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Contribution from the Department of Chemistry,
University of Massachusetts at Boston, Boston, Massachusetts 02125

Metal Complexes of Cyclic Triamines. 1. Complexes of 1,4,7-Triazacyclononane ([9]aneN3) with Nickel(II), Copper(II), and Zinc(II)

RITA YANG and LEVERETT J. ZOMPA*

The equilibria which exist between the potentially tridentate cyclic amine 1,4,7-triazacyclononane, [9]aneN3, and Ni(II), Cu(II), and Zn(II) ions have been investigated in 0.1 M KNO3 at 25.0 °C. The bis complexes Cu([9]aneN3)2X2 and Ni([9]aneN3)2X2 as well as Ni([9]aneN3)X2 (where $X^- = NO_3^-$ and/or Cl$^-$) have also been isolated and characterized. The unexpectedly large formation constants determined for the 1:1 metal–ligand complexes and the large value of Dq for Ni([9]aneN3)2^{2+} suggest that this ligand imposes rather severe steric constraints on coordination.

Introduction

Metal complexes of cyclic amines have been extensively investigated during the last 15 years. Most studies have focused upon macrocyclic complexes which contain cyclic tetraamine ligands[1-3] and to a lesser extent complexes containing cyclic diamines.[4] The few studies of complexes containing cyclic triamines indicate that these complexes exhibit thermodynamic and kinetic stability normally associated with macrocyclic complexes.[5,6] Busch and co-workers[7] suggested that the unusual stability of macrocyclic complexes is due to the fixed geometrical placement of ligand donor atoms (the MJF effect). The MJF effect, however, was first illustrated with a cyclic triamine, tris(anhydro-*o*-aminobenzaldehyde) (TRI).[7] Our preliminary studies with a series of saturated cyclic triamines indicated that these compounds form unusually stable metal complexes.[6]

In this study we present further evidence of the complexing strength of cyclic tridentate amines. Formation constants for the mono complexes of 1,4,7-triazacyclononane ([9]aneN3)[8] with nickel(II), copper(II), and zinc(II), as well as the acidity constants of the triprotonated species H3([9]aneN3)$^{3+}$ are presented. The mono and bis complexes of [9]aneN3 with nickel(II) and the bis complex of copper(II) have been isolated and characterized. The unusual stability of the [9]aneN3 complexes is demonstrated by comparison of the formation constants obtained in this study with those of other potentially tridentate amines.

The permutation of the normal Irving–Williams[9] order of stability for the copper(II) and nickel(II) complexes and the unusually large value for the ligand field parameter (Dq) for [Ni([9]aneN3)2]$^{2+}$ are presented as evidence to support our conclusion that the stability of the [9]aneN3 complexes is due largely to the stereorestrictive mode of coordination imposed by this ligand.

Experimental Section

Materials. All reagents and solvents used were reagent grade and were used without further purification. Standard solutions of nickel(II), copper(II), and zinc(II) as the nitrates were standardized by complexometric titration techniques.[10]

1,4,7-Triazacyclononane *N,N′,N″*-Tri-*p*-tosylate. A solution of 6.58 g (0.035 mol) of 1,2-dibromoethane in 80 ml of dimethylformamide (DMF) was added dropwise to a hot (100 °C) solution containing 21.34 g (0.035 mol) of disodiodiethylenetriamine *N,N′,N″*-tri-*p*-tosylate[11] in 180 ml of DMF. After stirring and heating of the solution at 100 °C for 16 h, it was cooled to room temperature. Concentration to one-tenth of the original volume followed by the addition of 1 l. of water gave a white gummy solid which was extracted with 300 ml of hot benzene. After treatment with activated carbon the benzene

solution was dried over anhydrous sodium sulfate. The benzene was then removed to give a yellow-brown oil which was dissolved in hot ethanol. After cooling and standing of the mixture for 24 h, 4.14 g (0.007 mol), 20% yield, of 1,4,7-triazacyclononane *N,N′,N″*-tri-*p*-tosylate was collected as colorless needles, mp 222–223 °C.[11] NMR: δ_{TMS}(CDCl3) 7.60 (q, 12 H, phenyl), 3.45 (s, 12 H, methyl), 2.40 (s, 9 H, ethylene).

