinement details are given in Table I. The Enraf-Nonius Structure Determination Package[8] was used for data collection, data processing, and structure solution. Intensity data were corrected for decay, Lp, and absorption (empirical) effects. Data having $I > 3\sigma(I)$ were used in the structure solution and refinement.

Table II. Atomic Coordinates and Equivalent Isotropic Thermal Parameters for **1**

	x	y	z	B or B_{eq},^{a} Å^2
Cu	0	0	0	2.3 (1)
N(1)	0.0200 (2)	0.1228 (2)	−0.0777 (3)	2.75 (5)
N(2)	0.1339 (2)	−0.0406 (2)	−0.0952 (3)	2.93 (5)
C(1)	0.0552 (2)	0.1527 (2)	−0.2182 (3)	3.03 (6)
C(2)	0.1577 (2)	0.0976 (2)	−0.2286 (3)	3.27 (6)
C(3)	0.1410 (2)	−0.0018 (2)	−0.2490 (3)	3.05 (6)
C(4)	0.1067 (3)	−0.1364 (2)	−0.0959 (4)	3.63 (7)
C(5)	−0.0825 (3)	0.1647 (2)	−0.0540 (4)	3.94 (7)
C(6)	−0.0409 (3)	0.1402 (2)	−0.3640 (4)	3.92 (7)
C(7)	0.0896 (3)	0.2504 (2)	−0.2071 (4)	4.40 (8)
C(8)	0.2340 (3)	−0.0454 (3)	−0.3069 (4)	4.15 (8)
C(9)	−0.3971 (3)	0.0963 (3)	−0.3495 (5)	5.3 (1)
C(10)	−0.5295 (3)	0.1339 (3)	−0.1612 (5)	5.8 (1)
Cl	−0.27369 (8)	0.36208 (6)	−0.1760 (1)	4.75 (2)
S	−0.45010 (7)	0.04398 (6)	−0.2041 (1)	4.28 (2)
O(1)	−0.1726 (2)	0.3853 (2)	−0.0753 (4)	6.88 (8)
O(2)	−0.2603 (3)	0.3186 (2)	−0.3100 (3)	7.36 (8)
O(3)	−0.3414 (2)	0.4379 (2)	−0.2200 (4)	7.51 (8)
O(4)	−0.3255 (3)	0.3018 (3)	−0.0944 (4)	9.9 (1)
O(5)	−0.3550 (2)	0.0338 (2)	−0.0641 (3)	6.24 (7)
H(N1)	0.063 (2)	0.135 (2)	−0.015 (3)	3.5
H(N21)	0.092 (2)	−0.021 (2)	−0.064 (4)	3.6
H(N22)	0.188 (2)	−0.033 (2)	−0.032 (4)	3.6
H(C3)	0.070 (2)	−0.006 (2)	−0.310 (3)	3.8
H(C21)	0.181 (2)	0.116 (2)	−0.295 (3)	4.0
H(C22)	0.223 (2)	0.112 (2)	−0.126 (4)	4.0
H(C41)	0.158 (2)	−0.166 (2)	−0.109 (3)	4.3
H(C42)	0.044 (3)	−0.147 (2)	−0.183 (3)	4.3
H(C51)	0.136 (3)	−0.146 (2)	0.129 (4)	4.5
H(C52)	0.080 (3)	−0.222 (2)	0.049 (4)	4.5
H(C61)	−0.071 (3)	0.078 (2)	−0.365 (4)	4.2
H(C62)	−0.090 (2)	0.183 (2)	−0.364 (3)	4.2
H(C63)	−0.020 (3)	0.140 (2)	−0.443 (4)	4.2
H(C71)	0.116 (3)	0.266 (2)	−0.286 (4)	5.3
H(C72)	0.030 (3)	0.284 (2)	−0.217 (4)	5.3
H(C73)	0.145 (3)	0.262 (2)	−0.131 (4)	5.3
H(C81)	0.313 (3)	−0.041 (2)	−0.227 (4)	4.9
H(C82)	0.216 (3)	−0.099 (2)	−0.338 (4)	4.9
H(C83)	0.232 (3)	−0.020 (2)	−0.392 (4)	4.9
H(C91)	−0.372 (3)	0.153 (2)	−0.307 (4)	5.7
H(C92)	−0.446 (3)	0.106 (2)	−0.403 (4)	5.7
H(C93)	−0.360 (3)	0.066 (3)	−0.373 (4)	5.7
H(C101)	−0.495 (3)	0.176 (2)	−0.134 (4)	6.6
H(C102)	−0.589 (3)	0.151 (3)	−0.231 (4)	6.6
H(C103)	−0.557 (3)	0.125 (3)	−0.081 (4)	6.6

