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Synthesis and Characterization of Copper(II), Nickel(II), and Cobalt(III) Complexes with 1,4,8,11-Tetraazacyclohexadecane and 1,4,8,11-Tetraazacycloheptadecane

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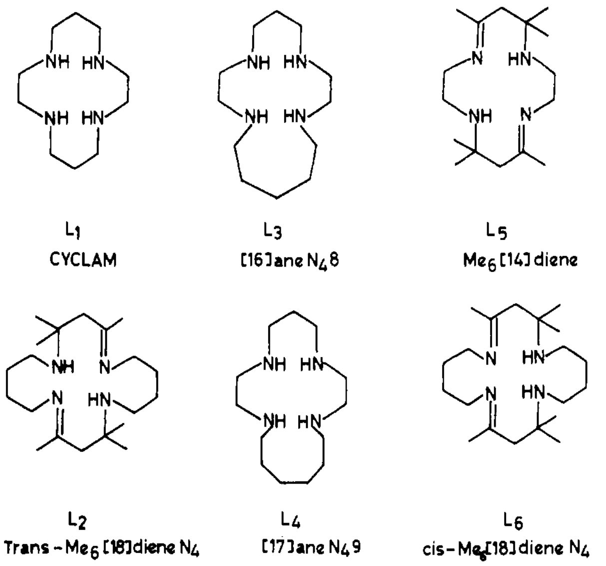
Two new macrocyclic ligands, 1,4,8,11-tetraazacyclohexadecane and 1,4,8,11-tetraazacycloheptadecane, and their Cu(II), Ni(II), and Co(III) complexes, which carry eight- and nine-membered chelate rings, have been synthesized. In aqueous solution the nickel(II) complexes form dihydrates and thus show planar $\rightleftharpoons$ octahedral equilibrium. The Cu(II) complexes undergo rapid dissociation in acidic solutions. The kinetic data are consistent with the general mechanism proposed for the acid-catalyzed dissociation of polyamine complexes. the six-coordinate cobalt(III) complexes are very stable, and the chloro complexes undergo facile axial substitution. In the cis cobalt(III) complexes with acetylacetone and glycine, the macrocycles attain a folded conformation with a C_2 axis.

Introduction

A large number of tetraaza macrocycles and their metal complexes[1] have been studied during the last 15 years. Detailed investigations on the spectral,[2,3] magnetic,[4] thermodynamic,[5-8] kinetic,[9-13] and electrochemical[14] aspects of the 12- to 16-membered tetraaza macrocyclic complexes show that the size of the chelate ring has a marked influence on the stability of these complexes. Most of the work has been done on the complexes involving 14-membered macrocycles, which consist of five- and six-membered chelate rings, and show a very high degree of stability. $[NiL_1]^{2+}$ (with a 5,6,5,6 chelate-ring sequence) persists in strongly acidic solutions for months,[9] while in the case of $[NiL_2]^{2+}$ (with a 7,6,7,6 chelate-ring sequence)[15] this stability is markedly decreased[12] due to the increased strain in the bigger seven-membered chelate rings. In order to investigate the effect of larger chelate rings on the stability of their complexes, two new macrocycles capable of generating eight- and nine-membered chelate rings in their metal complexes have been prepared. The larger sized chelate rings involve a severe strain by analogy with cycloalkanes but are stabilized to a considerable extent by the macrocyclic effect,[16] which makes possible the synthesis of such complexes. This paper reports the synthesis of two new macrocycles and their copper(II), nickel(II), and cobalt(III) complexes.

The macrocycles, 1,4,8,11-tetraazacyclohexadecane [L_3] and 1,4,8,11-tetraazacycloheptadecane [L_4], have been abbreviated as [16]ane$N_4$8 and [17]ane$N_4$9, respectively. During the concluding stages of this work, a few nickel(II) macrocyclic complexes carrying eight- and nine-membered chelate rings have been reported.[17] The formation of such rings has been confirmed by X-ray crystal structure studies on three such complexes[18] (Chart I).

