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Comparison of Copper(II) Complexes Containing Various Saturated 12-Membered Macrocycles

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Copper(II) complexes have been prepared containing the 12-membered cyclic ring 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane ($Me_4[12]aneN_4$). They include $[Cu(Me_4[12]aneN_4)Cl]Cl\cdot 1.5H_2O$ and $[Cu(Me_4[12]aneN_4)H_2O](NO_3)_2\cdot H_2O$. $[Cu(Me_4[12]aneN_4)H_2O](NO_3)_2\cdot H_2O$ has been characterized by X-ray crystallography as well as by elemental analysis and spectroscopically. This complex crystallizes in the space group $P2_1/c$ with $a = 8.849(1)$, $b = 15.724(2)$, $c = 14.946(3)$ Å, $\beta = 91.09(1)°$, $Z = 4$, and $R = 0.057$ for 2318 observed reflections. The copper atom has a square pyramidal geometry with the copper 0.50 Å above the N_4 plane of the macrocycle. $[Cu(Me_4[12]aneN_4)Cl]Cl\cdot 1.5H_2O$ also has a square pyramidal geometry on the basis of a comparison of physical properties with the known square pyramidal $[Cu(bz_4[12]aneN_4)Cl]Cl\cdot 0.5H_2O$. A comparison was made of the electrochemistry of all the above complexes as well as $[Cu(bz_4[12]aneN_4)(NO_3)](NO_3)\cdot H_2O$, $[Cu([12]aneN_4)Cl]Cl$, and $[Cu([12]aneN_4)(NO_3)]NO_3$. All these copper(II) complexes are easier to reduce than copper(II) complexes containing larger sized tetraaza macrocyclic ligands. Copper(II) complexes containing twelve-membered tetraaza macrocycles with tertiary nitrogens are also easier to reduce than similar complexes containing secondary nitrogens. The copper(I) complexes containing 12-membered rings are more inert with regards to decomposition than the copper(I) complexes containing the 14-membered ring. The copper(I) complexes containing 12-membered rings with tertiary nitrogen groups are more stable than those containing a similar ring system but having secondary nitrogen groups.

Introduction

Twelve-membered saturated tetradentate macrocyclic ligands cannot readily bond to divalent transition metal ions in a co-planar manner.[1-8] However, the donor atoms of 14-membered or larger saturated tetradentate macrocyclic ligands can bond coplanar to divalent transition metals.[9-12] Currently the only systematic studies on the effects of structural parameters, such as steric factors, ring size and the influence of the coordinated apical ligand on the redox properties of copper(II) complexes which contain tetraaza cyclic ligands have been done on complexes in which the copper(II) is in the same plane as the donor atoms from the tetraaza macrocyclic ligand.[13-17] However, there have not been any systematic studies of copper(II) complexes in which the copper(II) was not in the plane of the tetraaza cyclic ligand. Employing 12-membered tetraaza cyclic ligands that cannot coordinate in a co-planar manner with copper(II) allows us to make useful comparisons with similar tetraaza cyclic ligands that do bond in a co-planar manner with the copper(II). Fabbrizzi and co-workers[13-17] have already demonstrated that copper(II) complexes can be reduced at higher positive potentials by employing tetraaza macrocycles which have either more or fewer atoms in their ring system than the 14-membered macrocyclic ligand. By varying substituents on the nitrogens and the nature of the apical ligands we will observe changes in the physical and chemical properties as well as the stereochemistry of the resulting complexes.

These twelve-membered tetraaza macrocycle copper(II) complexes serve as good models for testing the entatic state hypothesis for enzymatic reactions.[18] This hypothesis suggests that the active site in certain enzymes has a geometry that approximates the geometry of the transition state for the reactions in which that enzyme is involved. As a result these enzymatic reactions require low activation energy. The entatic state hypothesis requires the predisposition of donor atoms around the metal ion in the precursor metallo enzyme so that this molecule can be readily converted to the geometry of the product molecule with minimal alterations in the geometry around the metal ion. An example of this was noted by Corfield et al.[19] on a model system. They attributed the large self-exchange electron transfer rate constant for the copper(II) and copper(I) complexes of 1,4,7,10,13-pentathiacyclopentadecane to their relatively similar crystal structures.[19] The above Cu(I) complex differs from the square pyramidal Cu(II) complex by only one Cu–S bond broken in the basal plane of the copper(II) complex. In this example it appears that the Franck–Condon barrier for electron transfer is small and this small energy barrier results in a small activation energy.

The Franck–Condon barrier for the electron transfer reactions of $[Cu^{II}(R_4[12]aneN_4)]^{2+}$ to $[Cu^{I}(R_4[12]aneN_4)]^{1+}$ is expected

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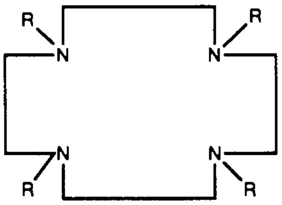
to be small if the geometries of the two complexes are similar. By breaking only one copper to nitrogen bond in $[Cu^{II}(R_4[12]aneN_4)]^{2+}$ upon electron reduction should result in a distorted tetrahedral geometry. Copper(I) complexes commonly have a tetrahedral geometry. This idea must remain speculative because the $Cu^{I}(R_4[12]aneN_4)$ complexes are too labile to permit growth of crystals and therefore crystal structures cannot be obtained. Nevertheless, we do know that the copper(II) ions in $[Cu^{II}(R_4[12]aneN_4)]^{2+}$ complexes are not in the plane of the $R_4[12]aneN_4$ donor atoms.[2,20] Therefore, the copper ion does not have to leave the plane of the four donor atoms upon electron transfer. Organic groups on the nitrogens, such as methyl or benzyl groups, should make conformational changes even more difficult. Such rigid geometries imposed by these ligands should, in theory, result in similar geometries of both the Cu(II) and Cu(I) complexes.