1,4,7-Triazacyclononane Trihydrobromide. The procedure of Koyama and Yoshino[12] was employed for the hydrolysis of the cyclic tosylate. A solution containing 3.55 g (6.01 mmol) of 1,4,7-triazacyclononane *N,N′,N″*-tri-*p*-tosylate in 180 ml of 30% hydrobromic acid–acetic acid was refluxed with stirring for 48 h. The solution was filtered while hot and concentrated to one-tenth its original volume. Addition of 150 ml of 25% ether–ethanol solution gave 1.65 g (4.44 mmol), 74% yield, of the amine trihydrobromide, mp 277–278 °C dec.[12] NMR: δ_{TMS}(D2O) 4.1 (s).

1,4,7-Triazacyclononane Trihydrochloride. A slurry of 1.12 g (3.01 mmol) of the hydrobromide salt in 3–4 ml of concentrated hydrochloric acid was heated until all solid dissolved. Sometimes several drops of water had to be added to produce complete solution. Upon cooling, this solution gave colorless crystals of the trihydrochloride salt. Two additional recrystallizations from hydrochloric acid gave 0.64 g (2.69 mmol), 89% yield, of the pure salt, mp 280–281 °C dec. Anal. Calcd for C6H18N3Cl3·0.5H2O: C, 29.10; H, 7.73; N, 16.97; Cl, 42.96. Found: C, 29.19; H, 7.25; N, 17.08; Cl, 42.93. NMR: δ_{TMS}(D2O) 4.0 (s).

Metal Complexes. All metal complexes were synthesized by the following procedure.

Ethanolic slurries of the amine hydrochloride (ca. 0.1 M) were neutralized with potassium hydroxide, cooled, and filtered. Then solutions containing a stoichiometric amount of the appropriate metal salt in ethanol (ca. 0.05 M) were added to the filtrate. Crystals of the metal complex were isolated after partial evaporation of the solvent. In some cases excess of ligand was added to the solutions. The crude product was usually recrystallized from ethanol. The analytical data are reported in Table I.

Spectroscopic and Magnetic Measurements. Solution and solid-state spectra were obtained with a Cary Model 14 recording spectrophotometer. Diffuse transmittance spectra were obtained using the Nujol mull technique.[13] Infrared spectra were recorded on a Perkin-Elmer 137 spectrophotometer employing KBr disks containing the sample. The NMR spectra were recorded with a Varian A-60 NMR spectrometer, using CDCl3 or D2O as solvent.

Magnetic susceptibilities were measured by the Faraday method at 20 °C on a Cahn Model 7600 system. The instrument was calibrated using Hg(Co(NCS)4)2.

Potentiometric Titrations. Solutions of H3([9]aneN3)Cl3 were prepared and standardized by titration with standard sodium hydroxide solution. Metal–ligand titrations were performed with equimolar quantities of metal and ligand. Three titrations were performed for each metal system with concentration ranging from 3 × 10^{-3} to 9 × 10^{-3} M. Because several weeks were required for equilibrium to be established in the nickel(II) system, the titration was performed out