Chart I



Experimental Section

Synthesis. The macrocyclic ligands were prepared essentially by using the method described.[19] The tetratosylate of 1,4,8,11-tetraazaundecane[19] (2,3,2-tet) and the ditosylate[20] of 1,5-pentanediol or 1,6-hexanediol were cyclized in DMF with NaH, and the product was recrystallized from formic acid. The purity of the cyclized product was monitored by infrared spectroscopy, which showed the absence of any ν_{NH} band around 3200 cm^{-1} for the pure product. The cyclized product was hydrolyzed with concentrated H_2SO_4 and the free ligand obtained by extracting with $CHCl_3$ after the pH was raised to about 14 with NaOH. Evaporation of the chloroform layer on a rotary evaporator yielded the ligands as light yellow sticky solids. Mass spectra showed *m/e* 228.37 for [16]ane$N_4$8 and 242.41 for [17]ane$N_4$9 (calcd *m/e* 228.38 for $C_{12}H_{28}N_4$ and 242.41 for $C_{13}H_{30}N_4$). The infrared spectra ($CHCl_3$ solution in NaCl cells) show a sharp ν_{NH} band at 3240 cm^{-1} for both ligands.

The ligands were converted into their hydrochloride salts by dissolving about 4 g of the ligand in 5 mL of methanol, cooling to 0 °C, and adding dropwise an excess of ice-cold concentrated HCl (ca. 20 mL) with stirring, followed by 100 mL of ice-cold ethanol. The white

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product corresponding to L·4HCl, was filtered, washed with ethanol and then ether, and dried under vacuum.

[Cu([16]aneN$_4$8)](ClO$_4$)$_2$ and [Cu([17]aneN$_4$9)](ClO$_4$)$_2$. A 25-mL methanolic solution of 2.0 mmol of copper(II) perchlorate hexahydrate was added to an equimolar amount of the ligand solution in 25 mL of methanol (acidified with 1 drop of $HClO_4$) and heated on a steam bath for 1 h. The volume of the blue solution was then reduced to ca. 3 mL, and excess ether was added to precipitate the complex, which was filtered. The crude product was purified by dissolving in a minimum amount of hot methanol and precipitating the complex with ether. The pure product was filtered, washed with 2-propanol and then ether, and dried under vacuum.

[Ni([16]aneN$_4$8)](ClO$_4$)$_2$ and [Ni([17]aneN$_4$9)](ClO$_4$)$_2$. A 25-mL methanolic solution of 2.0 mmol of nickel(II) perchlorate hexahydrate was mixed with an equimolar amount of the ligand in 25 mL of methanol and heated on a steam bath for about 2 h. The yellow solution was filtered hot and the volume reduced to ca. 5 mL on a steam bath. Excess ether was added on cooling to precipitate the complex, which was filtered. The crude product was recrystallized from a 50% methanol–ethanol mixture, washed with 2-propanol and then ether, and dried under vacuum.

***trans*-[Co([16]aneN$_4$8)Cl$_2$]ClO$_4$ and *trans*-[Co([17]aneN$_4$9)Cl$_2$]ClO$_4$.** A 2.0-g sample of freshly prepared sodium tris(carbonato)cobaltate(III) and 2.0 g of the ligand hydrochloride were mixed in 60 mL of 1:1 (v/v) methanol–water mixture, and the resultant mixture was heated on a steam bath slowly until the effervescence ceased and then heated for a further 30 min. To the deep red slurry was added 15 mL of concentrated HCl, and the green solution was heated on a steam bath for 1 h. The solution was then cooled and treated with 1 mL of 70% $HClO_4$. The volume of the resulting solution was reduced on a steam bath until the product started to separate and then allowed to stand overnight. The bright green product was filtered, washed with ethanol and then ether, and dried under vacuum. Another crop of the product was recovered by further concentration of the mother liquor.

***trans*-[Co([16]aneN$_4$8)(NO$_2$)$_2$]ClO$_4$ and *trans*-[Co([17]aneN$_4$9)(NO$_2$)$_2$]ClO$_4$.** A 1.0-mmol sample of *trans*-[CoLCl$_2$]ClO$_4$ was dissolved in 10 mL of hot 50% methanol and treated with 0.14 g of sodium nitrite. The mixture was heated slowly on a steam bath until it turned brownish yellow (ca. 20 min), and 1.0 g of $LiClO_4 \cdot H_2O$ was added. The volume was then reduced to half on a steam bath, and the solution was allowed to cool. The brownish yellow product that crystallized out was filtered, washed with ethanol and then ether, and dried under vacuum.