At present, the only known copper(II) complexes containing the 12-membered cyclic ring, 1,4,7,10-tetraazacyclododecane ($[12]aneN_4$), are $[Cu([12]aneN_4)NO_3]NO_3$ and $[Cu([12]aneN_4)Cl]Cl$.[1]



R=H, [12]ane N_4
$R=CH_3$, $Me_4[12]aneN_4$
$R=CH_2C_6H_5$, $bz_4[12]aneN_4$

Similar complexes of copper(II) with 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane ($Me_4[12]aneN_4$) and 1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane ($bz_4[12]aneN_4$) have also been prepared, e.g., $[Cu(Me_4[12]aneN_4)](ClO_4)_2$, $[Cu(bz_4[12]aneN_4)(NO_3)]NO_3 \cdot H_2O$ and $[Cu(bz_4[12]aneN_4)Cl]Cl \cdot 0.5H_2O$.[1,21] For the purposes of this study we have also prepared and characterized $[Cu(Me_4[12]aneN_4)Cl]Cl \cdot 1.5H_2O$ and $[Cu(Me_4[12]aneN_4)H_2O](NO_3)_2 \cdot H_2O$.

Experimental Section

Materials. $[12]aneN_4$, $Me_4[12]aneN_4$, $bz_4[12]aneN_4$, $[Cu([12]aneN_4)NO_3]NO_3$, $[Cu([12]aneN_4)Cl]Cl$, $[Cu(bz_4[12]aneN_4)(NO_3)]NO_3 \cdot H_2O$ and $[Cu(bz_4[12]aneN_4)Cl]Cl \cdot 0.5H_2O$ were prepared by published procedures.[1,21]

Preparation of Copper(II) Complexes. Chloro(1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane)copper(II) Chloride Trihemihydrate, $[Cu(Me_4[12]aneN_4)Cl]Cl \cdot 1.5H_2O$. $CuCl_2 \cdot 2H_2O$ (0.1930 g, 1.132 mmol) was placed into a round bottom flask and dissolved in 25 mL of absolute ethanol. $Me_4[12]aneN_4$ (0.2384 g, 1.043 mmol) dissolved in five mLs of absolute ethanol (transparent yellow) was added over 15 s to the above solution. The solution went from a dark olive color to a light blue. The mixture was stirred for one hour.

The resulting blue solution was concentrated by rotary evaporation to a deep blue oil. Diethyl ether was added dropwise to the oil until a powder blue solid precipitated from solution. After suction filtration the solid was dissolved in a minimal amount of hot absolute ethanol and diethyl ether was added dropwise to the ethanol to give a light blue solid. The solid was suction-filtered and rinsed with diethyl ether before placing it in a vacuum desiccator containing P_2O_5 and dried under vacuum for two days. Isolated 0.1985 grams (48.41% yield) Anal. Calcd for $C_{12}H_{31}N_4Cl_2O_{1.5}Cu$: C, 36.97; H, 8.02; N, 14.37; Cu, 16.3. Found: C, 36.93; H, 7.67; N, 14.45; Cu, 16.2.

Aqua(1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane)copper(II) Nitrate Hydrate, $[Cu(Me_4[12]aneN_4)(H_2O)](NO_3)_2 \cdot H_2O$. $Cu(NO_3)_2 \cdot 2H_2O$(0.2528 g, 1.046 mmol) was placed in a 50 mL one-neck round bottom flask and dissolved with 25 mL of absolute ethanol. $Me_4[12]aneN_4$ (0.2338 g, 1.025 mmol), dissolved in 5 mL of absolute ethanol, was added to the above solution over a one minute period. The initially light blue, solution turned blue then royal-blue during the addition of the ligand. The contents of the flask were then stirred for one hour.

After one hour of stirring the royal blue solution was placed in a 125 mL Erlenmeyer flask, sealed with a stopper and stored in the refrigerator overnight. Dark blue slate like crystals were observed the next day. The crystals were suction-filtered using a glass frit and dissolved in a minimal amount of hot absolute ethanol. Diethyl ether was added dropwise to the flask until a medium blue precipitate was observed. The solid was suction-filtered and rinsed with diethyl ether before placing in a vacuum desiccator containing P_2O_5 and the solid was dried under vacuum for two days. Isolated 0.365 grams (78.43% yield) of a medium blue solid. Anal. Calcd for $C_{12}H_{32}N_4O_8Cu$: C, 31.89; H, 7.14; N, 18.59; Cu, 14.1. Found: C, 32.32; H, 7.26; N, 18.76; Cu, 13.6.

Solvent Distillation. Acetonitrile was distilled twice; first it was refluxed for three hours, then distilled from calcium hydride, and then refluxed and distilled from phosphorous pentoxide (five grams per liter, under nitrogen).

Instrumentation. Magnetic moments were determined using the Faraday method. Data were obtained using a Cahn Electrobalance Model RG Np. 2000 at room temperature; $Hg[Co(SCN)_4]$ was used as the standard. Periodic checks of accuracy as well as precision were done against potassium hexacyanoferrate(III) (which has a $\mu_{eff} = 2.40\ \mu_B$), the average value obtained was 2.39 μ_B.

Ultraviolet and visible absorption spectra were recorded either on a Cary 219 spectrophotometer or a Beckman Acta IV. Solid spectra were obtained by grinding 10–20 mg of complex (in 1–2 drops of mineral oil) with a mortar and pestle. The mull was then smeared on Whatman No. 1 filter paper.

Infrared spectra were taken on a Nicolet-20DX spectrophotometer either as KBr pellets or Nujol mulls.

Conductivity measurements were obtained at 25° using an Industrial Instrument conductivity bridge model RO-18; the cell constant was determined using 0.100 M potassium chloride solution.

Chemical Analysis. All C, H, and N analyses were obtained from Galbraith Laboratories, Knoxville, TN. Copper analyses were performed using a Perkin-Elmer 306 atomic absorption spectrophotometer which was optimized using the appropriate standards from Alfa products.

Electrochemistry. Electrochemical analyses were done in acetonitrile using a Princeton Applied Research Model 173 three electrode potentiostat and a Model 175 Universal programmer. The concentration of the metal complexes used in the electrochemical analyses varied between 0.5 and 1.5 mmolar; the supporting electrolyte was 0.1 M tetrabutylammonium perchlorate. All values are reported with respect to a saturated calomel electrode (SCE).

An IBM voltammetric cell was used for both the cyclic voltammetric and coulometric analysis. All electrochemical studies were done under dry nitrogen.

The voltammograms obtained at scan rates less than 1.0 V/s were recorded on a Houston Instrument Model 2000 Omnigraphic X-Y recorder. Coulometry in acetonitrile was carried out with the PARC EG&G and a Princeton Applied research Model 179 digital coulometer.

Cyclic voltammetric analyses of all complexes were performed using a coiled platinum wire (extending from the end of its glass tubing sleeve) as the counter electrode and a platinum disk sealed into a glass tube as the working electrode.