Table I. Analytical Data of [9]aneN$_3$ Complexes

Complex	Dec. pt, °C	μ_{eff}, μ_B	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found	% Cl Calcd	% Cl Found
Cu([9]aneN$_3$)$_2$Cl$_2$·4.5H$_2$O	190		30.41	30.28	8.29	7.99	17.73	17.49	14.96	14.91
Cu([9]aneN$_3$)$_2$(NO$_3$)$_2$	200	1.92	32.31	32.23	6.78	7.07	25.13	24.98		
Ni([9]aneN$_3$)$_2$Cl$_2$·4H$_2$O	300		31.33	31.11	8.33	8.54	18.27	18.40	15.41	15.77
Ni([9]aneN$_3$)$_2$(NO$_3$)$_2$·H$_2$O	220	2.80	31.39	30.96	7.03	6.99	24.40	24.79		
Ni([9]aneN$_3$)Cl$_2$·2.5H$_2$O	295[a]		23.70	23.36	6.64	6.50	13.83	13.82	23.34	23.63

[a] This complex undergoes a color change from violet to green at 109–111 °C.

Table II. Acid Dissociation Constants of H$_3$([9]aneN$_3$)$^{3+}$ and Stability Constants of Its Metal Complexes in 0.1 M KNO$_3$ at 25.0 °C

Reaction	Constant
H$_3$L^{3+} ⇌ H$_2$L^{2+} + H$^+$	pK_{a_1} = strong
H$_2$L^{2+} ⇌ HL$^+$ + H$^+$	pK_{a_2} = 6.82 ± 0.02
HL$^+$ ⇌ L + H$^+$	pK_{a_3} = 10.42 ± 0.02
Cu^{2+} + L ⇌ CuL^{2+}	log β_{CuL} = 15.52 ± 0.01
CuL^{2+} + OH$^-$ ⇌ CuLOH$^+$	log K_{CuLOH} = 8.25 ± 0.02
Zn^{2+} + L ⇌ ZnL^{2+}	log β_{ZnL} = 11.62 ± 0.06
Ni^{2+} + L ⇌ NiL^{2+}	log β_{NiL} = 16.24 ± 0.08

of the cell by the method previously described.[14] An Orion Model 801 digital pH meter was used in combination with glass and calomel electrodes. Electrode response was standardized with buffer solutions at pH 4.01 and 7.00. All measurements were performed at 25 °C in 0.1 M KNO$_3$. Under these conditions values of $-$log [H$^+$] were estimated by applying a correction of -0.11 pH unit to the meter reading.[15] A value of 1.63×10^{-14} for K_w was employed.[16] The test solutions were protected from air by a stream of humidified purified nitrogen. Equilibrium constants were calculated from the titration data by means of the generalized program SCOGS.[17]

Results

The potentiometric titration curve of H$_3$([9]aneN$_3$)Cl$_3$ showed steep inflections at a = 1 and 2 (where a indicates the moles of base added per mole of ligand present). The first acid dissociation is that of a strong acid.

The copper(II)–ligand (1:1) system gave inflections at a = 3 and 4. The titration data are in agreement with the formation of Cu([9]aneN$_3$)$^{2+}$ as the only complex species in the a = 0–3 region of the titration curve.[18] From a = 3 to a = 4 the data are consistent with the hydrolysis of the complex to Cu([9]aneN$_3$)OH$^+$. Beyond a = 4 a precipitate formed and further measurements were not made. The zinc(II)–ligand (1:1) system showed inflections at a = 1 and 3. The titration data indicate that no detectable metal–ligand interaction occurs in the a = 0–1 region. In the ensuing buffer region, a = 1–3, Zn([9]aneN$_3$)$^{2+}$ is the only detectable complex species. Beyond a = 3 hydrolysis of the complex occurs accompanied by precipitate formation. Because of the slow attainment of equilibrium, studies of this hydrolysis reaction were not made. The titration curve for the nickel(II)–ligand (1:1) system appears similar to that for the copper(II)–ligand (1:1) system. Using the out-of-cell technique,[14] measurements were made in the region a = 0–3. Again, Ni([9]aneN$_3$)$^{2+}$ is the only detectable complex species. Equilibrium constants determined in this study are listed in Table II.