***trans*-[Co([16]aneN$_4$8)(Cl)NO$_2$]ClO$_4$ and *trans*-[Co([17]aneN$_4$9)(Cl)NO$_2$]ClO$_4$.** A 1.0-mmol sample of *trans*-[CoL(NO$_2$)$_2$]ClO$_4$ was warmed for about 10 min at 60 °C in 10 mL of dilute HCl during which time the initially yellow solution turned pink. The solution was then cooled, and 2 mL of 70% $HClO_4$ was added carefully, which resulted in the immediate precipitation of a pink complex. The product was filtered, washed with ethanol and then ether, and dried under vacuum.

***cis*-[Co([16]aneN$_4$8)(acac)](ClO$_4$)$_2$ and *cis*-[Co([17]aneN$_4$9)(acac)](ClO$_4$)$_2$.** A 1.0-mmol sample of *trans*-[CoLCl$_2$]ClO$_4$ was suspended in 5 mL of methanol, mixed with 0.2 g of acetylacetone, and heated on a steam bath for 5 min after which 10 drops of diethylamine were added. The solution immediately turned deep red. After the mixture was heated for another 10 min, 0.5 g of $LiClO_4 \cdot H_2O$ was added and the solution cooled in ice. A deep red product separated, which was filtered, washed with 2-propanol and then ether, and dried under vacuum.

***cis*-[Co([16]aneN$_4$8)(Gly)](ClO$_4$)$_2$ and *cis*-[Co([17]aneN$_4$9)(Gly)](ClO$_4$)$_2$.** A 1.0-mmol sample of *trans*-[CoLCl$_2$]ClO$_4$ was suspended in 5 mL of a 1:1 (v/v) methanol–water mixture and mixed with 0.1 g of glycine. This was then heated to about 70 °C on a steam bath, and 10 drops of diethylamine was added. The red solution was heated for a few minutes, and 0.2 g of $LiClO_4 \cdot H_2O$ was added. On cooling, excess ethanol (ca. 20 mL) was added, and the oily red product was separated by decantation. Tituration of the oily product several times with absolute ethanol gave a red solid, which was filtered, washed with ethanol and then ether, and dried under vacuum.

***trans*-[Co([16]aneN$_4$8)(ethanolamine)Cl](ClO$_4$)$_2$.** This compound was prepared by the general route described by Hay.[21] *trans*-[Co([16]aneN$_4$8)Cl$_2$]ClO$_4$ was moistened with a few drops of water in a mortar and mixed with a slight excess of ethanolamine (ca. 18.0 mmol), and the mixture was ground to a fine red paste. To this was added about 10 mL of ethanol, and the mixture was stirred thoroughly. The red oily product was separated by decantation. The oily product was washed several times with ethanol and then ether and dried under vacuum to yield a sticky solid.

Table I. Elemental Analyses for the Complexes[a]

compd	% C calcd	% C found	% H calcd	% H found	% N calcd	% N found
L_3	63.0	63.1	12.2	12.0	24.5	24.7
[CuL$_3$](ClO$_4$)$_2$	29.3	29.0	5.7	5.5	11.4	11.4
[NiL$_3$](ClO$_4$)$_2$	29.6	29.5	5.7	5.6	11.5	11.5
trans-[CoL$_3$Cl$_2$]ClO$_4$	31.4	31.3	6.1	5.9	12.2	12.1
trans-[CoL$_3$(NO$_2$)$_2$]ClO$_4$	30.1	29.9	5.8	5.8	17.5	17.8
trans-[CoL$_3$(NO$_2$)Cl]ClO$_4$	30.7	30.7	6.0	5.9	14.9	14.9
cis-[CoL$_3$(acac)](ClO$_4$)$_2$	34.8	34.8	6.2	6.0	9.5	9.4
cis-[CoL$_3$(Gly)](ClO$_4$)$_2$	29.9	29.8	6.6	6.5	12.4	12.5
L_4	64.4	64.3	12.4	12.5	23.1	23.0
[CuL$_4$](ClO$_4$)$_2$	30.9	30.7	5.9	5.6	11.0	11.2
[NiL$_4$](ClO$_4$)$_2$	31.1	31.2	6.0	5.9	11.2	11.1
trans-[CoL$_4$Cl$_2$]ClO$_4$	33.1	33.0	6.4	6.5	11.8	11.8
trans-[CoL$_4$(NO$_2$)$_2$]ClO$_4$	31.6	31.7	6.1	5.9	17.0	16.8
trans-[CoL$_4$(NO$_2$)Cl]ClO$_4$	32.3	32.3	6.2	6.1	14.5	14.4
cis-[CoL$_4$(acac)](ClO$_4$)$_2$	36.0	36.0	6.3	6.2	9.3	9.2
cis-[CoL$_4$(Gly)](ClO$_4$)$_2$	31.3	31.2	6.4	6.3	12.1	12.0

[a] L_3 = [16]aneN$_4$8 = $C_{12}H_{28}N_4$; L_4 = [17]aneN$_4$9 = $C_{13}H_{30}N_4$; acac = acetylacetonato; Gly = glycinato.