Crystallography. A saturated solution of aqua(1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane)copper(II) nitrate hydrate, $[Cu(Me_4[12]aneN_4)(H_2O)](NO_3)_2 \cdot H_2O$, was dissolved in ethanol and placed in a closed desiccator over diethyl ether. After several days the compound crystallized as blue rods. Preliminary examination and data collection were performed at 21 °C with Mo Kα radiation (λ = 0.710 73 Å) on an Enraf-Nonius CAD4 diffractometer. Intensities were corrected for absorption (μ = 11.0 cm^{-1}) and decay. The structure was solved by conventional Patterson and Fourier methods and refined on F in full-matrix least-squares to R = 0.057. In the final cycles of refinement, the hydrogen atoms of the macrocycle were included as riding atoms in ideal positions with isotropic temperature factors set to 1.3U(equiv) of the bonding atom. The hydrogen atoms of the water molecules were not found. From the thermal parameters, one of the nitrate groups appears to be disordered; however, no satisfactory disorder model could be found. Scattering factors were taken from Cromer and Waber[22] and anomalous dispersion coefficients were those of Cromer.[23] The crystal data,

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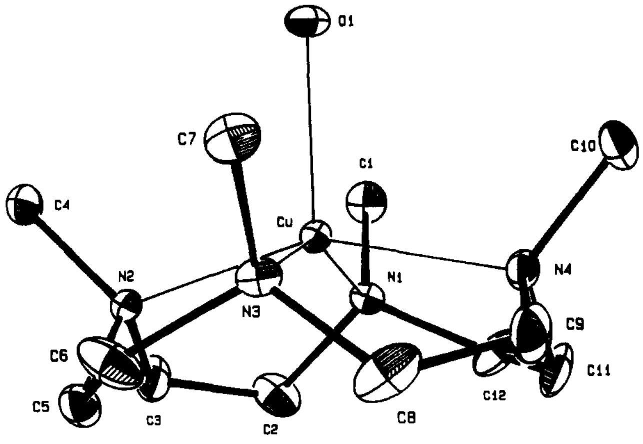

Figure 1. View of the $[Cu(Me_4[12]aneN_4)H_2O]^{2+}$ cation. (Hydrogen atoms are not shown.)

Table I. Crystallographic Data for $[Cu(Me_4[12]aneN_4)H_2O](NO_3)_2{\cdot}H_2O$

formula	$C_{12}H_{32}CuN_6O_8$
mol wt	451.96
F(000)	956
dimensions	0.28 × 0.18 × 0.16 mm
peak width at half-height	0.18°
λ(Mo Kα)	0.710 73 Å
temp	21 ± 1°
space group	$P2_1/c$
a	8.849(1) Å
b	15.734(2) Å
c	14.950(3) Å
β	91.09(1)°
V	2081.1 Å^3
Z	4
ρ	1.44 g/cm^3
μ	11.0 cm^{-1}
scan type	ω–2θ
$2\theta_{max}$	52.0°
monochromator	graphite cryst, incident beam
attenuator	Zr foil, factor 19.5
take off angle	2.8°
detecture aperture	1.5–1.6 mm horizontal, 4.0 mm vertical
cryst-detector dist	21 cm
scan rate	1–7°/min (in Ω)
scan width, deg	0.8 + 0.34 tan θ
reflcns measd:	5460 tot., 4236 unique
solution	Patterson method
hydrogen atoms	refined as riding atoms
refinement	full-matrix least-squares
minimization function	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
weights	$4F_o^2/\sigma^2(F_o^2)$
reflcns included	2318 with $F_o > 3.0\sigma(F_o^2)$
params refined	244
unweighted agreement factor	0.057
weighted agreement factor	0.071

measurement methods, structure solution, and refinement are summarized in Table I. All calculations were carried out on a VAX 11/750 using VAXSDP.[24]

Final atomic parameters are reported in Table II, and selected derived bond lengths and angles in Tables III and IV. A normal ORTEP[25] plot of the complex cation is given in Figure 1. A complete structure report including tables of observed and calculated structure factors, anisotropic temperature factors, bond lengths, and angles is available on request.

Results

$[Cu(Me_4[12]aneN_4)H_2O](NO_3)_2{\cdot}H_2O$ has a square-pyramidal geometry with the copper bonded above the plane of the four nitrogen atoms (Figure 1). The methyl groups on the nitrogens are all oriented on the same side of the N_4 plane. Water is bonded 2.144 Å from the copper and is on the same side of the plane as the four methyl groups. In DMF, DMSO, CH_3CN and water, $[Cu(Me_4[12]aneN_4)H_2O](NO_3)_2{\cdot}H_2O$ is a two-to-one electrolyte; and therefore, the nitrates are also not bonded to the copper(II)

Table II. Positional Parameters and Their Estimated Standard Deviations

atom	*x*	*y*	*x*	*B* (Å^2)[a]
Cu	0.20861(7)	0.08233(4)	0.21815(4)	3.56(1)
O1	0.1682(5)	−0.0402(3)	0.1595(3)	5.7(1)
O2	0.3660(6)	0.6676(3)	0.6383(4)	8.7(2)
O3	0.2699(6)	0.4587(3)	0.3501(5)	9.1(2)
O4	0.3196(5)	0.3286(3)	0.3341(5)	9.4(2)
O5	0.0977(5)	0.3682(3)	0.3494(5)	9.3(2)
O6	0.3100(9)	0.6109(5)	−0.9741(5)	12.8(3)
O7	0.3390(9)	0.7309(6)	−1.0177(6)	18.0(3)
O8	0.1658(8)	0.6523(5)	−1.0637(5)	14.3(2)
N1	0.3637(5)	0.1374(3)	0.1377(3)	4.4(1)
N2	0.3809(5)	0.0670(3)	0.3090(3)	4.3(1)
N3	0.0682(5)	0.0855(3)	0.3246(3)	4.8(1)
N4	0.0536(5)	0.1554(3)	0.1526(3)	4.9(1)
N5	0.2699(6)	0.6717(4)	−1.0201(4)	6.2(1)
N6	0.2298(6)	0.3855(3)	0.3425(4)	5.0(1)
C1	0.4293(8)	0.0822(5)	0.0698(5)	6.9(2)
C2	0.4778(8)	0.1691(5)	0.2001(5)	8.1(2)
C3	0.5114(9)	0.1189(5)	0.2732(6)	9.0(2)
C4	0.4341(8)	−0.0204(4)	0.3257(5)	6.5(2)
C5	0.3236(8)	0.1068(5)	0.3894(5)	7.4(2)
C6	0.1708(9)	0.0890(6)	0.4052(5)	9.6(3)
C7	−0.0340(8)	0.0133(5)	0.3375(5)	6.5(2)
C8	−0.0161(9)	0.1628(5)	0.3100(5)	9.2(2)
C9	−0.0572(9)	0.1803(6)	0.2222(5)	9.4(2)
C10	−0.0320(9)	0.1155(5)	0.0791(5)	7.7(2)
C11	0.1414(8)	0.2284(5)	0.1236(6)	9.5(2)
C12	0.2864(8)	0.2012(5)	0.0930(5)	7.9(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(8\pi^2/3) \times$ Tr(orthogonalized U tensor).