Electronic absorption spectra of the nickel(II) and copper(II) complexes of [9]aneN$_3$ in water are shown in Table III. The bis nickel(II) complexes show absorption maxima at nearly the same position, being independent of supporting anion (Cl$^-$ and NO$_3^-$) and solvent (H$_2$O and DMF). The diffuse-transmittance spectra also showed no change in absorption maxima from the solution spectra. The solution spectra of the bis copper(II) complexes are again essentially independent of supporting anion. However, the diffuse-transmittance spectra show small shifts toward higher energy for both bands. The visible band shifts to 16 400 and 16 670 cm^{-1} and the near-infrared band to 9010 and 9090 cm^{-1} for

Table III. Electronic Absorption Spectra of [9]aneN$_3$ Complexes[a]

NiL$_2$Cl$_2$	11 500 sh, 12 500 (9), 20 000 (9), 32 300 (12)
NiLCl$_2$	10 400 (14), 11 400 sh, 17 400 (4), 29 940 (5)
NiL$_2$(NO$_3$)$_2$	11 500 sh, 12 500 (7), 19 800 (5), 32 500 (16)[b]
CuL$_2$Cl$_2$	8100 (48), 16 130 (360)
CuL$_2$(NO$_3$)$_2$	8100 (48), 16 130 (360)

[a] Absorption maxima are reported in cm^{-1} and numbers in parentheses are molar extinction coefficients in aqueous solution at 20 °C. [b] Includes absorbance due to NO$_3^-$.

Table IV. Comparison of Acid Dissociation and Formation Constants for Some Tridentate Amines

	[9]aneN$_3$[a]	cis,cis-tach[b]	ptn[c]	dien[d]
pK_{a_1}	Strong	7.17	3.72	4.25
pK_{a_2}	6.82	8.66	7.95	8.98
pK_{a_3}	10.42	10.16	9.59	9.70
log β_{NiL}	16.2	9.9	9.3	10.7
log β_{CuL}	15.5	10.6	11.1	16.0
log β_{ZnL}	11.6	6.9	6.8	8.9

[a] This study. [b] Reference 14. [c] J. E. Prue and G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 995 (1950). [d] G. Schwarzenbach and J. E. Prue, *ibid.*, **33**, 985 (1950); M. Ciampolini and P. Paoletti, *J. Phys. Chem.*, **65**, 1224 (1961).
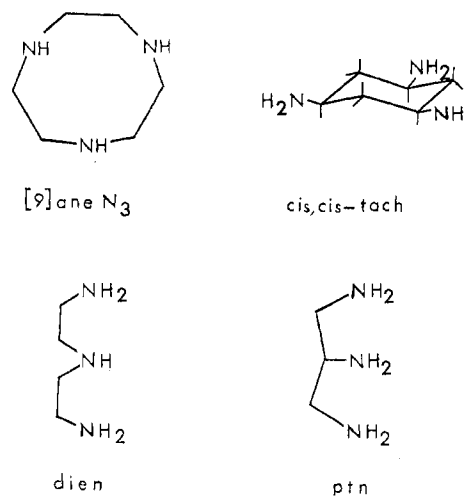

Figure 1. Structures of ligands.

the chloride and nitrate salts, respectively.

Infrared spectra of the bis copper(II) and bis nickel(II) nitrate salts appear to support the presence of ionic nitrate.[19] Absorbances assigned to ionic nitrate occur at 1370 cm^{-1} (vs, br), 825 cm^{-1} (m, sp), and 710 cm^{-1} (vw, sp).

Discussion

A comparison of acidity and formation constants of [9]-aneN$_3$ with other potentially tridentate saturated amines is made in Table IV. The structures of these compounds are shown in Figure 1.

The strong-acid behavior of H$_3$[9]aneN$_3$$^{3+}$ can be explained by the close proximity of the NH$_2^+$ groups which results from the cyclic nature of the amine. The second acid dissociation

is also at least an order of magnitude more acidic than that of the compared amines, probably because the species H_2-[9]aneN$_3$$^{2+}$ has only an ethylene moiety separating the NH$_2$$^+$ groups.