^{a} The equivalent isotropic thermal parameter B_{eq} is defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

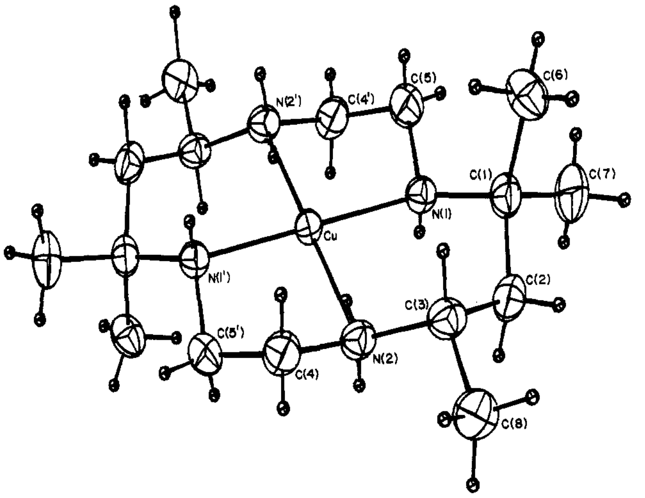

Figure 1. View of the dication in **1** with N(2) shown protonated and with a Cu atom shown in the dopant site.

The structure was solved by direct methods[9] and refined on F by using full-matrix least-squares techniques. An E map based on 400 phases revealed all atoms of the tet a ligand and most of the solvate atoms. The remaining solvate atoms were located on subsequent difference Fourier maps that also revealed a small peak at the origin assumed to be a Cu atom on a partially occupied site. From its peak height, the multiplicity of Cu was set at 0.035 (7% occupancy) and was subsequently refined [final value 0.035 (1)]. Following anisotropic refinement, 21 H atoms were located on a difference map and 3 were added at calculated positions. The remaining 0.93 H atom [H(N22)] required for charge balance was located unambiguously 0.87 Å from N(2) as the largest peak on a difference map and was added to the model with full multiplicity. H atom temperature factors were set as $B_H = 1.3B_{eq}(N)$, where N is the atom bonded to H. Several cycles of refinement, including H atom

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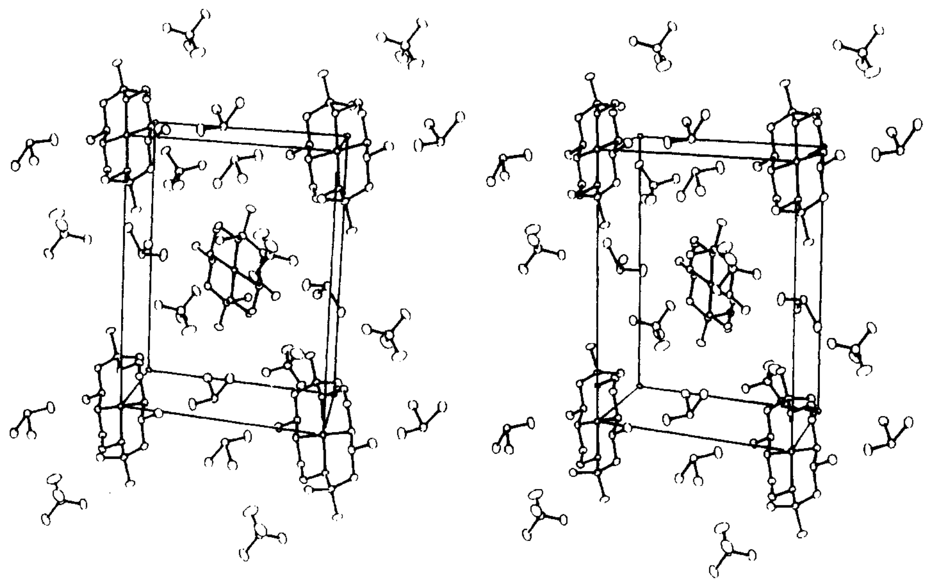


