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Copper(II) Complexes Containing a 12-Membered Macrocyclic Ligand

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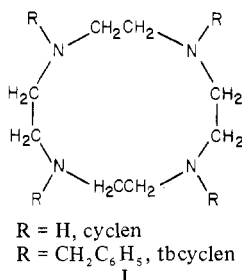
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Copper(II) complexes of 1,4,7,10-tetraazacyclododecane (cyclen) and 1,4,7,10-tetraazacyclododecane (tbcyclen) have been prepared. They include $\text{Cu}(\text{cyclen})\text{X}_2$ ($\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{NO}_3^-$), $\text{Cu}(\text{tbcyclen})\text{X}_2 \cdot n\text{H}_2\text{O}$ ($\text{X}^- = \text{NO}_3^-, \text{Cl}^-, \text{Br}^-, \text{NCS}^-$), $\text{Cu}(\text{tbcyclen})\text{ClClO}_4 \cdot 1/2\text{H}_2\text{O}$, and $\text{Cu}(\text{tbcyclen})\text{ClBr} \cdot \text{H}_2\text{O}$. Based on several chemical substitution reactions plus conductivity, electron spin resonance, and electronic spectral data, these complexes are proposed to be five-coordinate and to approximate a square-pyramidal geometry. The $\text{Cu}(\text{tbcyclen})\text{X}_2$ complexes exhibit an electronic absorption band maximum in the 700–800- μm range and these bands have unusually high extinction coefficients for a copper(II) complex bonded to only nitrogen and oxygen donor atoms. However, all these complexes have "normal" ESR spectra for copper(II) complexes. Many of the attributes of the type II copper(II) atoms in proteins are observed with the $\text{Cu}(\text{II})$ -tbcyclen or -cyclen complexes.

Introduction

It has been suggested that metal ions located at the active site of certain metalloenzymes are in a strained low-symmetry environment which approximates the transition state for the reactions in which that enzyme is involved. Metal ions in such a low-symmetry environment and having weak metal-donor bonds are believed to be partially responsible for certain anomalous physical properties observed in some metalloenzymes. The type I copper(II) proteins have anomalous electronic and ESR spectra.³ It has been hypothesized that these anomalous electronic and ESR spectra are due to either an unusual symmetry around the copper(II)^{2,4,5} or to a charge-transfer effect from copper(II) to a coordinated mercapto group.^{4,6-8} Several synthetic copper(II) complexes containing sulfur donors have exhibited electronic spectra similar to that observed in the type I copper proteins.^{4,6-8} However, at present there are few examples of kinetically stable synthetic copper(II) complexes containing a weak field ligand in which copper ion is in an unusually low symmetry environment.

We have previously prepared and reported a series of nickel(II) and cobalt(II) complexes employing the ligand 1,4,7,10-tetraazacyclododecane (tbcyclen) (I).^{9,10} Based on models of these compounds and on their



chemical and physical properties, it was concluded that these cobalt(II) and nickel(II) complexes are in a low-symmetry environment and that the metal to nitrogen bonds are both strained and weak. In preparing similar copper(II) complexes of tbcyclen and cyclen (1,4,7,10-tetraazacyclododecane) (I), we have produced copper(II) compounds having some of the environmental attributes hypothesized for a metal ion in the active site of a metalloenzyme. Since a charge-transfer effect from the copper to the donor atom is unlikely with saturated nitrogen donors, we have been able to study the physical properties of these copper(II) complexes as a function of only geometric effects. This has allowed us to determine whether a distorted geometry and strained metal to donor bonds alone will result in anomalous physical properties.

Results and Discussion

We have prepared a series of copper(II) complexes having the stoichiometry $\text{Cu}(\text{tbcyclen})\text{X}_2$, where $\text{X}^- = \text{NO}_3^-, \text{Cl}^-$, or

Table I. Electronic Spectra of Copper(II) Complexes of 1,4,7,10-Tetraazacyclododecane (cyclen) and 1,4,7,10-Tetraazacyclododecane (tbcyclen)

Complex	λ_{max} , nm (ϵ)			
	Solid	CH_3OH	CH_3NO_2	H_2O
$\text{Cu}(\text{cyclen})(\text{NO}_3)_2$	595	590 (300)		590 (257)
$\text{Cu}(\text{tbcyclen})(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$	625	625 (880)	660 (580)	614 (500)
$\text{Cu}(\text{cyclen})\text{Cl}_2 \cdot \text{H}_2\text{O}$	770	655 (230)		594 (271)
$\text{Cu}(\text{tbcyclen})\text{Cl}_2 \cdot 1/2\text{H}_2\text{O}$	775	725 (510)	750 (595)	615 (640)
$\text{Cu}(\text{cyclen})\text{Br}_2$	680	655 (152)		590 (273)
$\text{Cu}(\text{tbcyclen})\text{Br}_2 \cdot \text{H}_2\text{O}$	770	740 (700)	750 (740)	