The stability of the mono(1,4,7-triazacyclononane) complexes is clearly evident in Table IV. With the exception of Cu(dien)$^{2+}$, formation constants for the [9]aneN$_3$–M complexes are several orders of magnitude larger than those of the other ligands compared. The tridentate complexes of cis,-cis-tach and ptn, like [9]aneN$_3$, are sterically constrained to facial coordination. On the other hand, dien may coordinate either facially or meridionally thereby avoiding the weaker bond to the axial position of copper(II). The preference of copper(II) for meridional coordination is well-known.[20] Therefore, some destabilization of Cu([9]aneN$_3$)$^{2+}$ is to be expected. Nonetheless, the difference in stabilities between Cu(dien)$^{2+}$ and Cu([9]aneN$_3$)$^{2+}$ is extremely small. For complexes containing saturated tridentate amines which form five-membered chelate rings with copper(II), the meridional complex appears to be more stable by a factor of 10^5 over the facial complex (i.e., see log β_{CuL} for dien and ptn—Table IV).

A rather unusual feature of [9]aneN$_3$ chemistry is the permutation of the normal Irving–Williams order[9] for the copper(II) and nickel(II) complexes. The ratio of log β_{CuL}/log β_{NiL} generally ranges from 1.1 to 1.5 for facial vs. meridional coordination of tridentate saturated amines.[21] This ratio is only 0.96 for [9]aneN$_3$. Again the steric requirements of [9]aneN$_3$ are probably responsible for the destabilization of the copper(II) complex.

The stability constants for the nickel(II) and zinc(II) complexes of [9]aneN$_3$ are among the largest recorded for tridentate N-donor ligands. This unusual stability is apparently not due to the secondary-amine nature of the nitrogen donor atoms but involves the cyclic nature of the ligand. The factors responsible for the macrocycle effect most likely operate in the case of certain cyclic tridentate ligands where stereochemical factors favor tridentate coordination. It is interesting to note that in the M–[9]aneN$_3$ (1:1) systems studied protonated complex species are not present in measurable concentrations even in the early stages (acidic solution) of titration. Similar behavior has been observed in cis,cis-tach-M systems.[14] This would appear to indicate that [9]aneN$_3$ has a favorable conformation for tridentate chelation. Similar properties have also been observed for ([10]–[12])aneN$_3$ complexes.[6]

Although enthalpic[7,22] and entropic[23] arguments have been presented to account for the stability of macrocyclic complexes, it does not appear that one factor is unequivocally more important than the other. Microcalorimetric studies are currently being performed on several M–aneN$_3$ systems in order to determine if enthalpic and/or entropic effects are responsible for their unusual stability.

The electronic spectrum of Ni([9]aneN$_3$)$_2$$^{2+}$ shows three absorption maxima typical of an octahedral complex. The spectrum is nearly identical in water, in DMF, and in the solid state and upon dilution in aqueous solution obeys Beer's law. Since infrared evidence points toward the presence of ionic nitrate in Ni([9]aneN$_3$)$_2$(NO$_3$)$_2$, it appears that the ([9]-aneN$_3$)$_2$Ni^{II} complexes contain the NiN$_6$ chromophores.[24] The value of Dq for these complexes, taken from the energy of the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition, is 1250 cm^{-1}. The shoulder on the low-energy band ($^3A_{2g} \rightarrow {}^3T_{2g}$) is attributed to the spin-forbidden $^3A_{2g} \rightarrow {}^1E_{2g}$ transition.[25] It has been reported[26] that this shoulder appears on the low-energy side of the band if $Dq > 1200$ cm^{-1}. This is consistent with the spectrum of the Ni([9]aneN$_3$)$_2$$^{2+}$ complex.