Measurements. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer. Electronic spectra were recorded on a Perkin-Elmer 402 spectrophotometer. For the planar $\rightleftharpoons$ octahedral equilibrium studies, different temperatures were maintained within ±0.1 °C by a circulating-water thermostat. The temperatures were measured inside the cell before and after each spectral measurement. Conductance measurements were carried out on a Systronics conductivity bridge, Type 302, at 25 ± 0.1 °C.

Dc polarograms were recorded on a Cambridge pen recording polarograph at 25 ± 0.1 °C with a dropping mercury electrode against a saturated calomel electrode. 0.1 M KCl and 0.1 M $NaClO_4$ were used as supporting electrolyte. A solution of 0.02% Triton X-100 was used as a maxima suppressor.

The acid-catalyzed dissociation of the copper(II) complexes was studied by using perchloric acid solutions adjusted to I = 1.0 M ($NaClO_4$). The kinetic runs were carried out with a solution of 0.05 g of the copper(II) complexes dissolved in 50 mL of 1.0 M $NaClO_4$. The kinetic runs were monitored at 37 735 cm^{-1} for [Cu([16]aneN$_4$8)](ClO$_4$)$_2$ and at 38 460 cm^{-1} for [Cu([17]aneN$_4$9)](ClO$_4$)$_2$ on a Durrum-Gibson stopped-flow system interfaced with a desk top microcomputer. The rates at each acid concentration were computed from the average of at least six runs, each having a correlation coefficient of 0.999 calculated over more than 3 half-lives.

Results and Discussion

Syntheses of Ligands and Their Metal Complexes. The results of these studies show that the ligands 1,4,8,11-tetraazacyclohexadecane ([16]aneN$_4$8) and 1,4,8,11-tetraazacycloheptadecane ([17]aneN$_4$9) can be readily obtained through the cyclization of the tosylated segments (tetratosyl of 1,4,8,11-tetraazaundecane and ditosyl of 1,5-pentanediol or 1,6-hexanediol) with a yield of ca. 40% (Table I). Both ligands undergo complexation quite easily with copper(II), nickel(II), and cobalt(III). The cobalt(III) complexes are quite stable and undergo axial ligand substitution reactions by the usual metathesis procedures. The facile and stable complexation is apparently promoted by the 2,3,2-tet sequence (5,6,5 chelate-ring sequence), which holds the four nitrogens in a "synthetically preoriented" geometry favorable for coordination, despite the presence of bulky cyclic segments that give eight- and nine-membered chelate rings. The alternating sequence of five- and six-membered chelate rings has been shown to be enthalpically preferred.

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Table II. Electronic Spectral and Conduction Data

complexes	ν, cm^{-1} (ϵ)	Λ, S cm^2 mol^{-1}
$[CuL_3](ClO_4)_2$	18 587 (90)	171
$[CuL_4](ClO_4)_2$	17 600 (213)	150
$[NiL_3](ClO_4)_2$	22 222 (15)	171
$[NiL_4](ClO_4)_2$	22 222 (21)	191
trans-$[CoL_3Cl_2]ClO_4$	15 723 (36)	
trans-$[CoL_3Cl_2]ClO_4$	15 873 (13)	
trans-$[CoL_3(NO_2)_2]ClO_4$	21 459 (303)	
trans-$[CoL_4(NO_2)_2]ClO_4$	21 739 (186)	
trans-$[CoL_3(NO_2)_2]ClO_4$	19 920 (77)	
trans-$[CoL_4(NO_2)_2]ClO_4$	20 619 (84)	
cis-$[CoL_3(acac)](ClO_4)_2$	19 608 (108)	
cis-$[CoL_4(acac)](ClO_4)_2$	19 608 (170)	
cis-$[CoL_3(Gly)](ClO_4)_2$	20 161 (45)	
cis-$[CoL_4(Gly)](ClO_4)_2$	20 202 (38)	
trans-$[CoL_3(ethanolamine)Cl]$-$(ClO_4)_2$	20 000	