Table III. Bond Distances (Å)[a]

Cu–O1	2.145(4)	O7–N5	1.11(1)	N3–C7	1.466(9)
Cu–N1	2.036(5)	O8–N5	1.159(9)	N3–C8	1.441(9)
Cu–N2	2.037(5)	N1–C1	1.464(9)	N4–C9	1.50(1)
Cu–N3	2.038(5)	N1–C2	1.450(9)	N4–C10	1.464(9)
Cu–N4	2.028(5)	N1–C12	1.486(9)	N4–C11	1.456(9)
O3–N6	1.209(7)	N2–C3	1.520(9)	C2–C3	1.38(1)
O4–N6	1.206(7)	N2–C4	1.473(8)	C5–C6	1.40(1)
O5–N6	1.206(7)	N2–C5	1.455(9)	C8–C9	1.38(1)
O6–N5	1.23(1)	N3–C6	1.497(9)	C11–C12	1.40(1)

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

Table IV. Selected Angles (deg)[a]

O1–Cu–N1	104.5(2)	Cu–N2–C3	105.4(4)	C9–N4–C11	111.2(6)
O1–Cu–N2	106.4(2)	Cu–N2–C4	117.1(4)	C10–N4–C11	112.7(6)
O1–Cu–N3	104.0(2)	Cu–N2–C5	103.4(4)	O6–N5–O7	118.7(7)
O1–Cu–N4	101.9(2)	C3–N2–C4	108.6(5)	O6–N5–O8	109.2(7)
N1–Cu–N2	86.6(2)	C3–N2–C5	109.8(5)	O7–N5–O8	131.9(8)
N1–Cu–N3	151.5(2)	C4–N2–C5	112.2(5)	O3–N6–O4	121.6(5)
N1–Cu–N4	86.0(2)	Cu–N3–C6	105.1(4)	O3–N6–O5	119.4(6)
N2–Cu–N3	86.7(2)	Cu–N3–C7	118.1(4)	O4–N6–O5	118.9(5)
N2–Cu–N4	151.6(2)	Cu–N3–C8	102.9(4)	N1–C2–C3	116.8(7)
N3–Cu–N4	86.9(2)	C6–N3–C7	106.8(5)	N2–C3–C2	115.7(6)
Cu–N1–C1	115.9(4)	C6–N3–C8	113.3(6)	N2–C5–C6	113.9(6)
Cu–N1–C2	103.6(4)	C7–N3–C8	110.8(5)	N3–C6–C5	116.3(6)
Cu–N1–C12	106.5(4)	Cu–N4–C9	105.0(4)	N3–C8–C9	116.0(7)
C1–N1–C2	111.7(5)	Cu–N4–C10	117.0(4)	N4–C9–C8	116.4(7)
C1–N1–C12	109.3(5)	Cu–N4–C11	103.4(4)	N4–C11–C12	115.7(6)
C2–N1–C12	109.4(5)	C9–N4–C10	107.3(5)	N1–C12–C11	115.3(7)

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

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Table V. Electronic Spectral Data for the Complexes

compd	solid: λ_{max} (nm)	H$_2$O: λ_{max} (nm) (ϵ, M^{-1} cm^{-1})	ref
[Cu([12]aneN$_4$)NO$_3$]NO$_3$	595	590 (257)	12
[Cu(bz$_4$[12]aneN$_4$)](NO$_3$)$_2$·H$_2$O	625	614 (500)	12
[Cu(Me$_4$[12]aneN$_4$)H$_2$O](NO$_3$)$_2$·H$_2$O	611	602 (499)	this study
[Cu([12]aneN$_4$)Cl]Cl·H$_2$O	770	594 (271)	12
[Cu(Me$_4$[12]aneN$_4$)Cl]Cl·1.5H$_2$O	775	602 (499)	this study
[Cu(bz$_4$[12]aneN$_4$)Cl]Cl·0.5H$_2$O		615 (640)	12

Table VI. Electrochemical Data of Copper(II) Complexes Containing 12-Membered Macrocyclic Ligand in CH$_3$CN versus SEC at 25 °C

rate (mV s^{-1})	E_a (V)	E_c (V)	ΔE (V)	$E_{1/2}{}^a$ (V)	i_a (μA)	i_c (μA)	i_a/i_c
			[Cu[12]aneN$_4$](NO$_3$)$_2$·H$_2$O				
200		–0.54				17.5	
200		–1.13				25.7	
			Cu([12]aneN$_4$)Cl$_2$				
200		–0.62				6	
200		–1.24				4	
			[Cu(Me$_4$[12]aneN$_4$)(H$_2$O)](NO$_3$)$_2$·H$_2$O				
500	–0.25	–0.34	0.09	–0.30	38	70	0.54
200	–0.26	–0.34	0.09	–0.30	14	48	0.29
200	–0.49	–0.59	0.10	–0.54	18	58	0.31
100	–0.25	–0.33	0.08	–0.29	14	45	0.31
100	–0.50	–0.59	0.09	–0.55	6	56	0.11
			[Cu(Me$_4$[12]aneN$_4$)Cl]Cl·1.5H$_2$O				
500	–0.51	–0.625	0.105	–0.57	38	145	0.26
200	–0.45	–0.580	0.130	–0.52	40	98	0.41
100	–0.50	–0.600	0.100	–0.55	33	72	0.46
50	–0.48	–0.570	0.090	–0.53	35	56	0.63
			Cu(tb$_4$[12]aneN$_j$(NO$_3$)$_2$·H$_2$O				
100	–0.09	–0.16	0.07	–0.125	13	18	0.72
100	–0.30	–0.40	0.10	–0.35	7	9	0.78
100	–0.94	–1.20	0.26	–1.07	10	20	0.50
200	–0.09	–0.17	0.08	–0.13	18.5	23.5	0.78
200	–0.30	0.41	0.11	–0.35	6	13.5	0.44
			Cu(tb$_4$[12]aneN$_4$)Cl$_2$·0.5H$_2$O				
100		–0.40				40	
100	–0.30				20		
100	–0.15						
200	–0.3	–0.40			15	23	

[a] $E_{1/2}$ is the average of the cathodic and anodic peak potentials.

in solution. The magnetic moment, 1.75 μ_B, is consistent with with one unpaired electron and divalent copper.