Br^- , and $\text{Cu}(\text{cyclen})\text{X}_2$, where $\text{X}^- = \text{NO}_3^-, \text{Cl}^-$, or Br^- . Since $\text{Cu}(\text{tbcyclen})\text{ClClO}_4 \cdot 1/2\text{H}_2\text{O}$ and $\text{Cu}(\text{tbcyclen})\text{ClBr} \cdot \text{H}_2\text{O}$ were prepared from $\text{Cu}(\text{tbcyclen})\text{Cl}_2 \cdot 1/2\text{H}_2\text{O}$, we suggest that one of the two chlorides in $\text{Cu}(\text{tbcyclen})\text{Cl}_2 \cdot 1/2\text{H}_2\text{O}$ is coordinated to the copper(II) and the other chloride is functioning as a noncoordinating counteranion. However, the reaction of $\text{Cu}(\text{tbcyclen})\text{Cl}_2 \cdot 1/2\text{H}_2\text{O}$ with the relatively stronger ligand, thiocyanate, resulted in the displacement of the coordinated chloride from the coordination sphere and $\text{Cu}(\text{tbcyclen})(\text{SCN})_2 \cdot 2\text{H}_2\text{O}$ was isolated. All the other $\text{Cu}(\text{tbcyclen})\text{X}_2$ complexes were prepared from the reactions of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, or CuBr_2 and the cyclic tetradentate ligand.

The copper(II)-cyclen and -tbcyclen complexes are all various shades of blue and blue-green; their optical spectral parameters are listed in Table I. Differences in these parameters reflect slight changes in stereochemistry and the composition of the coordination sphere, as was also found for the nickel(II) and cobalt(II) complexes.^{9,10}

The magnetic moments for all the above complexes indicate one unpaired electron per copper (Table II). These observed magnetic moments only slightly exceed the spin-only value expected for copper(II) complexes.¹¹ Therefore, there is no positive evidence of any antiferromagnetic or ferromagnetic interactions at room temperature for any of the complexes prepared in this study, and we have not considered it likely that these complexes are polynuclear. Professor Little¹² has attempted to collect x-ray data for $\text{Cu}(\text{tbcyclen})(\text{NO}_2)_3 \cdot \text{H}_2\text{O}$ but observed that his crystals did not diffract strongly enough. Nevertheless, $\text{Cu}(\text{tbcyclen})(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ was determined to be monomeric,¹³ and Professor Little's results are consistent with our interpretation of the magnetic moments.

The conductivity of the Cu -tbcyclen and Cu -cyclen complexes in CH_3NO_2 and CH_3OH indicates that these compounds are one-to-one electrolytes (Table III). In water all the complexes are two-to-one electrolytes. Therefore the conductivity data are consistent with our synthetic data which suggest that in the solid state one anion is coordinated to the copper(II) while the other anion is not. However, plots of equivalent conductance vs. the equivalent concentration in

Table II. Magnetic Properties of Copper Complexes

Compd	$\langle g \rangle^c$	$\langle A \rangle^c$	g_{\parallel}^c	A_{\parallel}^c	g_{\perp}^e	A_{\perp}^e	μ_{eff}
Cu(tbcyclen)Cl ₂ ·H ₂ O ^a	2.102	77.5	2.230 ^d	160	2.038	36	2.07
Cu(tbcyclen)Br ₂ ·H ₂ O ^a	2.102	77.5	2.210	163	2.049	35	--
Cu(tbcyclen)(NO ₃) ₂ ·H ₂ O ^a	2.096	77.5	2.212	170	2.038	31	1.90
Cu(cyclen)(NO ₃) ₂	2.117	80.0	2.172	175	2.089	32	1.84

^a tbcyclen complex ESR spectra recorded in 50% aqueous acetone at room temperature and at 77 K in a 50% acetone-H₂O glass.

^b Cyclen complex ESR spectrum recorded in Zn(cyclen)(NO₃)₂ matrix; 2%. Spectral features unresolved in aqueous acetone at 77 K.

^c Errors in measured quantities: ± 0.002 in g ; ± 2 G in A ($\pm 1\%$). ^d Medium effects: 2.215–2.230 in DMF, MeNO₂, acetone/H₂O.

^e Calculated from $\langle g \rangle$, $\langle A \rangle$, g_{\parallel} , and A_{\parallel} .