Table III. Infrared Spectral Data[a]

compd	ν_{NH}, cm^{-1}	$\nu_{ClO_4^-}$, cm^{-1}	other ligand bands (ν, cm^{-1})
L_3	3240		
$[CuL_3](ClO_4)_2$	3220	1100, 620	
$[NiL_3](ClO_4)_2$	3220	1100, 620	
trans-$[CoL_3Cl_2]ClO_4$	3200	1100, 620	
trans-$[CoL_3(NO_2)_2]ClO_4$	3210	1100, 620	3150 sh (sym NO_2) 1405 (asym NO_2) 822 (asym NO_2)
trans-$[CoL_3(NO_2)Cl]ClO_4$	3200	1100, 620	1420 (asym NO_2) 822 (asym NO_2)
cis-$[CoL_3(acac)](ClO_4)_2$	3230 3100	1100, 625	1570 C=O and 1520 C=C of acac
cis-$[CoL_3(Gly)](ClO_4)_2$	3170	1100, 625	1340 (asym COO^-)
L_4	3240		
$[CuL_4](ClO_4)_2$	3220	1100, 620	
$[NiL_4](ClO_4)_2$	3200	1100, 620	
trans-$[CoL_4Cl_2]ClO_4$	3200	1100, 620	3150 sh (asym NO_2)
trans-$[CoL_4(NO_2)_2]ClO_4$	3200	1080, 620	1410 (asym NO_2) 822 (asym NO_2)
trans-$[CoL_4(NO_2)Cl]ClO_4$	3200	1080, 620	1415 (asym NO_2) 822 (asym NO_2)
cis-$[CoL_4(acac)](ClO_4)_2$	3220 3090	1100, 628	1570 C=O and 1520 C=C of acac
cis-$[CoL_4(Gly)](ClO_4)_2$	3180	1100, 628	1340 (asym COO^-)

[a] sh = shoulder.

Copper(II) Complexes. The copper(II) complexes are bluish violet and show a single d–d band in the visible region (Table II). The position of this band compares quite well with those of the bands shown by other copper(II) tetraaza macrocyclic complexes. The presence of only a single N → Cu charge-transfer band in the UV region shows that the four nitrogen atoms are equivalent in these complexes.[3] The infrared spectra (Table III) show a sharp ν_{NH} band (ca. 3200 cm^{-1}) and the characteristic perchlorate bands (ca. 1100 and 620 cm^{-1}). The perchlorate is ionic in the solid complexes since no splitting in the perchlorate band (1100 cm^{-1}) is observed. Conductance measurements in aqueous solutions correspond to those of 2:1 electrolytes (Table II).

Nickel(II) Complexes. The nickel(II) complexes are brownish yellow in color. They show a broad band at ca. 22 000 cm^{-1} with a low extinction coefficient, which increases with an increase of temperature or ionic strength. This behavior is consistent with the planar ⇌ octahedral equilibrium

$$NiL^{2+} + 2H_2O \overset{K}{\rightleftharpoons} NiL(H_2O)_2^{2+}$$

which shifts to the left on increasing either the temperature or ionic strength. Such an equilibrium is known for a number of other nickel(II) tetraaza macrocyclic complexes.[4,17,22,23]

Table IV. Thermodynamic Parameters for Planar ⇌ Octahedral Equilibria in Nickel(II) Complexes

compd	% planar[a]	% octahedral[a]	$-\Delta H$, kJ mol^{-1}	$-\Delta S$, J K^{-1} mol^{-1}
$[NiL_3](ClO_4)_2$	75	25	8.2	35.7
$[NiL_4](ClO_4)_2$	40	60	3.3	7.5

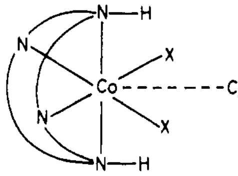
[a] 25 °C.

The equilibrium constant ($K = [NiL(H_2O)_2^{2+}]/[NiL]^{2+}]$) and the thermodynamic parameters have been determined at an ionic strength of 0.1 (maintained with $NaClO_4$) from the temperature dependence of the electronic spectra. With an increase in temperature the intensity of the band at ca. 22 000 cm^{-1} due to the square-planar species shows an increase. At 25 °C there is 75% of the nickel complex of [16]ane$N_4$8 and 40% of the [17]ane$N_4$9 complex in the planar form. The thermodynamic parameters (Table IV) are in the range expected for such equilibria.[23,24] The higher stability of the four-coordinate $[Ni([16]aneN_48)]^{2+}$ complex is primarily due to the stereochemical configuration of the eight-membered chelate ring. The nine-membered chelate ring in $[Ni([17]aneN_49)(H_2O)_2]^{2+}$ has stereochemical features that provide less hindrance to the formation of the six-coordinate species. Molecular models show that, in the case of the eight-membered chelate ring of [16]ane$N_4$8, the methylene protons adjacent to the nitrogen atoms of this chelate ring hinder coordination at the apical sites.[17]