Although we do not have a crystal structure of [Cu(Me$_4$[12]aneN$_4$)Cl]Cl·1.5H$_2$O, the electronic spectra of this complex and [Cu(bz$_4$[12]aneN$_4$)Cl]Cl·0.5H$_2$O are similar (Table V). [Cu(bz$_4$[12]aneN$_4$)Cl]Cl·0.5H$_2$O has a structure similar to [Cu(Me$_4$[12]aneN$_4$)H$_2$O](NO$_3$)$_2$·H$_2$O except that a chloride is bonded to the copper instead of a water molecule.[12] Since [Cu(Me$_4$[12]aneN$_4$)Cl]Cl·1.5H$_2$O is a one-to-one electrolyte in DMF, DMSO, and CH$_3$CN, one chloride must be bonded to the copper(II) while the other chloride functions as a counteranion. It is reasonable to assume that the chloride is also bonded to the copper(II) in the solid state. The magnetic moment of [Cu(Me$_4$[12]aneN$_4$)Cl]Cl·1.5H$_2$O is 1.84 μ_B at 25 °C, and this is consistent with the presence of one unpaired electron and a positive two oxidation state for copper.

The cyclic voltammogram of [Cu([12]aneN$_4$)NO$_3$]NO$_3$ in CH$_3$CN run at a sweep rate of 200 mV s^{-1} exhibited cathodic peaks at –0.54 V and –1.13 V (Table VI). No coupled oxidation peak was observed if the switching potential is set just beyond the –0.54 V peak. In fact no anodic peaks were observed between ±2 V regardless of the position of the switching potentials employed within these limits.

Demetalation does not occur after reduction even at voltages past –1.5 V. If rapid demetalation did occur, Cu(I) would be liberated. Free copper(I) should be reduced in acetonitrile to Cu(0) at –0.55 V. If copper metal plated out on the electrode a stripping peak involving the two electron oxidation of copper should be observed. This was not observed. Also the controlled-potential coulometric measurements at –0.6 V should show the consumption of more than one electron per mole of copper if free Cu(I) is produced on coulometic time frame. The liberated Cu(I) would consume a second electron. However, controlled-potential electrolysis at –0.6 V involved the consumption of one electron per copper. Therefore we conclude that rapid demetalation did not occur.

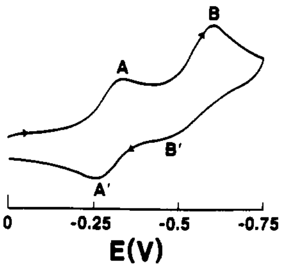

Figure 2. Cyclic voltammogram of [Cu(Me$_4$[12]aneN$_4$)H$_2$O](NO$_3$)$_2$·H$_2$O versus SCE at a platinum electrode at a scan rate of 200 mV s^{-1}, 25 °C in CH$_3$CN with 0.1 M (TMA)ClO$_4$.

The cyclic voltammogram of [Cu([12]aneN$_4$)Cl]Cl[26] looks similar to that of [Cu([12]aneN$_4$)(NO$_3$)]NO$_3$.[26] Two reduction reactions are observed at –0.62 V and –1.24 V and there is no indication of any oxidation reaction between 0 and –2 V.

The cyclic voltammogram of Cu(Me$_4$[12]aneN$_4$)H$_2$O](NO$_3$)$_2$·H$_2$O showed two cathodic electron-transfer processes at –0.34 V (peak A) and –0.59 V (peak B) (Figure 2). However, when the scan was reversed at –0.75 V two anodic processes were observed at –0.49 V and –0.26 V (Figure 2). These two oxidations processes appear to be coupled to the above reductions. Employing a switching potential of –2 V and a scan rate of 200 mV s^{-1} i_a/i_c is 0.29 for first electron transfer reaction. However, employing the same switching potential but a scan rate of 1000 mV s^{-1} the i_a/i_c increases to 0.46. If, however, the switching potential is set at –0.75 V and the scan rate is set at 200 mV s^{-1} i_a/i_c increases to 0.55. Such data suggest that a chemical reaction must occur after the first electron transfer reaction. The approximate $E_{1/2}$ for first electron transfer reaction is –0.3 V. i_a/i_c for the second electron transfer process at 200 mV s^{-1} is difficult to measure. The approximate $E_{1/2}$ for the second electron transfer reaction is –0.54 V. Controlled-potential coulometry at –0.6 V indicates that 1.04 electrons are transferred. However, controlled potential coulometry at –0.3 V indicated that only 0.4 electrons per mole of complex were consumed. We do not have an adequate explanation for the 0.4 electrons observed for the first electron transfer reaction. Upon the addition of excess chloride ions to a solution of [Cu(Me$_4$[12]aneN$_4$)(H$_2$O)](NO$_3$)$_2$·H$_2$O in CH$_3$CN peaks A and B disappeared and a new cathodic peak appeared at –0.62 V. A similar cathodic peak was observed for [Cu(Me$_4$[12]aneN$_4$)Cl]Cl·1.5H$_2$O. These data suggest that a copper(II) to chloride bond was formed in this solution.

Only one broad unsymmetrical cathodic peak for the reduction of [Cu(Me$_4$[12]aneN$_4$)Cl]Cl·1.5H$_2$O is observed at –0.58 V. Since this peak is broad and unsymmetrical it is possible that several reduction processes may exist at voltages more negative than –0.58 V. Coulometric measurements done on [Cu(Me$_4$[12]aneN$_4$)Cl]Cl·1.5H$_2$O at –0.65 V indicated that one electron was consumed.