Table III. Conductivity Data for Copper-tbcyclen and -cyclen Compounds (Concentration = 1×10^{-3} M)

Compd	Conductance, mho cm ² mol ⁻¹		
	CH ₃ -NO ₂	CH ₃ OH	H ₂ O
Cu(tbcyclen)(NO ₃) ₂ ·H ₂ O	89	99	244
Cu(tbcyclen)Cl ₂ · $\frac{1}{2}$ H ₂ O	81	68	208
Cu(tbcyclen)ClClO ₄ · $\frac{1}{2}$ H ₂ O	89		
Cu(tbcyclen)Br ₂ ·H ₂ O	88	77	
Cu(tbcyclen)Br·ClH ₂ O	110		
Cu(tbcyclen)(NCS) ₂ ·2H ₂ O	106		
Cu(cyclen)(NO ₃) ₂		141	206
Cu(cyclen)Cl ₂ · $\frac{1}{2}$ H ₂ O		92	221
Ni(cyclen)(NO ₃) ₂		122	198
Ni(tbcyclen)(NO ₃) ₂		59	168

nitromethane for the Cu-tbcyclen complexes and for the Cu-cyclen complexes in methanol resulted in curves. Such curves indicate that the coordinated anion is being partially displaced by the solvent.¹⁴

The molar conductivities of Cu(tbcyclen)(NO₃)₂·H₂O and Cu(tbcyclen)Cl₂· $\frac{1}{2}$ H₂O are less than the molar conductivities of Cu(cyclen)(NO₃)₂ and Cu(cyclen)Cl₂· $\frac{1}{2}$ H₂O in methanol. The same is true for the analogous nickel(II) complexes in methanol.¹⁵ This may be due to the greater mobility of the smaller cations containing cyclen compared to tbcyclen. However, in water the numerical values of the molar conductivities of all these complexes are similar, although somewhat higher. It is therefore, possible that ion mobilities may not be the only factor involved; the degree of ion association may also play a role. The cyclen complexes must exhibit a larger degree of ion association in water than that of the tbcyclen complexes in order to compensate for the greater ion mobility of cyclen complexes. Ion association in water might occur for the metal(II)-cyclen complexes by means of the anion hydrogen bonding to the coordinated water or to cyclen. It seems reasonable to expect that the hydrophobic benzyl groups on the nitrogen prevent the water from interacting with the tbcyclen complexes. Since methanol does not solvate or hydrogen bond as effectively as water, the Cu-cyclen complexes do not ion associate to as great a degree as the Cu-tbcyclen complexes in methanol.

No $\nu(\text{N-H})$ stretching peaks are observed in the 3100–3550-cm⁻¹ region of the infrared spectra for the Cu-tbcyclen complexes. The absence of peaks in this area is consistent with the assumption that only tertiary amines are present in the macrocycle. The presence of *N*-benzyl groups can be inferred from a series of three peaks at 3020–3080 cm⁻¹ in all spectra, which were assigned to the aromatic C-H stretch for monosubstituted benzene.¹⁶ In addition, two intense peaks at 705 and 750 cm⁻¹ are assigned to C-H out-of-plane bending modes for monosubstituted benzene while a peak at 1500 cm⁻¹ is assigned to the aromatic C-C stretching mode.¹⁶ In contrast, and as expected, bands in the 3500–3100-cm⁻¹ region are observed for the Cu-cyclen complexes and no bands are observed in the aromatic C-H stretching region.

A broad diffuse band of medium to low intensity in the 3350–3450-cm⁻¹ region is observed in the infrared spectrum

for all copper-tbcyclen compounds and assigned to the antisymmetric and symmetric O-H stretching modes for lattice water.¹⁷ In addition, a weak absorption is found in the region 1600–1650 cm⁻¹ and assigned to the H-O-H bending mode for lattice water.¹⁷ The presence of absorption bands at 887 and 855 cm⁻¹, indicative of coordinated water, could not be confirmed because of overlapping tbcyclen bands.¹⁶ However, no absorption bands at 535 and 400 cm⁻¹ were observed in the infrared spectrum for any of the copper-tbcyclen complexes as would be expected for coordinated water. Therefore, it would seem unlikely that copper-tbcyclen complexes contain coordinated water.

The presence of noncoordinated perchlorate in Cu(tbcyclen)ClClO₄· $\frac{1}{2}$ H₂O is inferred from the broad band in the region 1070–1105 cm⁻¹¹⁶ and the absence of an intense absorption band around 930 cm⁻¹ which is indicative of coordinated perchlorate. These observations are consistent with conductivity data which support a one-to-one electrolyte. The chloride is coordinated to the copper(II) while the perchlorate acts as a counteranion.

