Notes

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Thermodynamic Studies of the Axial Ligation Reactions of Isomeric (5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)copper(II) Complexes with Anions

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Previously, we have reported the equilibrium constants for the formation of adducts of copper(II) tetraamine complexes with anionic ligands in aqueous solution represented by eq 1.[1-4]

$$[\mathrm{CuL}]^{2+} + \mathrm{X}^- \overset{K}{\rightleftarrows} [\mathrm{CuLX}]^+ \qquad (1)$$

Here, L is the macrocyclic tetraamine *C-meso*-(tet a) or *C-rac*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet b)[1-3] or the linear tetraamine *N,N'*-bis(2-aminoethyl)-1,3-propanediamine (2,3,2-tet).[4]

In the current investigation, we have attempted to gain more detailed understanding of the ways in which the different structures of the coordinated macrocyclic ligands convey properties on their metal complexes. To accomplish this, we have extended our studies to the reactions of copper(II) complexes containing unsaturated nitrogen donors with various anions. The complex ion (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)copper(II), $[\mathrm{Cu}(1,7\text{-CT})]^{2+}$, can exist in two diastereoisomeric forms, depending on the configurations of the two asymmetric nitrogen centers. The crystal structure determinations of these two complexes have recently been completed,[5,6] and these structures are shown in Figure 1. The equilibrium constants of the reactions of these two complexes with several mononegative bases in aqueous solution have been studied by spectrophotometric techniques, and the results are reported herein.

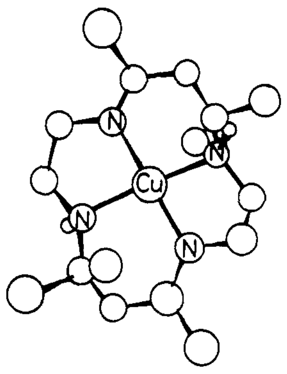
Experimental Section

Reagents. The macrocyclic complexes $[\mathrm{Cu}(N\text{-}meso\text{-}1,7\text{-CT})](\mathrm{ClO_4})_2$ and $[\mathrm{Cu}(N\text{-}rac\text{-}1,7\text{-CT})](\mathrm{ClO_4})_2$ were the same as those reported earlier.[5-8] All other chemicals used in this work were of GR grade from Merck.

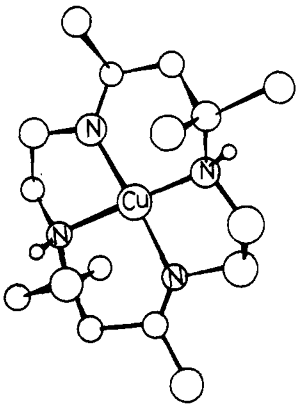
Instrumentation. A Cary 17 spectrophotometer with a thermostated cell compartment was used to record absorption spectra. The temperature was maintained within ±0.1 °C. Equilibrium constants were obtained by a linear least-squares fit of the data on a CDC Cyber-172 computer.

Results and Discussion

General Trends of the Equilibrium Constants. The equilibrium constants for the reaction of $[\mathrm{Cu}(N\text{-}meso\text{-}1,7\text{-CT})]^{2+}$ or $[\mathrm{Cu}(N\text{-}rac\text{-}1,7\text{-CT})]^{2+}$ with various mononegative bases obtained by the method described previously[1,3] are compiled in Table I.



$[\mathrm{Cu(N\text{-}meso\text{-}1,7\text{-}CT)}]^{2+}$



$[\mathrm{Cu(N\text{-}rac\text{-}1,7\text{-}CT)}]^{2+}$

Figure 1. Crystal structures of $[\mathrm{Cu}(N\text{-}meso\text{-}1,7\text{-CT})]^{2+}$ and $[\mathrm{Cu}(N\text{-}rac\text{-}1,7\text{-CT})]^{2+}$.