Two anodic peaks at –0.29 V and –0.45 V were observed for [Cu(Me$_4$[12]aneN$_4$)Cl]Cl·1.5H$_2$O. However as the switching

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(26) These complexes appear to be one to one electrolytes in organic solvents. However, the molar conductivity for [Cu([12]aneN$_4$)NO$_3$]NO$_3$ is relatively high for a one to one electrolyte.[1] This suggest that is is likely that more than one species exist in solution.

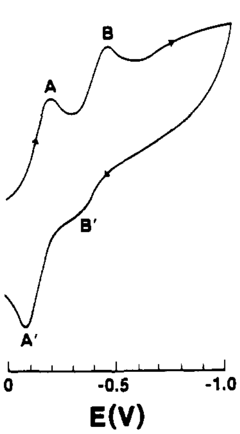

Figure 3. Cyclic voltammogram of [Cu(tb$_4$[12]aneN$_4$)H$_2$O](NO$_3$)$_2$·H$_2$O versus SCE at a platinum electrode at a scan rate of 200 mV s^{-1}, 25 °C in CH$_3$CN with 0.1 M (TBA)ClO$_4$.

potential becomes more negative, the relative peak heights of the anodic peak is altered. This suggest that a chemical reaction must have occurred after the one electron reduction of the starting compound. The resulting [Cu(Me$_4$[12]aneN$_4$)Cl]^0 should be unstable and as a result either the chloride might dissociate from the copper(I) or a nitrogen to copper bond might break.

[Cu(bz$_4$[12]aneN$_4$)](NO$_3$)]NO$_3$·H$_2$O showed reduction peaks at −0.17 V, −0.41 V and −1.20 V at a scan rate of 200 mV s^{-1} but no anodic peaks within the same range of voltages. However, if the scan is reversed at −1.0 V instead of −2 V, anodic peaks were observed at −0.30 V, −0.09 V (Figure 3). i_a/i_c for the first electron transfer reaction is 0.78 and i_a/i_c for the second electron transfer reaction is 0.43. The approximate $E_{1/2}$ values are −0.13 V and −0.35 V. No stripping peak was observed. Electrolysis data obtained at −0.23 V indicates that this process involves only 0.24 electrons per mole of copper. We do not have an adequate explanation for this observation.

[Cu(bz$_4$[12]aneN$_4$)]Cl$_2$·0.5H$_2$O showed cyclic voltammetric cathodic response at −0.4 V and upon reversing the scans resulted in voltammetric anodic responses at −0.3 V and −0.15 V (Table VI).

Discussion

[Cu(Me$_4$[12]aneN$_4$)H$_2$O](NO$_3$)$_2$·H$_2$O, [Cu([12]aneN$_4$)-NO$_3$]NO$_3$ and [Cu(bz$_4$[12]aneN$_4$)Cl]Cl·0.5H$_2$O have square pyramidal geometries and the *N*-methyl and *N*-benzyl groups are oriented on the same side of the N$_4$ plane.[2,20] In addition, all three compounds contain a copper(II) bonded about 0.5 Å from the N$_4$ plane, and the Cu–N bond distances vary only from 2.02 Å to 2.07 Å. The copper(II) complex containing the 12-membered cyclic tetrathiaether, [Cu([12]aneS$_4$)(H$_2$O)](ClO$_4$)$_2$, has a square-pyramidal geometry with the copper displaced 0.53 A above the S$_4$ plane with the water bonded in the axial position 2.11 Å from the copper(II).[11]

Although the structures of all these R$_4$[12]aneN$_4$ copper(II) complexes are remarkably similar, their physical properties are quite different. For example, the band maximum of the lowest energy transition in the electronic spectra of the solids varies from 595 nm to 775 nm (Table V), and these complexes also exhibit great differences in electrochemical behavior as a function of the R group on the coordinated amines and the nature of the anion (Table VI). However, the nature of the anion has more influence on the physical properties of these complexes than the nature of the R group on the coordinated nitrogen. Complexes having different 12-membered macrocycles and the same counteranion have similar electronic spectra (Table V) and cyclic voltammograms (Table VI). In contrast, complexes having an identical 12-membered macrocyclic ligand but a different counteranion will have considerably different electronic spectra and electrochemistry. For example, the electronic spectra for all the solid chloride compounds have a band maximum around 770 nm while the nitrate compounds have a band maximum around 600 nm. Another example is that the first reduction response at a given scan rate for a copper(II) complex containing a 12-membered macrocycle is about 0.25 V more negative for the chloride complexes than nitrate complexes (Table VI).

We observed electrochemically that small amounts of chloride ion added to the nitrate complexes resulted in the formation of a copper(II)–chloride bond. For example, if chloride ions are added to [Cu(Me$_4$[12]aneN$_4$)H$_2$O](NO$_3$)$_2$·H$_2$O dissolved in CH$_3$CN the reduction response at −0.17 V in the cyclic voltammogram disappears and a new peak is observed at −0.62 V. This peak has been assigned the one electron reduction of [Cu(Me$_4$[12]aneN$_4$)Cl]$^+$. In contrast a carbon monoxide atmosphere had only a minor effect on the cyclic voltammogram on any of the complexes used in this study. In summary, these complexes appear to be highly reactive toward chloride ions.

Other copper(II) complexes exhibit similar physical and chemical properties to that of the copper(II) complexes containing the R$_4$[12]aneN$_4$ ligands. For example, Cu(cyclops)$^+$ (cyclop = 1,1-difluoro-4,5,11,12-tetramethyl-1-bora-3,6,10,13-tetraza-2,14-dioxocyclotetradeca-3,5,10,12-tetraenato) reacts with Lewis bases to form square pyramidal adducts. The copper(II) is above the plane of the four nitrogens.[27] The optical absorption spectra of the Cu(cyclops)L$^+$ complexes are sensitive to the nature of the L group. The chloride adduct of Cu(cyclops)$^+$ has a higher wavelength maximum (Cu(cyclops)Cl, 665 nm in Nujol) than the pyridine adduct of Cu(cyclops)$^+$ ([Cu(cyclops)pyridine]ClO$_4$, 593 nm in Nujol). A similar trend was observed with the [Cu(R$_4$[12]aneN$_4$)]$^{2+}$ complexes. Another similarity of the copper(II) complexes of R$_4$[12]aneN$_4$ type ligands to that of the Cu(cyclops)$^+$ complexes is that the Cu(cyclops)$^+$ bonds more strongly to anionic donors than to neutral donors.