Two bands at 2105 and 2060 cm⁻¹ in the spectrum of Cu(tbcyclen)(NCS)₂·2H₂O are assigned to the C-N stretching mode of NCS⁻. The presence of two bands for the C-N stretch indicates that the two thiocyanates are not equivalent. The band at 2060 cm⁻¹ is likely to be due to ionic thiocyanate and the 2105-cm⁻¹ band is likely to be due to the nitrogen coordinated thiocyanate. The C-S stretching frequency and the NCS⁻ bending frequency are better indicators for distinguishing the two isomers.¹⁷ Unfortunately such assignments cannot be made because of interference by the tbcyclen ligand. However, it is well known that first-row transition metals prefer to coordinate to the nitrogen in thiocyanate rather than the sulfur. X-ray analysis of Cu(tren)(NCS)₂ has shown that one thiocyanate is bonded through nitrogen and the other thiocyanate is not coordinated.¹⁹ The C-N frequencies for Cu(tren)(NCS)₂, 2094 and 2060 cm⁻¹, are similar to the frequencies observed for Cu(tbcyclen)(NCS)₂.¹⁹ In view of the information cited above, the infrared data for Cu(tbcyclen)(NCS)₂ are consistent with the assumption that one thiocyanate is coordinated through nitrogen while the other thiocyanate is ionic. Furthermore, conductivity data for this compound are characteristic of a one-to-one electrolyte. However, it is also possible that both thiocyanates are coordinated to the copper(II): one strongly bonded through the nitrogen and the other thiocyanate weakly bonded.

In the infrared spectrum of Cu(tbcyclen)(NO₃)₂·H₂O, absorption peaks were observed at 1480, 1330, and 820 cm⁻¹. These absorption bands do not appear in the spectrum of other copper-tbcyclen complexes and are assigned to a coordinated nitrate. The Cu(cyclen)(NO₃)₂ has bands at 1420, 1360, 1310, 1250, and 810 cm⁻¹. The bands at 1420 and 1310 cm⁻¹ are in the position expected for a monodentate nitrate.²⁰ For example, Ni(en)₂(NO₃)₂ and Ni(tet-a)(NO₃)₂ both contain monodentate nitrate and have bands at 1420 and 1305 cm⁻¹ for the former compound and 1412 and 1307 cm⁻¹ for the latter compound.^{20,21} The 1360- and 810-cm⁻¹ bands for Cu(cyclen)(NO₃)₂ are at approximately the positions expected for ionic nitrate.²⁰ However, the band at 1250 cm⁻¹ can be

assigned to either monodentate or bidentate nitrate.

Cu(cyclen)(NO₃)₂ and Cu(cyclen)Br₂ show only one band in the N-H stretching region, at 3210 and 3150 cm⁻¹, respectively. However, Cu(cyclen)Cl₂·H₂O shows a strong band at 3150 cm⁻¹ and two weak bands at 3380 and 3440 cm⁻¹. In all the metal complexes in which the cyclen is folded around the metal ion, there are many bands (of equal intensity) in the N-H stretching region.²¹ Many bands are expected in the cis octahedral geometry because the axial and equatorial nitrogen atoms are in different geometric environments. However, the metal-cyclam complexes show only one band in the N-H region.²² These complexes have a planar geometry and therefore all N-H's are likely to be in identical environments. The fact that only one band was observed for the complexes suggests that the cyclen bonded to copper(II) may be *less* folded and *more* planar than the nickel(II), chromium(III), and cobalt(III) complexes of cyclen.^{9,10,21,23} Consistent with this model is that in all the nitrate complexes containing the coordinated folded cyclen or tbcyclen, the nitrate group appears to be bonded in a bidentate manner. However, in the copper(II) complexes the nitrate seems to be monodentate. Finally, it has been observed that the Cu(tbcyclen)(NO₃)₂·H₂O decomposes at a slower rate than the Ni(tbcyclen)(NO₃)₂.²⁴ Since copper(II) complexes usually are *more* labile than nickel(II) complexes having the same geometry, it can be assumed that the nickel(II) and copper(II) complexes do not have the same geometry. The more folded the macrocyclic ligand is around the metal ion the faster the compound should decompose.²⁵ Based on these data it appears that the tbcyclen on copper(II) is less folded and coordinated in a more coplanar manner with the copper(II) than the tbcyclen bonded to nickel(II). Since the copper(II) in these complexes appears to have a coordination number of five (assuming that cyclen and tbcyclen are functioning as tetradentate ligands) and since the kinetic and infrared data suggest that the tbcyclen is bonded in a planar manner to the copper(II), therefore this suggests that these complexes might have a square-pyramidal geometry rather than a trigonal-bipyramidal configuration.

The ESR spectra of all of the copper(II) complexes described herein (Table II) are typical of the majority of copper(II) complexes.^{26,27} Spectra recorded at room temperature and at 77 K, in the solid-state and in frozen and mobile solution, exhibit no inconsistencies. The parallel Cu hyperfine coupling constant, $A_{||}$, is in the 160–175 G range and this is normal for N- or O-bonded Cu(II) in tetragonal environments.²⁸

As found here, $g_{||} > g_{\perp}$ is typical of tetragonal Cu(II) where the tetragonal distortion takes the form of elongation of the axial bonds.²⁸ Based on this it appears that we can exclude a trigonal-bipyramidal geometry or a tetragonal structure involving compression of axial bond lengths. These would both lead to $g_{\perp} > g_{||}$.²⁸ Since the kinetic and infrared data suggest that the tbcyclen and the cyclen are not coordinated in a folded manner and the ESR data eliminate a trigonal-bipyramidal configuration, it appears likely that these complexes have a square-pyramidal geometry.