Table I. Equilibrium Constants ($\mathrm{M^{-1}}$) for $\mathrm{CuL^{2+} + X^- \rightleftarrows CuLX^+}$ (25 °C, $\mu = 0.1$ M ($\mathrm{NaNO_3 + NaX}$))

$\mathrm{L^-}$	$[\mathrm{Cu}(N\text{-}rac\text{-}1,7\text{-CT})]^{2+}$	$[\mathrm{Cu}(N\text{-}meso\text{-}1,7\text{-CT})]^{2+}$
$\mathrm{Cl^-}$	1.1 ± 0.1	1.0 ± 0.1
$\mathrm{Br^-}$	2.0 ± 0.1	1.8 ± 0.1
$\mathrm{I^-}$	6.5 ± 0.1	6.2 ± 0.2
$\mathrm{N_3^-}$	7.8 ± 0.2	7.5 ± 0.1
$\mathrm{SCN^-}$	13.6 ± 0.2	12.6 ± 0.2
$\mathrm{NO_2^-}$	2.1 ± 0.1	2.0 ± 0.1
$\mathrm{OAc^-}$	0.4 ± 0.1	0.4 ± 0.1

As preliminary observations on the equilibrium constants listed in Table I and those reported in earlier studies,[1-4] the following two general trends are particularly noteworthy.

(1) For each of these copper(II) complexes, the axial ligation constant increases in the order $\mathrm{OAc^-} < \mathrm{Cl^-} < \mathrm{Br^-} < \mathrm{NO_2^-} < \mathrm{I^-} < \mathrm{N_3^-} < \mathrm{SCN^-}$.

(2) For each of these anions, the axial ligation constant increases in the order $[\mathrm{Cu}(N\text{-}meso\text{-}1,7\text{-CT})]^{2+} < [\mathrm{Cu}(N\text{-}rac\text{-}1,7\text{-CT})]^{2+} < [\mathrm{Cu(tet\ a)(red)}]^{2+}$, $[\mathrm{Cu}(2,3,2\text{-tet})]^{2+} < [\mathrm{Cu(tet\ b)(red)}]^{2+} < [\mathrm{Cu(tet\ a)(blue)}]^{2+} < [\mathrm{Cu(tet\ b)(blue)}]^{2+}$.

The implications of these observations are examined in detail below.

Softness and Basicity of the Anions. There are two important factors influencing the tendency of the anions to

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Table II. Softness Parameter and Basicity toward the Proton

X^-	softness parameter[a]	pK_a[b]	X^-	softness parameter[a]	pK_a[b]
Cl^-	1.65	−4	SCN^-	4.26	−0.7
Br^-	2.79	−7	NO_2^-	1.83	3.4
I^-	4.03	−10	OAc^-	H[c]	4.7
N_3^-	2.19	4.7			

[a] Reference 9. [b] Reference 10. [c] Hard.

Table III. Electronic Absorption Bands of Copper(II) Complexes in Aqueous Solution

complex	$\bar{\nu}_{max}$, $cm^{-1} \times 10^3$	ϵ_{max}, $M^{-1}\ cm^{-1}$
$[Cu(N\text{-}rac\text{-}1,7\text{-}CT)]^{2+}$	19.8	105
$[Cu(N\text{-}meso\text{-}1,7\text{-}CT)]^{2+}$	20.0	122
$[Cu(tet\ b)(blue)]^{2+}$[a]	12.0, 14.7 (sh)	269, 172
$[Cu(tet\ a)(blue)]^{2+}$[a]	15.4	213
$[Cu(tet\ b)(red)]^{2+}$[a]	19.1	174
$[Cu(tet\ a)(red)]^{2+}$[a]	19.6	135
$[Cu(2,3,2\text{-}tet)]^{2+}$[b]	19.3	51
$Cu^{2+}(aq)$[a]	12.6	11

[a] Reference 2. [b] Reference 4.

complex with these copper(II) macrocyclic complexes: one is the softness of the anion, and the other, the basicity of the anion. The softness parameters[9] and the pK_a values of the conjugate acids of these anions in aqueous solution[10] are listed in Table II.

The fact that OAc^- has the least ligation tendency, in spite of its high basicity, suggests that these copper(II) macrocyclic complexes can be considered soft. In addition, the equilibrium constant of the adduct formation increases as the softness of the halide ion increases, i.e., $Cl^- < Br^- < I^-$. This sequence also indicates that the copper macrocyclic complexes are soft acids.