Hancock and co-workers[28] also made similar observations. They noted that copper(II) complexes in which the copper(II) is not in the same plane as the donor atoms of the tetradentate macrocycle have a stronger affinity for Lewis bases than copper(II) complexes in which the copper(II) is in the same plane as the donor atoms. The former group of compounds includes the copper(II) complexes containing [12]aneN$_4$ and [13]aneN$_4$. In contrast, planar Cu(II) complexes of [14]aneN$_4$ and [15]aneN$_4$ are relatively weak Lewis acids toward such bases such as hydroxide, ammonia, chloride and others.[28] Hancock and co-workers[28] also observed that the Me$_4$[14]aneN$_4$ complex of copper(II) resulted in higher formation constants with anionic ligands such as thiocyanate or cyanide than the copper(II) complex of [14]aneN$_4$.

Young and co-workers[29] have observed that the copper(II) complexes containing cyclic polythiaethers will form adducts with weak anionic Lewis bases such as ClO$_4^-$, BF$_4^-$, CF$_3$SO$_3^-$. These cyclic polythiaethers are weak field ligands as are the R$_4$[12]aneN$_4$ ligands. The geometry of the copper(II) complex of [12]aneS$_4$ is similar to the geometry of the copper(II) complexes of R$_4$[12]aneN$_4$.[11]

The physical and chemical properties of all the above copper(II) complexes including those of the [12]aneN$_4$ are due in some manner to the fact that the copper(II) is located above the plane of the four donor atoms in the tetradentate ligand. Because the copper(II) is not in the plane of the four nitrogen atoms, the donor atoms in the macrocycle will impart less electron density to the copper(II) than a larger macrocycle, such as the [14]aneN$_4$. Because the donor atoms in larger macrocyclic ligands can bond to the copper(II) in a planar manner, they can form stronger

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copper to donor atom bonds. Tertiary amines are usually weaker donors than the secondary amines and as a result they will be weaker-field ligands.[30] Since the tertiary amine macrocycles will donate less electron density to the copper(II) than those that contain secondary amine donor atoms, the copper(II) ion bonded to a tertiary amine ligand will also be more electrophilic. This macrocyclic induced electrophilicity (MIE) will manifest itself on the vacant apical position. It is for this reason that copper(II) complexes in which the copper(II) is bonded above the plane of four donor atoms are relatively strong Lewis acids and as a result they are especially reactive toward anionic Lewis bases such as chloride versus neutral Lewis Bases such as water, acetonitrile or carbon monoxide.

Shorter Cu(II)–X bonds in the axial position are expected with weaker field cyclic ligands. The Cu–O bond length in $[Cu(Me_4[12]aneN_4)H_2O](NO_3)_2H_2O$ is smaller, 2.144 Å, than the Cu–O bond length in $[Cu([12]aneN_4)NO_3]NO_3$, 2.183 Å.[20] $Me_4[12]aneN_4$ is a weaker field ligand than $[12]aneN_4$. (However, water is a stronger ligand than the nitrate group. This factor will also contribute to the shorter Cu–O bond in the former compound.) The $[12]aneS_4$ must be a weaker ligand than the $[12]aneN_4$ because the Cu–O bond length, 2.11 Å for $[Cu([12]aneS_4)H_2O](ClO_4)_2$ is smaller than those measured for other copper(II) complexes containing the $R_4[12]aneN_4$ ligands.[11]

The stronger the axial interaction of a Lewis base with CuL^{+n}, the more the copper(II) is displaced from the N_4 plane.[27] For example, NCO^- and Cl^- are stronger bases than water or the nitrate group, as a result the copper(II) is displaced 0.55–0.58 A from the N_4 plane in the NCO^- and Cl^- complexes whereas the displacement is only 0.50–0.51 A when the axial ligands are H_2O or NO_3^-.[27] The electrochemical data also indicate that the chloride ion forms stronger bonds with copper(II) than with either water or nitrate groups. The validity of the above statement is corroborated by noting that the chloride complexes containing a given 12-membered macrocycle are more difficult to reduce than the nitrate complexes containing the same macrocycle (Table VI).

The strength of the copper(II) to amine bond has been correlated to the d–d band observed in the electronic spectra for the various copper(II)–macrocyclic complexes.[13,31] On the basis of this type of correlation the $bz_4[12]aneN_4$ is the weakest macrocyclic ligand and the $[14]aneN_4$ is the strongest ligand. The relative ordering of ligand field strength based on this correlation is listed as follows:

$$\begin{aligned} &bz_4[12]aneN_4(614\,nm)^{11} < Me_4[12]aneN_4(602\,nm) = \\ &\quad [16]aneN_4(600\,nm)^{10} < [15]aneN_4(595\,nm)^{10} < \\ &\quad [12]aneN_4(590\,nm)^{1} < [13]aneN_4(525\,nm)^{10} < \\ &\qquad\qquad [14]aneN_4(495\,nm)^{10} \end{aligned}$$

The electrochemical data are consistent with the spectral data in that the copper(II) complexes containing the ligand $bz_4[12]aneN_4$ are the easiest to reduce while the copper(II) complexes of $[12]aneN_4$ are the most difficult to reduce. The copper(II) complexes containing the 12-membered macrocyclic ligands are easier to reduce than 13–16 membered rings[13,14] because the four nitrogens atoms of the $R_4[12]aneN_4$ ligands are not in the same plane as is the copper(II) ion. As a result they are weaker field ligands than larger sized macrocycles. It has also been reported that the Cu(II) ion in $Cu[13]aneN_4^{2+}$ lies above the N_4 plane of the $[13]aneN_4$ ligand and as a result of this it is easier to reduce this compound than the $[14]aneN_4$ copper(II) complex.[14]

The geometry of the resulting labile copper(I) complexes that are bonded to 12-membered macrocycles is open to speculation. If these copper(I) complexes have a tetrahedral geometry then only one copper to nitrogen bond must break upon reducing the copper(II) to copper(I) for the copper–$[12]aneN_4$ complexes in order to form distorted tetrahedral geometries. However, it is also possible that the coordination number does not change when copper(II) is reduced to copper(I). For example Goodwin and co-workers[32] have observed the retention of the pentacoodinated species upon reducing copper(II)–2,6-bis[1-((2-pyridin-2-ylethyl)imino)ethyl]pyridine. The retention of the stereochemistry around the copper ion can be retained upon reduction of the Cu(II)–$R_4[12]aneN_4$ complexes by moving the copper ion further from the basal plane. In either case the reason that it is easier to reduce the copper(II)–$[12]aneN_4$ complexes compared to the $[14]aneN_4$ complexes is because the former complexes do not have to appreciably alter bond angles after the electron transfer. As a result there should be a lower energy barrier for forming copper(I) complexes from the copper(II)–$[12]aneN_4$ complexes compared to forming copper(I) complexes from the copper(II)–$[14]aneN_4$ complexes.