The infrared spectra show the ν_{NH} band at 3200 cm^{-1} and that of the ionic perchlorate at 1100 cm^{-1}. In aqueous solutions the conductance corresponds to those of 2:1 electrolytes.

Cobalt(III) Complexes. Both [16]ane$N_4$8 and [17]ane$N_4$9 give green cobalt(III) complexes (*trans*-$[CoLCl_2](ClO_4)_2$), which show a single d–d band (ca. 15 800 cm^{-1}) typical of a *trans*-CoN_4Cl_2 chromophore (Table II). These cobalt(III) complexes undergo axial ligand substitution reactions to give products that show visible spectral bands typical of CoN_6, CoN_5Cl, CoN_5O, or CoN_4O_2 chromophores.

In the case of cis complexes, the macrocycles should have a folded geometry with a rac(N) configuration that provides a fold axis. Diethylamine has been used to prepare these complexes since secondary NH protons exchange rapidly[25] above pH 6, which allows conversion of meso(N) to the rac(N) configuration required for the formation of cis complexes. The ligand then has a folded conformation with a C_2 axis.



The base-catalyzed configurational conversion occurs while the ligand is coordinated and has been explained on the basis of a concerted mechanism involving reaction of coordinated hydroxide ion with amine hydrogens.[26,27] The infrared spectrum (Table III) show bands corresponding to the appropriate axial ligands.

Stereochemistry. Both macrocycles are capable of forming a novel sequence of chelate rings (5,6,5,8 and 5,6,5,9) on complexation. The four chiral nitrogen centers associated with each macrocycle are capable of yielding as many as 10 dia-

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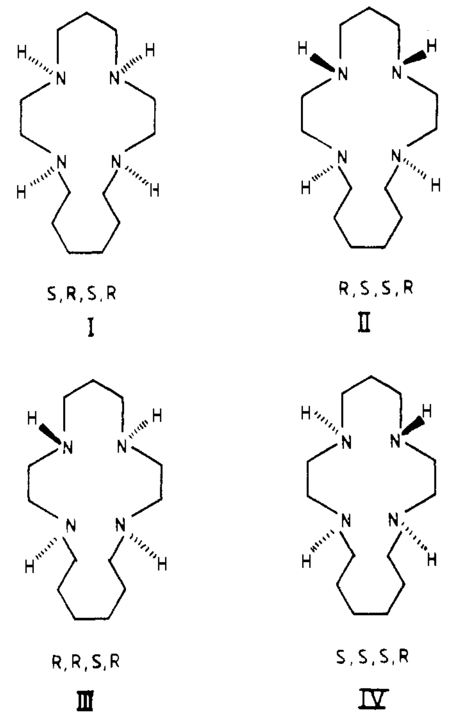
Table V. Kinetic Data for the Dissociation of the Copper(II) Complexes

compd	k_H, M^{-1} s^{-1}	k_0, s^{-1}	k, s^{-1}	K, M^{-1}	ref
$[Cu(teta)]^{2+}$	5.9×10^{-8}	···	···	···	12
$[Cu(teta)]^{2+}$ (unstable red)	7.0×10^{-7}	···	···	···	12
$[Cu(teta)]^{2+}$ (blue)	6.2×10^{-4}	···	···	···	12
$[CuL_5]^{2+}$	2.0×10^{-4}	···	···	···	12
$[CuL_2]^{2+}$	3.6×10^{-4}	0.80×10^{-4}	4.8×10^{-3}	10.2	12
$[CuL_6]^{2+}$	25				12
$[CuL_3]^{2+}$	1.13	0.027	0.48	2.7	this work
$[CuL_4]^{2+}$	0.60	0.122	0.53	1.3	this work
$[Cu(2,3,2\text{-tet})]^{2+}$	6.7×10^{-1}	···	···	···	12

Chart II



S,R,S,R

I

R,S,S,R

II

R,R,S,R

III

S,S,S,R

IV

stereoisomers each, similar to the ones possible for *meso*(*C*)-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane.[28] Molecular models show that out of the possible 10 N-diastereoisomers, only four isomers (Chart II) are virtually free from torsional strain and have minimum hydrogen–hydrogen interactions in the chelate rings. All hydrogens are gauche in each ring in these isomers. In the case of the eight- and nine-membered chelate rings, both of the imine hydrogens are in rac(N) configuration.