The value of Dq for this species is much greater than most saturated amines. This probably reflects the constraining nature of the ligand, where the amine donors rigidly force a distorted octahedral structure and present a stronger ligand field to the metal ion. The Racah parameter B for the Ni-([9]aneN$_3$)$_2$$^{2+}$ ($B = 993$ cm^{-1}) is unusually high for an octahedral complex. Similar values of B have been reported for the nickel(II) complexes of cis,cis-1,3,5-tris(pyridine-2-carbaldimino)cyclohexane, Ni((py)$_3$tach)$^{2+}$ ($B = 1000$ cm^{-1}), and 1,1,1-tris(pyridine-2-carbaldiminomethyl)ethane, Ni-((py)$_3$tame)$^{2+}$ ($B = 980$ cm^{-1}).[27] In the case of Ni-((py)$_3$tach)$^{2+}$ the electronic spectrum was interpreted on the basis of a trigonal-prismatic model.[28] A detailed study[29] of the NiN$_6$ chromophore in complexes ranging from trigonal-prismatic (D_{3d}) to trigonal-antiprismatic (D_{3h}) stereochemistry indicates that Ni([9]aneN$_3$)$_2$$^{2+}$ could indeed exhibit trigonal splitting in its spectrum. The parameters employed by Holm and co-workers[29] in constructing the trigonal energy-level diagram do not allow definite assignment of the ligand field bands for this complex and therefore no definite conclusion can be drawn about its degree of distortion from octahedral stereochemistry. However, the small values of the molar extinction coefficients for Ni([9]aneN$_3$)$_2$$^{2+}$ would seem to suggest that the microsymmetry is more trigonal antiprismatic (centrosymmetric) than trigonal prismatic.

The magnetic moment of Ni([9]aneN$_3$)$_2$(NO)$_2$·H$_2$O is 2.81 μ_B. This value is consistent with six-coordinate complexes of nickel(II).[20]

The electronic spectrum of CuL$_2$$^{2+}$ shows two bands. These bands may arise from a trigonal distortion of the copper(II) complex. In this case the T$_{2g}$ state will split into E and A$_1$ states.

The infrared spectrum of Cu([9]aneN$_3$)$_2$(NO$_3$)$_2$ appears to indicate that the nitrate is ionic and therefore not directly bonded to copper(II). However, the change in absorbance maxima from the solid-state spectrum to the aqueous solution spectrum may indicate partial dissociation of the complex. Spectra of the 1:1 complex in aqueous solution are pH dependent. In the pH range 2–5 where CuL^{2+} is the dominant complex species the visible absorption maximum appears at 15 200 cm^{-1}. At pH 9–10 where CuLOH$^+$ is totally formed the maximum shifts to 15 800 cm^{-1}. The aqueous solution spectrum of CuL$_2$$^{2+}$ has an absorption maximum at 16 000 cm^{-1}. Thus, it would appear that in aqueous solution one of the ligands is not completely coordinated.

The magnetic moment of Cu([9]aneN$_3$)$_2$(NO$_3$)$_2$ is 1.92 μ_B. This is consistent with most copper(II) complexes.

The unusual stability of the M–[9]aneN$_3$ complexes and the magnitude of Dq for the nickel(II) complex leads us to conclude that this ligand imposes rather rigid steric constraints on the metal. Lending further support for this argument is the observation that Ni([9]aneN$_3$)$^{2+}$ is unusually stable to acid hydrolysis. Solutions containing this complex in 1 M acid hydrolyze slowly over a matter of hours. Childers and Wentworth[29] have noted similar behavior with Ni(cis,cis-tach)$^{2+}$ and they argued that the stereoselectivity of cis,cis-tach hinders the normal dissociative mechanism of the complex. Busch and co-workers[7] have attributed the unusual kinetic inertness of Ni(TRI)$^{2+}$ to a similar process (the MJF effect).