Figure 2. Stereoview of the unit cell contents. H atoms have been omitted for clarity.

Table III. Selected Bond Distances (Å) and Angles (deg) in **1**[a]

Cu–N(1)	2.015 (2)	C(3)–C(8)	1.514 (3)
Cu–N(2)	2.117 (2)	C(4)–C(5′)	1.486 (3)
N(1)–C(1)	1.479 (3)	Cl–O(1)	1.388 (2)
N(1)–C(5)	1.473 (3)	Cl–O(2)	1.396 (2)
N(2)–C(3)	1.498 (3)	Cl–O(3)	1.417 (2)
N(2)–C(4)	1.485 (3)	Cl–O(4)	1.407 (2)
C(1)–C(2)	1.535 (3)	S–O(5)	1.488 (2)
C(1)–C(6)	1.533 (3)	S–C(9)	1.762 (4)
C(1)–C(7)	1.533 (3)	S–C(10)	1.769 (3)
C(2)–C(3)	1.521 (3)		
N(1)–Cu–N(2)	87.78 (7)	N(1)–C(1)–C(7)	112.0 (1)
N(1)–Cu–N(2′)	92.22 (7)	C(2)–C(1)–C(6)	111.3 (2)
Cu–N(1)–C(1)	130.6 (1)	C(2)–C(1)–C(7)	108.0 (2)
Cu–N(1)–C(5)	99.7 (1)	C(6)–C(1)–C(7)	108.6 (2)
Cu–N(2)–C(3)	117.8 (1)	C(1)–C(2)–C(3)	117.0 (2)
Cu–N(2)–C(4)	95.1 (1)	N(2)–C(3)–C(2)	108.4 (2)
C(1)–N(1)–C(5)	115.1 (2)	N(2)–C(3)–C(8)	110.4 (2)
C(3)–N(2)–C(4)	116.2 (2)	C(2)–C(3)–C(8)	112.2 (2)
N(1)–C(1)–C(2)	107.4 (2)	N(2)–C(4)–C(5′)	111.8 (3)
N(1)–C(1)–C(6)	109.8 (2)	N(1)–C(5)–C(4′)	111.5 (2)

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

Table IV. Selected Torsion Angles and Possible Hydrogen-Bonding Contacts for **1**

N(1)–C(1)–C(2)–C(3)	62.2 (3)	C(3)–N(2)–C(4)–C(5′)	−170.2 (3)
C(6)–C(1)–C(2)–C(3)	−58.0 (3)	C(5)–N(1)–C(1)–C(2)	−176.3 (2)
C(7)–C(1)–C(2)–C(3)	−177.0 (3)	C(5)–N(1)–C(1)–C(6)	−55.1 (3)
C(1)–C(2)–C(3)–N(2)	−75.3 (3)	C(5)–N(1)–C(1)–C(7)	65.5 (3)
C(1)–C(2)–C(3)–C(8)	162.4 (3)	C(1)–N(1)–C(5)–C(4′)	−175.4 (3)
C(4)–N(2)–C(3)–C(2)	174.3 (2)	N(2)–C(4)–C(4′)–N(1′)	68.8 (4)
C(4)–N(2)–C(3)–C(8)	−62.3 (3)		

donor	hydrogen	acceptor[a]	D–H···A, deg	D···A, Å	H···A, Å	D–H, Å
N(2)	H(N22)	O(5)^{i}	157 (2)	2.748 (2)	2.03 (2)	0.77 (2)
N(1)	H(N1)	O(2)^{ii}	172 (2)	3.253 (3)	2.56 (2)	0.70 (2)
N(1)	H(N1)	O(3)^{ii}	134 (2)	3.328 (2)	2.80 (2)	0.70 (2)