There are some differences in the spectra of the cyclen and tbcyclen complexes which are worth noting. $\Delta g (g_{||} - g_{\perp})$ is greater in the tbcyclen complexes than in the cyclen complexes. The spectral resolution is also somewhat greater in the immobilized tbcyclen complexes. These two features are consistent with a greater degree of distortion from octahedral geometry in the tbcyclen complexes, a finding which is not surprising considering the relative size of the ligands. The effect of the benzyl groups is seen also in solution spectra where molecular tumbling is noticeably hindered relative to the cyclen complexes. This is evident from the relative line

widths of the hyperfine lines which show a pronounced decrease with increasing magnetic field.

The ESR spectra are quite insensitive to both solvent effects and extraneous coordinating anions in solution. This may be because these solvent effects involve changes centered on filled orbitals and involve paired electrons whose wave functions mix only slightly with those of the unpaired electrons.

While the ESR spectra do not exhibit the anomalous features of the type I copper species, the electronic spectra are atypical (Table I). The absorption of both cyclen and tbcyclen complexes is considerably more intense than found in the typical copper(II) complexes which these otherwise appear to represent.²⁷ In the tbcyclen complexes extinction coefficients of 500–900 M⁻¹ cm⁻¹ were observed for the electronic transition in the 600–700-nm range while for the cyclen complexes extinction coefficients of 200–300 M⁻¹ cm⁻¹ were observed for the comparable transition. These high values for ϵ are quite remarkable, since no charge transfer is likely in this region of the spectrum. One would logically expect the origin to be in purely geometric ligand field effects. If an increasing ϵ is interpreted as indicating a greater degree of distortion and consequently greater d-p mixing, then the optical spectra are consistent with the ESR results which also suggest a greater degree of distortion in the tbcyclen than in the cyclen complexes. Not surprisingly, the optical spectra seem more sensitive than the ESR spectra in revealing these small differences.

The addition of various salts to nonaqueous solutions of Cu-cyclen and -tbcyclen resulted in significant and often large changes in the electronic spectra but not in the ESR spectra. The change in the electronic spectrum indicates that the coordinated anion can be readily displaced by a stronger ligand. For example, the band at 625 m μ for Cu(tbcyclen)(NO₃)₂·H₂O in methanol shifts to 725 m μ upon adding a fivefold excess of chloride ions. This band at 725 m μ was also observed for Cu(tbcyclen)Cl₂·¹/₂H₂O in methanol (Table I). A similar observation was made upon adding bromide ion to a methanol solution of Cu(tbcyclen)(NO₃)₂·H₂O. In addition, the extinction coefficient increased at 725 m μ to above 900 M⁻¹ cm⁻¹ upon the addition of either chloride or bromide to Cu(tbcyclen)(NO₃)₂·H₂O. We have observed that larger anions in the coordination sphere generally result in higher extinction coefficients. Large anions result in more crowding to accommodate the larger anion. By lowering the symmetry of the metal complex, there should be a greater degree of p-d mixing and therefore higher extinction coefficients are expected. (The addition of extraneous ions to copper(II)-cyclen complexes produces results similar to the Cu(II)-tbcyclen complexes. In all cases a red shift in the band maximum is observed. However, a larger excess of extraneous ion is required to reach a maximum extinction coefficient at the absorption maximum with the copper(II)-cyclen complexes compared to the analogous copper(II)-tbcyclen complexes.) The addition of strong field anions such as nitrite or cyanide to the copper-tbcyclen complexes resulted in the displacement of the tbcyclen from the coordination sphere of the copper.

Although all the previously prepared complexes of cyclen and tbcyclen have had either a cis octahedral geometry or a trigonal-bipyramidal stereochemistry, it is unlikely that these copper(II)-cyclen and -tbcyclen complexes have such geometries. A six-coordinate geometry has been eliminated based on previously discussed data. In addition, cis octahedral copper(II) complexes usually have two equally intense bands at 1100 and 710 m μ .^{29,30} Only one band has been observed for the copper(II) complexes prepared in this study.