This explanation is similar to the one given for the large electron transfer self-exchange constant for the copper(II) complex of 1,4,7,10,13-pentathiacyclopentadecane.[19] The research groups of Sykes, Pecht and Gray have observed that certain copper(II) containing proteins such as azarin and the plastocyanins undergo electron transfer at the copper(II) site with a minimum of reorganization energy.[33-35] They reported that the low reorganization energies are required in these reactions are due to similar geometries around both the copper(II) and copper(I) sites. If the above explanations for our data are valid, then these electron transfer reactions involving the $R_4[12]aneN_4$ complexes are good model systems for copper protein electron transfer reactions and the enthatic state hypothesis.

The copper(I) complexes containing the $[12]aneN_4$ type ligands is qualitatively more inert than copper(I) complexes containing the 14-membered tetraaza macrocyclic ligands with respect to demetalation. This conclusion is based on electrochemical observations that no stripping peak was observed in the CV of any of the copper(II) complexes containing $R_4[12]aneN_4$ ligands. Therefore, we conclude that there is no evidence of demetalation occurring upon reduction even if the switching potential is set at –2.0 V. In contrast a stripping peak was observed for the copper complex containing a fourteen-membered tetraaza macrocyclic ligand.[17]

The copper(I) complexes containing the weaker field 12-membered macrocyclic ligands, $Me_4[12]aneN_4$ and $bz_4[12]aneN_4$, appears to be more inert than the copper(I) complex of unsubstituted $[12]aneN_4$. This is based on the observation that the reductions of the copper(II) complexes of $Me_4[12]aneN_4$ and $bz_4[12]aneN_4$ are more reversible than that of the copper(II) complexes of $[12]aneN_4$. In the case of the $Cu([12]aneN_4)NO_3^+$ there is no evidence of a coupled oxidation reaction to the observed reduction reactions. However, if the switching potential for copper(II) complexes of $Me_4[12]aneN_4$ and $bz_4[12]aneN_4$ is set at less than -1 V then coupled anodic reactions were observed. The electrochemistry of the copper(II) complexes containing the 12-membered macrocyclic ligands and a coordinated chloride is similar to that of the nitrate complexes (Figure 4) in that there is no evidence for demetalation after the first reduction process and the copper(I) complexes containing the tertiary amines appear to be more inert than the secondary amine complexes with regards to demetalation.

It has been proposed that in order for a planar tetradentate macrocyclic metal complex to decompose, the macrocycle must

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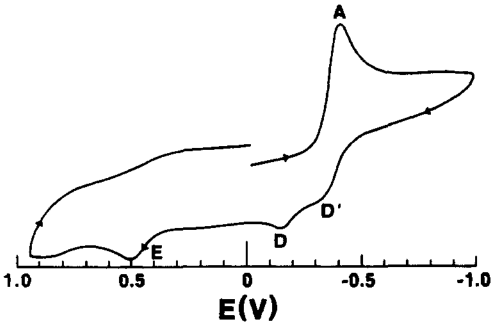

Figure 4. Cyclic voltammogram of [Cu(tb$_4$[12]aneN$_4$)H$_2$O]Cl$_2$ versus SCE at a platinum electrode, 25 °C in CH$_3$CN with 0.1 M (TBA)ClO$_4$ at a scan rate of 200 mV s^{-1}.

first fold in such a manner that the cyclic ligand and the metal ion are not in the same plane.[36] A necessary conclusion of this proposed mechanism is that non-planar complexes should decompose faster than planar complexes containing the same metal ion. The instantaneous product of the one electron reduction of a copper(II) complex bonded to four coplanar nitrogen donors must be a copper(I) complex having a similar geometry and the instantaneous product of a one electron reduction on a non-planar copper(II) complex must be a non-planar copper(I) complex. Since the folding step is not necessary for non-planar complexes, it is probable that these non-planar complexes will undergo ligand dissociation faster than complexes which must rearrange before the ligand can dissociate. However, the electrochemical data indicates that the copper(I) complexes bonded to the smaller macrocycles appear to be more inert than the copper(I) complexes containing the larger macrocycles.

There are several explanations for the relative inertness of the copper(I) complexes containing 12-membered rings. If the copper(I)–[14]aneN$_4$ complex contains more strained copper to nitrogen bonds than are contained in the [12]aneN$_4$ copper(I) complexes, then the former complexes should be less thermodynamically stable. As a result of these weaker bonds in the copper(I)–[14]aneN$_4$ complexes, they will decompose faster. Hancock and co-workers[37] have provided a theoretical basis for justifying the assumption that the copper(I)– [14]aneN$_4$ complexes have a lower thermodynamic stability compared to the copper(I)–[12]aneN$_4$ complexes. They noted that macrocyclic ligands which have the potential of forming six membered chelate rings, such as the [14]aneN$_4$ ligands, will be at minimum strain energy for smaller metal ions such as copper(II). However larger metal ions, such as copper(I), will be at a minimum strain energy with ligands that form five-membered rings, such as the [12]aneN$_4$ ligands. This means that the [12]aneN$_4$ ligands should form stronger bonds with larger metal ions such as copper(I) than the [14]aneN$_4$ ligand.

Steric and hydrophobic effects may also be responsible for the greater stability of the copper(I) complexes containing the tertiary amine ligands compared to copper(I) complexes containing the secondary amine ligands.

In summary, it is easier to reduce the copper(II) complexes containing a twelve-membered ring than those bonded to larger sized macrocycles and copper(II) complexes containing macrocycles with tertiary amine donors atoms are easier to reduce than those with secondary amine donor atoms. The copper(II)–R$_4$[12]aneN$_4$ complexes have a relatively strong affinity for chloride ion and the copper(I)–R$_4$[12]aneN$_4$ complexes appear to have a greater stability than the copper(I)–[14]aneN$_4$ complexes.

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