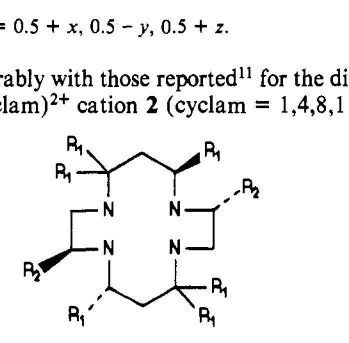
[a] i = $-x, -y, z$; ii = $0.5 + x, 0.5 - y, 0.5 + z$.

coordinates, led to convergence with $R_F = 0.057$, $R_{wF} = 0.078$, and GOF = 2.54. The highest seven peaks on a final difference map (0.31–0.39 e/Å^3) were located 0.84–0.99 Å from oxygen atoms O(1)–O(5). Final atomic parameters are listed in Table II. Tables of anisotropic thermal parameters and structure factors are available.[10]

3. Physical Measurements. Electronic spectra were recorded with a computer-interfaced spectrometer constructed by Aviv Associates around the monochromator of a Cary Model 14 spectrometer. EPR spectra of the polycrystalline Cu(II)-doped salt and glassed (80 K) DMF solutions of Cu(tet a)(ClO$_4$)$_2$ were measured with a Varian E-12 spectrometer calibrated with a Hewlett-Packard Model 5245-L frequency counter and a DPPH crystal (g = 2.0036).

Results and Discussion

The structure contains copper-doped diprotonated tet a cations [Cu$_{0.07}$H$_{1.86}$(tet a)]$^{2+}$ with C_i site symmetry separated by perchlorate anions and dimethyl sulfoxide solvate molecules. A view of the doped cation is shown in Figure 1, while a packing diagram, showing the interaction of the cation and anions, is given in Figure 2. Selected bond distances and angles are given in Table III. It should be emphasized that only 7% of the Cu sites are occupied and 93% of the cations are Cu-free diprotonated amines. The H atom positions show clearly that N(2) is protonated (quaternary) and N(1) is not. Bond distances in the cation are typical and compare favorably with those reported[11] for the diperchlorate salt of the H$_2$(cyclam)$^{2+}$ cation **2** (cyclam = 1,4,8,11-tetraazacyclotetradecane). Indeed, corresponding distances in the 14-membered macrocyclic rings in **2** and **1** differ by no more than 0.017 Å. The torsion angles (Table IV) indicate that the five- and six-membered rings that would be formed by treating the center of symmetry as a coordination site would have gauche and chair conformations, respectively. Thus, the observed conformation of the dication in **1** compares favorably with the low-energy forms of cyclam and of coordinated tet a calculated by Curtis et al.[12] and observed in several metal complexes.[12-14] In contrast, **2** would give rise to boat-shaped six-membered rings derived from a higher energy conformation of cyclam.[12]



(a) cyclam: R$_1$ = R$_2$ = H
(b) tet a: R$_1$ = CH$_3$; R$_2$ = H
(c) Me$_2$tet a: R$_1$ = R$_2$ = CH$_3$

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(10) Supplementary material.

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In the centrosymmetric dication **1**, the quaternary N(2) atom is 0.102 Å further from the center of symmetry than the ternary N(1) atom; a similar nonequivalency (0.13 Å) was observed for the corresponding N atoms in **2**. Assuming that the N positions for the Cu-containing cation are identical with those observed for the diprotonated cation **1**, the Cu–N distances are 2.117 (2) Å (quaternary) and 2.015 (2) Å (ternary). The latter distance is close to the values reported for Cu(Me$_2$tet a)(H$_2$O)$_2$(ClO$_4$)$_2$[13] (2.035 (3), 2.031 (4) Å) and Cu(tet a)(ClO$_4$)$_2$[14] (2.064 (3), 2.022 (2) Å). Although the Cu–N (quaternary) distance appears to be a bit long, we observed no evidence of disorder at the N(2) site, possibly owing to the low level of doping. Elongation of the Cu–N bond distances relative to those reported for the neat complexes is not consistent with the relatively large ligand field present at the dopant site (vide infra).