Hathaway and associates have suggested criteria for distinguishing square-pyramidal (SP) and trigonal-bipyramidal (TB) geometries for copper(II) complexes based on the position

of the absorption band in the visible spectrum.^{30,31} They suggest that square-pyramidal copper(II) complexes have an absorption band in the region 550–670 nm while trigonal-bipyramidal complexes absorb near 800–850 nm. Since the absorption peak for most of the complexes prepared in this study falls between these two ranges, their structures might be considered intermediate between SP and TB. However, tbcyclen and cyclen have been shown to be weak field ligands.^{9,10} Therefore the absorption around 700 m μ would be too high in energy for a trigonal-bipyramidal copper(II) complex and so a distorted square pyramid appears to be the most likely structure for most of these complexes.

Furlani³² has shown the energy difference between a trigonal bipyramid and a square pyramid is small, and variations between these two limiting geometries can occur by a normal vibration of either structure. Kepert³³ has also shown that nondistorted trigonal-bipyramid or square-pyramid structures are not likely. Although most of the complexes prepared in this study appear to approach a square pyramid, it is likely that Cu(cyclen)(NO₃)₂ and Cu(tbcyclen)(NO₃)₂·H₂O may have geometries with more square-pyramidal character than the other complexes. These two copper complexes have band maxima at higher energies than the other compounds. However, it should also be noted that Cu(cyclen)Br₂ has a maximum at higher energy than that of Cu(cyclen)Cl₂ in the solid state. This is inconsistent with the fact that the chloride is a stronger ligand than the bromide. Therefore caution must be exercised in explaining spectral data solely on ligand field effects. Small differences in the geometries of these complexes may explain differences in their spectra. This is especially true since the broad observed electronic transition actually consists of several components. Finally, it must be pointed out that the above stereochemical assignments based on electronic spectra can hardly be considered conclusive. The electronic spectra of copper(II) complexes are not especially good indicators of geometry.^{34,35} However, the electronic spectral data seems to be consistent with the infrared, ESR, and kinetic data.

Discussion

Linear tetradentate ligands containing amine groups will usually coordinate copper(II) in a planar manner.^{22,36} For example, in the complex Cu(trien)(SCN)₂ where (trien = triethylenetetramine) the nitrogen atoms of trien occupy the basal positions of a square pyramid.³⁷ In marked contrast trien will occupy both equatorial and axial positions when coordinated to cobalt(II).³⁸ However, a 12-membered macrocyclic ligand such as cyclen or tbcyclen (because of its cavity size) cannot coordinate coplanar with a metal ion.^{26,37} Therefore the geometrical requirements of the copper(II) ion and the 12-membered ring are in conflict and a compromise is required if these ligands are to coordinate. The physical data suggest that the copper(II) complexes of cyclen and tbcyclen are of low symmetry and that the geometry of most of the complexes in this study approaches that of an irregular square pyramid. Since it is highly unlikely that the copper is able to sit in the plane of the 12-membered ring, the copper(II) is probably somewhat displaced from the plane of the macrocyclic ligand.

Although the Jahn-Teller effect only requires a nondegenerate ground state for copper(II) and does not predict how a metal ion such as copper(II) will be distorted from octahedral symmetry by a polydentate ligand, the overwhelming geometric preference of a copper(II) complex is the elongated tetragonal-octahedral geometry.²⁷ Such a geometry would be unlikely for cyclen or tbcyclen, since it cannot coordinate coplanar with the metal ion. Also, spanning both the axial and equatorial sites of an elongated tetragonal distorted complex would be unlikely with the geometric constraints of a cyclic ligand. Therefore a reasonable compromise is a square pyramid with the copper(II) displaced from the plane.

Many complexes have recently been proposed as models for the various types of copper found in proteins.^{4,6-8} Few of these models are really satisfactory, but consideration of the whole range of these models has given us a better insight into the nature of the enzyme-bound copper. The complexes we have described are likewise deficient as models, but they do illustrate a few points which are worth noting.

The electronic absorption in the 600–750-nm range for all complexes prepared in this study has a surprisingly high extinction coefficient considering that the coordination sphere contains only nitrogen and oxygen atoms. However, the ESR spectra of all our complexes are normal and are not consistent with type I copper(II) proteins. Nevertheless our complexes suggest that distortion of the coordination sphere from relatively high symmetry can result in anomalous extinction coefficients for copper(II) complexes. Therefore there may be a geometrical component as well as a low-energy charge-transfer component to the anomalous physical properties of the type I copper(II) proteins.

Although these complexes are not especially good models for the type I copper proteins, they are better models for the type II copper(II) proteins. The pyramidal structure of the copper(II)-cyclen and copper(II)-tbcyclen complexes is consistent with the fact that the type II proteins have one or two empty coordination sites and can add even weak ligands such as a fluoride ion.^{3,40} Adding only 0.5 mol of NaBr or NaCl or NaN₃ per mole of Cu(tbcyclen)(NO₃)₂ in methanol causes an appreciable change in the electronic spectra. The type II copper(II) proteins are believed to have only nitrogen and oxygen donors and normal copper(II) ESR spectra. The electronic spectrum for galactose oxidase has a band maximum around 600 nm and extinction coefficient around 1000.^{41,42} All these properties of the type II complexes are consistent with our synthetic copper(II) complexes.