The tendency to form $CuLX^+$, $Br^- < NO_2^- < I^- < N_3^- < SCN^-$, indicates that not only the softness but also the inherent base strength of the anion affects its ligation tendency. The very large ligation tendency of SCN^- is attributed to its softness and basicity shown in Table II. The softness parameter of N_3^- or NO_2^- is smaller than that of Br^- or I^-. But the basicity toward H^+ of N_3^- is about 10^{12} times that of Br^- or 10^{15} times that of I^-. The basicity toward H^+ of NO_2^- is about 10^{10} times that of Br^-. As it turns out, the equilibrium constant of adduct formation varies in the order of $Br^- < NO_2^- < I^- < N_3^-$.

Cis Effect of $[CuL]^{2+}$. The tendency of axial coordination in $[CuL]^{2+}$ varies in the order $[Cu(N\text{-}meso\text{-}1,7\text{-}CT)]^{2+} < [Cu(N\text{-}rac\text{-}1,7\text{-}CT)]^{2+} < [Cu(tet\ a)(red)]^{2+}$, $[Cu(2,3,2\text{-}tet)]^{2+} < [Cu(tet\ b)(red)]^{2+} < [Cu(tet\ a)(blue)]^{2+} < [Cu(tet\ b)(blue)]^{2+}$. This sequence can be explained by the cis effect proposed by Busch.[11] The ability of $[CuL]^{2+}$ to form an adduct with an anion can be enhanced by the presence of a weak ligand field. The electronic absorption bands of these complexes in aqueous solution, which can be used as a measure of the equatorial ligand field strength, are given in Table III.

$[Cu(tet\ b)(blue)]^{2+}$ is unique among these complexes. The ligand of $[Cu(tet\ b)(blue)]^{2+}$ is in a folded rather than a planar configuration. The spectrum of this complex in aqueous solution exhibits two d–d bands, while the spectra of the other macrocyclic copper(II) complexes in which the ligand is in a planar or distorted-planar rather than a folded configuration exhibit a single λ_{max}. For the investigation of the effect of the strength of the ligand field of the copper(II) complexes on the values of the equilibrium constants for the reactions of these complexes with anions, the wave number of the maximum of the d–d band or the average of the wave numbers of the two bands was considered as an approximate measure of the strength of the ligand field. The results listed in Table I and those reported previously[1–4] indicate the equilibrium constant for the formation of the adduct increases with a decrease in the strength of the ligand in-plane field of $[CuL]^{2+}$.

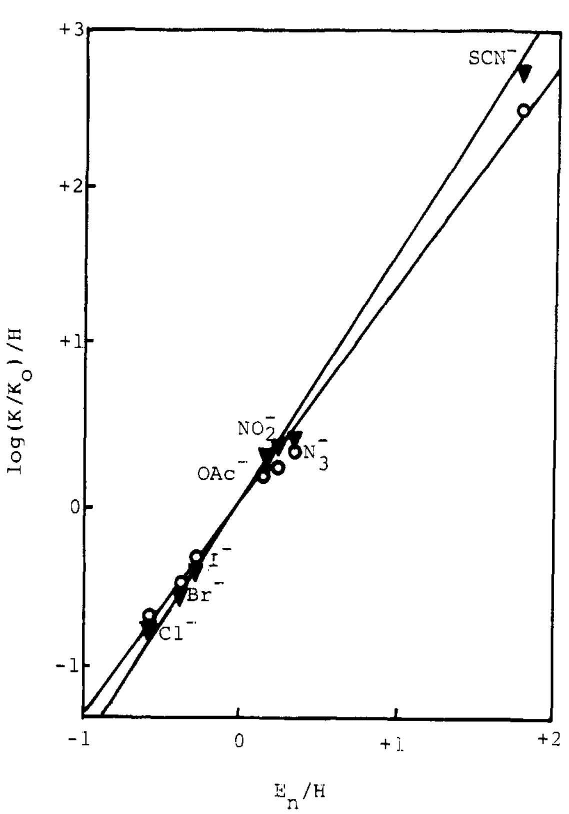

Figure 2. $(\log (K/K_0))/H$ vs. E_n/H plot in water at 25 °C: ○, $[Cu(N\text{-}meso\text{-}1,7\text{-}CT)]^{2+}$; ▲, $[Cu(N\text{-}rac\text{-}1,7\text{-}CT)]^{2+}$.