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Relationship between Electronic Spectra and Heat of Formation of Some Copper–Polyamine Complexes and the Macrocyclic Effect

L. FABBRIZZI,[1] P. PAOLETTI,*[1] and A. B. P. LEVER*[2]

The previously described relationship between ΔH_{aq} and $\nu(d-d)$ for a series of tetragonal copper(II) complexes[3,4] has been greatly extended to include the ammonia complexes $Cu(NH_3)_x^{2+}(aq)$ ($x = 1-4$), various monodiamine derivatives, some triamine complexes, and a macrocyclic derivative. In the light of the more extensive study, the significance of the relationship is reassessed. The good behavior of the copper complex with the macrocycle cyclen suggests that the "macrocyclic effect" is not due to an increased enthalpy contribution but rather to an increased entropy term. At least for the complexes studied here the difference in solvation enthalpy between open-chain and macrocyclic ligands does not seem to play an important role. This conclusion is also supported by data concerning the enthalpy of dehydration of hydrated open-chain and macrocyclic ligands. The strength of the copper–nitrogen bond in macrocyclic complexes may be greater than or less than the strength in analogous open-chain amine complexes depending upon details of the structure, in particular ring sizes.

Introduction

In some preceding work[3-5] we have illustrated a linear relationship between the enthalpy of formation in water and the energy of the electronic maxima in some polyamine complexes of copper (containing four amine nitrogen atoms in the equatorial plane). The complexes in question were prepared by the reaction of aqueous copper ion with one molecule of the tetraamine or two molecules of diamine. Some conclusions concerning the significance of this work were drawn. In this work we have extended the relationship to polyamine complexes containing three atoms of nitrogen (tridentate amines), two atoms of nitrogen (complexes containing two ammonia groups or one diamine ligand), and one atom of nitrogen, namely, the species $Cu(NH_3)^{2+}(aq)$. This series of complexes considerably extends the range of $-\Delta H$ and $\nu(d-d)$ values and permits a more detailed discussion of the significance of the observations.

We have also observed that the macrocycle cyclen (1,4,-7,10-tetraazocyclotetradodecane) obeys the same linear relationship. This fact allows us to review current thinking on the stability of cyclic complexes and to propose an alternative explanation for the "macrocyclic effect". Margerum[6] maintained that the macrocyclic effect is due to a greater degree of solvation for the tetraamines, relative to the analogous macrocycles, and as a consequence attributed this effect solely to an exceptionally favorable enthalpy term, the entropy term being counterbalanced. The studies reported here led

us to believe that ligand desolvation effects have been overestimated. It would appear that it is the entropy term, ΔS, which makes the major contribution to the extra stability of macrocyclic complexes, at least for copper(II). The variations in ΔH can favor or diminish the stability of macrocyclic complexes according to the sequence of chelate rings and the number of atoms contained therein. A combination of penta- and hexaatomic chelate rings is favorable. Macrocycles containing only five-membered rings (and presumably those containing only six-membered rings) have smaller ΔH values. Similar arguments have been applied to explain the thermodynamic stability of open-chain derivatives.[7]

Experimental Section

Materials. The amine ligands were obtained commercially (Fluka, Aldrich). The complexes, all as perchlorates, were obtained by reaction of $Cu(ClO_4)_2 \cdot 6H_2O$ with the ligand in ethanol solution followed by two recrystallizations from the same solvent. The analyses (C, H, N, and Cu) were satisfactory. The ligand *ms*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet a) was prepared by the literature method.[8] Recrystallization from aqueous alcohol gave the dihydrate. The complex Cu(tet a)(ClO₄)₂ was obtained through reaction of tet a with copper perchlorate in anhydrous alcohol.

Spectroscopic Measurements. Visible spectra were obtained with a Beckman DK2A, using quartz cells thermostated at 25 °C, and ultraviolet spectra, with a Cary 14. Solutions of the copper–triamine derivatives and –bis(diamine) derivatives were obtained by dissolving the appropriate perchlorate salt in water. Solutions of the species $Cu(diamine)^{2+}$ (mono(diamine)derivatives) were prepared by dis-