Experimental Section

Apparatus. All electronic spectra were recorded employing a Beckman DK-2 ratio spectrophotometer and a Beckman Acta IV. The spectra of the solids were measured in a Nujol mull using the diffuse transmittance technique.⁴³ Infrared spectra were taken on a Perkin-Elmer 337 instrument. The magnetic susceptibilities of all solid samples were determined by the Gouy method at room temperature. Susceptibilities of the ligand and anions were calculated from Pascal's constants.⁴⁴ Conductivity measurements were taken using an Industrial Instruments conductivity bridge. ESR spectra were recorded on a Varian E-4 spectrometer operating at X-band frequencies and were calibrated with DPPH. Nitrogen analyses were taken on a Coleman Model 29 nitrogen analyzer. Carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Preparations. Synthesis of Nitrato(1,4,7,10-tetraazacyclododecane)copper(II) Nitrate. To 100 mL of absolute ethanol in a 150-mL beaker was added 1.0 g (4.1 mmol) of Cu(NO₃)₂·3H₂O. This solution was allowed to boil and to it was slowly added 0.5 g (2.29 mmol) of solid cyclen⁴⁵ with rapid stirring. The solution changed from a light blue to a royal blue. The volume was reduced to less than 20 mL by boiling, and upon refrigeration for about 1 h, dark blue crystals formed. The crystals were filtered, purified by recrystallization in absolute ethanol, and dried. Anal. Calcd for Cu(C₈H₂₀N₄)(NO₃)₂: N, 23.33; H, 5.56; C, 26.67. Found: N, 23.22; H, 5.70; C, 27.03.

Synthesis of Bromo(1,4,7,10-tetraazacyclododecane)copper(II) Bromide. A solution of 0.4 g (2.3 mmol) of cyclen⁴⁵ in 100 mL of absolute ethanol in a 150-mL beaker was allowed to boil. A solution of 0.6 g (2.7 mmol) of CuBr₂ in 40 mL of absolute ethanol was also prepared. This dark red-brown solution was then slowly added with rapid stirring to the colorless cyclen solution and a royal blue color appeared immediately. The resulting solution was then reduced in volume to less than 40 mL by boiling, and blue crystals formed upon refrigeration. The product was then filtered, recrystallized from absolute ethanol, and dried. Anal. Calcd for Cu(C₈H₂₀N₄)Br₂: N, 14.17; H, 5.06; C, 24.28. Found: N, 14.03; H, 5.31; C, 24.55.

Synthesis of Chloro(1,4,7,10-tetraazacyclododecane)copper(II) Chloride Monohydrate. A solution of 0.5 g (2.91 mmol) of cyclen⁴⁵

was added to 100 mL of absolute ethanol and the solution was allowed to boil. To this colorless solution was added with rapid stirring a yellow-green solution of 0.5 g (2.93 mmol) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ dissolved in approximately 10 mL of absolute ethanol. Upon the addition of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ the resulting solution immediately turned a blue-green. The volume of this solution was reduced by boiling to less than 40 mL and upon refrigeration blue crystals formed. These were filtered and recrystallized using absolute ethanol. The product was then filtered and dried. Anal. Calcd for $\text{Cu}(\text{C}_8\text{H}_{20}\text{N}_4)\text{Cl}_2 \cdot \text{H}_2\text{O}$: N, 17.25; H, 6.83; C, 29.59. Found: N, 17.35; H, 6.79; C, 29.74.

Synthesis of Nitrate(1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane)copper(II) Nitrate Monohydrate. A solution of 0.114 g (6 mmol) of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in 125 mL of absolute ethanol was heated to boiling and 0.35 g (6 mmol) of tbcyclen⁴⁶ was added. The light blue color deepened as the copper complex was formed. The solution was refluxed for 1 h. Upon standing at room temperature, dark blue crystals formed which were filtered and washed with ethanol and dried in a desiccator. Anal. Calcd for $\text{Cu}(\text{C}_{36}\text{H}_{44}\text{N}_4)(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$: N, 11.40; H, 6.24; C, 58.57. Found: N, 11.78; H, 6.35; C, 58.48.

Synthesis of Chloro(1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane)copper(II) Chloride Hemihydrate. To a solution of 0.096 g (7 mmol) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in 100 mL of absolute ethanol, 0.31 g (6 mmol) of solid tbcyclen⁴⁶ was added slowly and allowed to boil for 15 min. As the boiling continued the contents of the beaker turned from a green to a blue-green. The solution was decanted into an Erlenmeyer flask and allowed to cool to room temperature after which it was refrigerated overnight. The next day the blue-green crystals were filtered, washed with absolute ethanol, and dried in a desiccator. Anal. Calcd for $\text{Cu}(\text{C}_{36}\text{H}_{44}\text{N}_4)\text{Cl}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$: N, 17.25; H, 6.83; C, 29.59. Found: N, 17.35; H, 6.79; C, 29.74.