$[Cu(N\text{-}meso\text{-}1,7\text{-}CT)]^{2+}$ and $[Cu(N\text{-}rac\text{-}1,7\text{-}CT)]^{2+}$ have smaller chelate-ring sizes than the complexes that contain the reduced form of the macrocyclic ligand, tet a or tet b; therefore, the in-plane fields of $[Cu(N\text{-}meso\text{-}1,7\text{-}CT)]^{2+}$ and $[Cu(N\text{-}rac\text{-}1,7\text{-}CT)]^{2+}$ are stronger, and the axial ligation constants of $[Cu(N\text{-}meso\text{-}1,7\text{-}CT)]^{2+}$ and $[Cu(N\text{-}rac\text{-}1,7\text{-}CT)]^{2+}$ are smaller than those of the complexes of tet a and tet b.

Application of the Edwards Equation. Like the formation of adducts of Cu(II) tetraamine complexes with anion,[2,4] the equilibrium constants of these reactions can be quantitatively correlated by the Edwards equation,[12] $\log K/K_0 = \alpha E_n + \beta H$, where K_0 is the constant for a reference base (say, water), H is a proton basicity factor of the base defined by $H = 1.74 + pK_a$, and E_n is a redox factor defined by $E_n = E° + 2.60$, where $E°$ is the standard oxidation potential for the process $2X^- \rightleftarrows X_2 + 2e^-$. The parameters α and β are constants characteristic of the acid. The terms α, β, and α/β are of value and can be used as a measure of the sensitivity to nucleophilic ligand character or polarizability, a measure of the sensitivity to basicity of ligand toward proton, and a measure of the softness of the acid, respectively.[13] A plot of $(\log K + 1.74)/H$ vs. E_n/H gives a straight line with slope α and intercept β for each of these copper(II) complexes as shown in Figure 2. The results obtained are given in Table IV along with the reported

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Table IV. Values of α and β for Copper(II) Complexes

complex	α	β	α/β
$[Cu(N\text{-}rac\text{-}1,7\text{-}CT)]^{2+}$	1.332	0.024	56[d]
$[Cu(N\text{-}meso\text{-}1,7\text{-}CT)]^{2+}$	1.304	0.024	54[d]
$[Cu(\text{tet b})(\text{blue})]^{2+}$[a]	2.189	0.033	66[d]
$[Cu(\text{tet a})(\text{blue})]^{2+}$[a]	1.913	0.031	62[d]
$[Cu(\text{tet b})(\text{red})]^{2+}$[a]	1.512	0.026	57[d]
$[Cu(\text{tet a})(\text{red})]^{2+}$[a]	1.395	0.025	56[d]
$[Cu(2,3,2\text{-tet})]^{2+}$[b]	1.440	0.024	60[d]
Cu^{2+}[c]	2.259	0.233	9.7[e]

[a] Reference 2. [b] Reference 4. [c] Reference 13. [d] Soft acid. [e] Borderline acid.

parameters for Cu^{2+} [13] and copper(II) tetraamine complexes.[2,4]

The linear relationship between the values of α and the maxima in the electronic absorption spectra of copper(II) complexes reported in previous papers[2,4] can be extended to these copper(II) macrocyclic complexes, which contain unsaturated nitrogen donors. A plot of α vs. $\bar{\nu}$ gives a strainght line for the copper(II) complexes listed in Table IV. This correlation indicates there appears to be no effect of the macrocyclic ligand other than that which can be described as the equatorial ligand field strength as measured by the energy of the average d–d transition. The values of β for $[Cu(N\text{-}meso\text{-}1,7\text{-}CT)]^{2+}$ and $[Cu(N\text{-}rac\text{-}1,7\text{-}CT)]^{2+}$ are very similar to those of the planar copper(II) tetraamine complexes, $[Cu(2,3,2\text{-tet})]^{2+}$, $[Cu(\text{tet a})(\text{red})]^{2+}$, and $[Cu(\text{tet b})(\text{red})]^{2+}$. The small values of β indicate these complexes are insensitive to the proton basicity of the anionic ligand.