The green *trans*-$[CoLCl_2]ClO_4$ complex has been prepared by two synthetic routes: (a) reaction of ligand hydrochloride with sodium tris(carbonato)cobaltate(III) and (b) aerial oxidation of a solution of cobalt(II) acetate and the ligand. Both routes yield a single product as shown by their identical infrared and visible spectra. The former route involves a cis carbonato species as the intermediate and can give a mixture of the N-diastereoisomers.[29,30] The latter route (involving aerial oxidation) gives the pure diastereoisomers, and under carefully controlled conditions, the N-diastereoisomers separate out at different stages of the preparative procedure by virtue of their different solubilities. This method has been successfully used to separate the various N-diastereoisomers of the cobalt(III) complexes of *meso*(*C*)- and *rac*(*C*)-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane.[31,32] These isomers give different infrared and visible spectra. Since both routes give the same isomers in the present case, the ligands must exist as single diastereoisomers in their thermodynamically most stable form.

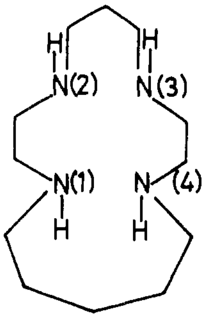


Figure 1.

X-ray studies[18] carried out on the nickel(II) complexes of 1,4,7,10-tetraazacyclohexadecane and tetraazacycloheptadecane, which carry eight- and nine-membered chelate rings, show that these rings are highly unsymmetrical. In the case of the eight-membered chelate-ring macrocyclic complex, this chelate ring is intermediate between boat–boat and crown. By analogy with this complex and the cyclooctane structure,[33] the eight-membered chelate ring should have a structure intermediate between boat–boat and crown form with the N(1) hydrogen equatorially oriented. All other imine hydrogens are axial (Figure 1). All the carbons should lie below the NiN_4 plane with the five-membered chelate rings adopting a gauche–gauche conformation and the central six-membered ring in the twisted-chair form.

The [17]ane$N_4$9 macrocycle, by analogy with 1,4,7,10-tetraazacycloheptadecane and cyclononane,[34] will have a twist-boat–chair conformation. Both of the five-membered chelates adopt the stable gauche–gauche conformation, and the central six-membered chelate ring adopts a twisted-chair form. Close hydrogen–hydrogen contacts are expected in the nine-membered chelate rings similar to the strong transannular hydrogen–hydrogen interaction noted in the crystal structure of cyclononane derivatives.[35,36]

Dissociation of Copper(II) Complexes. The 14-membered macrocyclic complexes are highly stable toward acids, and the dissociation proceeds at very slow rates even at very high acidities.[9,37] The enhanced stability of these complexes as compared to the analogous complexes with noncyclic ligands of the same denticity has been interpreted in terms of the macrocyclic effect.[35] It may be noted that this stability is

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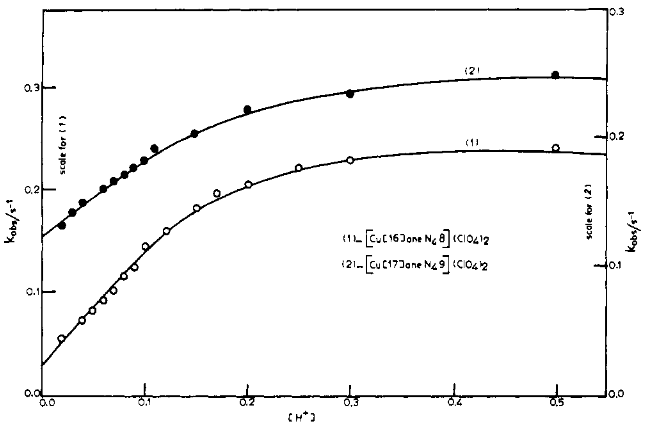

Figure 2. Plots of k_{obsd}/s^{-1} vs. $[H^+]$.

dependent on the ring size, extent of unsaturation, N-chirality, and nature of ring substituents.