Synthesis of Chloro(1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane)copper(II) Perchlorate Hemihydrate. To a mixture of 0.135 g (0.2 mmol) of $\text{Cu}(\text{tbcyclen})\text{Cl}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ in 10 mL of absolute ethanol, 4.4 mL of 0.1 M NaClO_4 (0.4 mmol) was added. A light blue precipitate formed within a few minutes as the solution became nearly colorless. The precipitate was filtered, washed with ethanol and water, and dried in a desiccator. Anal. Calcd for $\text{Cu}(\text{C}_{36}\text{H}_{44}\text{N}_4)\text{ClClO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$: N, 7.58; H, 6.09; C, 58.53. Found: N, 7.82; H, 6.32; C, 58.79.

Synthesis of Chloro(1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane)copper(II) Bromide Monohydrate. To a solution of 0.0675 g (1 mmol) of $\text{Cu}(\text{tbcyclen})\text{Cl}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ in 10 mL of absolute ethanol, 1.5 mL of 0.1 M NaBr (1.5 mmol) was added. The solution was warmed and stirred for 5–10 min after which it was left to cool overnight. A bright blue-green precipitate formed on the bottom of the beaker. This was filtered and washed with ethanol and water and dried in a desiccator. Anal. Calcd for $\text{Cu}(\text{C}_{36}\text{H}_{44}\text{N}_4)\text{ClBr} \cdot \text{H}_2\text{O}$: N, 7.24; H, 5.82; C, 55.88. Found: N, 6.90; H, 5.77; C, 55.16.

Synthesis of Isothiocyanato(1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane)copper(II) Thiocyanate Dihydrate. To a mixture of 0.0676 g (1 mmol) of $\text{Cu}(\text{tbcyclen})\text{Cl}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ and 10 mL of absolute ethanol, 2 mL of 0.1 M NaSCN (2 mmol) was added. A blue-green precipitate formed within a few minutes. The solution became colorless after standing at room temperature for a few hours. The precipitate was filtered, washed with ethanol and water, and dried in a desiccator. Anal. Calcd for $\text{Cu}(\text{C}_{36}\text{H}_{44}\text{N}_4)(\text{NCS})_2 \cdot 2\text{H}_2\text{O}$: N, 11.23; H, 6.42; C, 61.00. Found: N, 11.31; H, 6.06; C, 61.20.

Synthesis of Bromo(1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane)copper(II) Bromide Monohydrate. A solution of 0.43 g (0.19 mmol) of CuBr_2 in 40 mL of absolute ethanol was heated to boiling and 0.1 g (0.19 mmol) of tbcyclen⁴⁶ was added. The orange solution turned dark green and as the complex formed the solution became a lighter green. The green precipitate was filtered and washed with ethanol and dried in a desiccator. Anal. Calcd for $\text{Cu}(\text{C}_{36}\text{H}_{44}\text{N}_4)\text{Br}_2 \cdot \text{H}_2\text{O}$: N, 7.58; H, 6.31; C, 59.25. Found: N, 7.44; H, 5.77; C, 58.41.

Note Added in Proof. A crystal structure determination has recently shown the complex $[\text{Cu}(\text{tbcyclen})\text{Cl}]\text{NO}_3$ to be a distorted five-coordinate square pyramid. Complete details on the structure will be reported in a future communication.

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Registry No. $\text{Cu}(\text{tbcyclen})(\text{NO}_3)_2$, 64413-42-9; $\text{Cu}(\text{tbcyclen})\text{Cl}_2$, 64381-79-9; $\text{Cu}(\text{tbcyclen})\text{ClClO}_4$, 64381-78-8; $\text{Cu}(\text{tbcyclen})\text{Br}_2$, 64381-76-6; $\text{Cu}(\text{tbcyclen})\text{Br} \cdot \text{Cl}$, 64381-75-5; $\text{Cu}(\text{tbcyclen})(\text{NCS})_2$, 64381-74-4; $\text{Cu}(\text{cyclen})(\text{NO}_3)_2$, 64413-40-7; $\text{Cu}(\text{cyclen})\text{Cl}_2$, 64381-72-2; $\text{Cu}(\text{cyclen})\text{Br}_2$, 64381-71-1; $\text{Ni}(\text{cyclen})(\text{NO}_3)_2$, 63528-01-8; $\text{Ni}(\text{tbcyclen})(\text{NO}_3)_2$, 36119-28-5.

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