Both the perchlorate and DMSO lattice species are well-ordered. The Cl–O bond distances and angles lie in the range 1.388 (2)–1.417 (2) Å and 106.7 (2)–112.8 (1) deg, respectively. As might be expected, the O atom thermal parameters (Table II) are somewhat larger than those of the macrocycle atoms. A strong hydrogen-bonding interaction exists between the DMSO O(5) atom and the quaternary N(2) atom. Possible hydrogen bonds also exist between the ternary N(1) atom and two of the perchlorate O atoms, O(2) and O(3). These H-bonding interactions are summarized in Table IV.

The shortest possible apical bonding distance from the center of symmetry (the Cu(II) site) involves O(3) of the ClO$_4$ ion (Cu···O(3) = 2.905 (2) Å). This distance is substantially longer than the Cu–O distance (2.594 (5) Å) found for neat Cu(tet a)(ClO$_4$)$_2$[13] and for many related CuN$_4$ diperchlorate complexes whose axial coordination is not hindered by bulky equatorial ligands.[14] For the homologous Cu(Me$_2$tet a)(ClO$_4$)$_2$,[15] the apical Cu–O distance increases to 2.815 (5) Å, presumably owing to steric effects arising from the additional methyl groups. For the tetrakis(1,4,5-trimethylimidazole)copper(II) diperchlorate complex, apical ligation has been completely suppressed by steric effects; the shortest Cu···O(ClO$_4$) contacts exceed 4 Å.[16] There is no crystallographic evidence to suggest that the long axial Cu···O distance in the doped material is an artifact due to disorder; this view is supported by the spectroscopic evidence presented below. In other words, the position of the lattice perchlorate group is in harmony with the H-bonding requirements of the diprotonated tet a cation and is not locally perturbed by weak apical interactions with the copper dopant.

Spectroscopic studies of the solid doped material reveal that the pink color arises from a symmetrical LF absorption centered at 485 (1) nm. This absorption is considerably blue-shifted from that of the neat Cu(tet a)(ClO$_4$)$_2$ complex, whose mull spectra at room temperature consist of a prominent LF absorption at 506 (1) nm. Red solutions of the complex in DMSO exhibit the LF absorption at 528 (1) nm ($\epsilon = 134$). The highest energy LF absorptions of Cu(II) complexes are exhibited by planar CuN$_4$ chromophores; the presence of additional apical bonding causes the LF absorptions of the resulting square-pyramidal and tetragonal Cu(II) species to red-shift.[17] We attribute the anomalously high LF absorption to the above-noted *attenuation* of the apical Cu(II)···O(ClO$_4$) interactions, which are constrained by the nature of the host lattice.

The doped material exhibits EPR spectra typical of those for magnetically dilute tetragonal Cu(II) systems. There is no indication that more than one type of lattice site is occupied (i.e., only a single set of Cu-hyperfine absorptions on the $g_\parallel$ signal is observed). The appearances of the spectra are similar to those of the often studied bis(ethylenediamine)copper(II) and related CuN$_4$ species, which exhibit a prominent angular anomaly at high field.[18,19] The spectral parameters of the doped solid at room temperature are $g_\parallel = 2.185$, $g_\perp =$ ca. 2.05, and $A_\parallel^{Cu} = 203 \times 10^{-4}$ cm^{-1}. The spectra of approximately 4.5 mM Cu(tet a)(ClO$_4$)$_2$ in glassed DMF (80 K) are essentially identical, with $g_\parallel = 2.192$, $g_\perp =$ ca. 2.06, and $A_\parallel^{Cu} = 203 \times 10^{-4}$ cm^{-1}. In contrast to the electronic spectral data, the EPR spectra are insensitive to whatever differences may exist between these Cu(II) chromophores present in the doped material and in DMF solutions.

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Supplementary Material Available: Table SI, listing anisotropic thermal parameters (1 page); a table of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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