The copper(II) complexes undergo very rapid dissociation in acidic solutions (Table V). A plot of k_{obsd} vs. hydrogen ion concentration (Figure 2) shows an initial linear dependence of k_{obsd} on $[H^+]$, but at higher hydrogen ion concentrations, the reaction becomes independent of $[H^+]$ concentration. The plots show an intercept corresponding to a solvolytic path associated with these dissociation reactions. The acid-catalyzed path is consistent with the kinetic scheme[12]

$$CuL^{2+} + H^+ \overset{K}{\rightleftharpoons} CuLH^{3+}$$

$$CuLH^{3+} \xrightarrow{k} Cu^{2+} + LH^+$$

The overall rate expression for this mechanism can be represented as

$$k_{obsd} = k_0 + kK[H^+]/(1 + K[H^+])$$

where k_0 is the solvolytic route.

The double reciprocal plots of $1/(k_{obsd} - k_0)$ vs. $1/[H^+]$ are linear, the slopes of which give $1/kK$ and the intercept $1/K$. A rate constant k_H at low hydrogen concentrations may be used for comparative purposes, which can be defined as the slope of the plot between k_{obsd} and $[H^+]$ at low acidities.

The general mechanism proposed for the acid-catalyzed dissociation of polyamine complexes,[39] as adapted for macrocyclic complexes,[12] adequately accounts for the dissociation pattern exhibited by these complexes. The protonation of the bound nitrogen in these complexes is difficult and is reflected in the low K_{MHL} values, which are comparable to the K_{MHL} values reported for other macrocyclic complexes.[12,40] It is assumed that, in this mechanism, cleavage of the second metal–nitrogen bond is rate determining.[26] The higher rates for the decomposition of these complexes as compared to the 14-membered and 18-membered complexes can be accounted for on the basis of the strain introduced by the bulky eight- and nine-membered chelate rings. The 18-membered complexes, which are associated with a 7,6,7,6 chelate-ring sequence (L_2), have a symmetrical geometry and lesser strain in the molecules and hence dissociate at a lower rate. The order of dissociation rates for the the various copper(II) macrocyclic complexes is in the order of their stability, as reflected by the position of the visible d–d adsorption band.[41] The rate of dissociation can be directly related to the strain energy of the macrocycle.[42]

Table VI. Polarographic Data for Copper(II) Complexes

compd	$E_{1/2}$ vs. SCE, V in 0.1 M KCl	 in 0.1 M $NaClO_4$
$[CuL_3](ClO_4)_2$	−0.61	−0.55
$[CuL_4](ClO_4)_2$	−0.44	−0.54

Polarographic Studies. The copper(II) complexes show a single, diffusion-controlled, one-electron-transfer, reversible reduction wave. The reversible reduction can be assigned to the $Cu^{2+} \rightleftharpoons Cu^+$ couple. The half-wave potentials show a systematic variation in their values with size (Table VI). The reduction potential decreases with increasing ring size and is in the order of the magnitude of their ligand field strengths.[3]

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Registry No. L_3, 85828-16-6; L_4, 296-12-8; $[CuL_3](ClO_4)_2$, 92787-17-2; $[NiL_3](ClO_4)_2$, 92787-19-4; *trans*-$[CoL_3Cl_2]ClO_4$, 92787-21-8; *trans*-$[CoL_3(NO_2)_2]ClO_4$, 92787-23-0; *trans*-$[CoL_3(NO_2)Cl]ClO_4$, 92787-25-2; *cis*-$[CoL_3(acac)](ClO_4)_2$, 92787-27-4; *cis*-$[CoL_3(gly)](ClO_4)_2$, 92787-29-6; $[CuL_4](ClO_4)_2$, 92787-31-0; $[NiL_4](ClO_4)_2$, 92787-33-2; *trans*-$[CoL_4Cl_2]ClO_4$, 92787-35-4; *trans*-$[CoL_4(NO_2)_2]ClO_4$, 92787-37-6; *trans*-$[CoL_4(NO_2)Cl]ClO_4$, 92787-39-8; *cis*-$[CoL_4(acac)](ClO_4)_2$, 92787-41-2; *cis*-$[CoL_4(gly)](ClO_4)_2$, 92787-43-4; *trans*-$[CoL_3(B)Cl](ClO_4)_2$ (B = ethanolamine), 92787-45-6; 2,3,2-tet, 73396-37-9; 1,5-pentanediol ditosylate, 24293-28-5; 1,6-hexanediol ditosylate, 4672-50-8.

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