In aqueous solution, copper(II) ion is on the borderline between hard and soft. Addition of two amines and two imines softens the copper(II) and makes it a soft acid, in accord with the symbiosis pointed out by Jørgensen.[14,15] Like copper(II) tetraamine complexes, the softness of $[Cu(N\text{-}meso\text{-}1,7\text{-}CT)]^{2+}$ or $[Cu(N\text{-}rac\text{-}1,7\text{-}CT)]^{2+}$ is mainly due to the low value of β, insensitivity to the proton basicity factor of the anionic ligand.

On the basis of these results we are able to conclude that the major effect of the macrocyclic ligand is that which can be described as the equatorial ligand field strength as measured by the energy of the average d–d transition.

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Registry No. $[Cu(N\text{-}meso\text{-}1,7\text{-}CT)]^{2+}$, 48186-23-8; $[Cu(N\text{-}rac\text{-}1,7\text{-}CT)]^{2+}$, 48186-22-7; Cl^-, 16887-00-6; Br^-, 24959-67-9; I^-, 20461-54-5; N_3^-, 14343-69-2; SCN^-, 302-04-5; NO_2^-, 14797-65-0; OAc^-, 71-50-1.

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Syntheses and X-ray Crystal Structures of Two New Classes of Macrocyclic Ligands Having both Phosphorus and Nitrogen Donor Atoms

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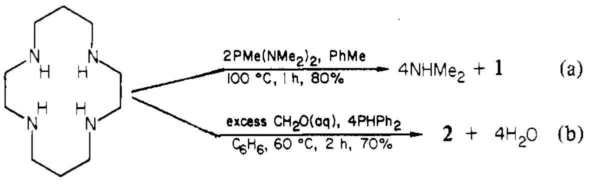
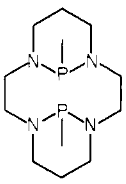
The study of macrocyclic polyhetero ligand systems has attracted much interest, and they have been shown to possess interesting chemical and physical properties.[1,2] However, their syntheses usually involve the use of high-dilution techniques that can, in some cases, limit their availability.[3] In this paper we report one-step high-yield syntheses of two new derivatives of macrocyclic ligands containing phosphorus and nitrogen donor atoms. The syntheses are based upon the derivatization of the cyclam $[14]aneN_4$[4] by simple routes as shown in eq a and b.



cyclam or $[14]aneN_4$
(1,4,8,11-tetraaza-
cyclotetradecane)



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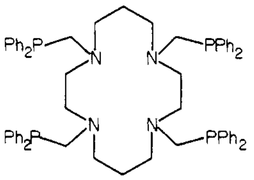

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Experimental Section

Materials. 1,4,8,11-Tetraazacyclotetradecane[5] and bis(dimethylamino)methyl phosphine, $[P(Me)(NMe_2)_2]$,[6] were synthesized according to literature procedures. Diphenylphosphine (Strem), triethylamine (Aldrich), and formaldehyde (37% aqueous) (Mallinckrodt) were used as purchased. Toluene, hexane, and benzene were dried over Na/K amalgam before use. NMR spectra were obtained by using a Nicolet NT-200 spectrometer operating at 200 or 81 MHz.

$[N_1N_{11},N_4N_8\text{-}(\mu\text{-PMe})_2[14]aneN_4]$. Bis(dimethylamino)methylphosphine (2.67 g, 20 mmol) in toluene (20 mL) was added to a stirred slurry of 1,4,8,11-tetraazacyclotetradecane (2.00 g, 10 mmol) in toluene (50 mL). After the addition was completed, the mixture was heated at reflux for 3 h, filtered through Celite, and cooled in an acetone/dry ice bath. The product was isolated as a white solid and recrystallized from a 1:2 toluene/hexane mixture. The white crystals were stored under N_2; a second crop was isolated from the filtrate by reducing the volume to 5 mL: yield 2.13 g (74%); mp 157–159 °C; ^1H NMR ($CDCl_3$) δ 1.22 (d, CH_3, $J = 6$ Hz), 2.65 (m, CCH_2C, 4 H), 3.33

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