Acknowledgment. We are indebted to the Science Research Council and the University of London Intercollegiate Research Service for financial support. We also thank Mr. J. R. Campbell for measuring the excitation profile of ARG and TSI.

Registry No. WR, 50600-57-2; RG, 58559-78-7; ARG, 12081-56-0; TSI, 60428-74-2.

References and Notes

(1) J. S. Miller and A. J. Epstein, in *Prog. Inorg. Chem.*, **20**, 2 (1976); R. P. van Duyne, *J. Am. Chem. Soc.*, **100**, 1958 (1978).

(2) (a) R. J. H. Clark and W. R. Trumble, *J. Chem. Soc., Chem. Commun.*, 318 (1975); (b) *Inorg. Chem.*, **15**, 1030 (1976); (c) *J. Chem. Soc., Dalton Trans.*, 1145 (1976).

(3) P. Day in "Low Dimensional Cooperative Phenomena", H. J. Keller, Ed., Plenum Press, New York, N.Y., 1975, p 191.

(4) R. J. H. Clark, M. L. Franks, and W. R. Trumble, *Chem. Phys. Lett.*, **41**, 287 (1976).

(5) R. J. H. Clark and M. L. Franks, *J. Chem. Soc., Dalton Trans.*, 198 (1977).

(6) M. Textor and H. R. Stieger, *Z. Anorg. Allg. Chem.*, **423**, 185 (1976).

(7) H. Reihlen and E. Flohr, *Ber. Dtsch. Chem. Ges.*, **67**, 201 (1934).

(8) J. A. Koningstein and B. F. Gächter, *J. Opt. Soc. Am.*, **63**, 892 (1973).

(9) R. J. H. Clark in "Advances in Infrared and Raman Spectroscopy", Vol. 1, R. J. H. Clark and R. E. Hester, Ed., Heyden, London, 1975, p 143.

(10) W. Kiefer in "Advances in Infrared and Raman Spectroscopy", Vol. 3, R. J. H. Clark and R. E. Hester, Ed., Heyden, London, 1977, p 1.

(11) B. M. Craven and D. Hall, *Acta Crystallogr.*, **14**, 475 (1961).

(12) K. L. Brown and D. Hall, *Acta Crystallogr., Sect. B*, **32**, 279 (1976).

(13) M. Tsuboi and A. Y. Hirakawa, *Science*, **188**, 359 (1975); Y. Nishimura, A. Y. Hirakawa, and M. Tsuboi in "Advances in Infrared and Raman Spectroscopy", Vol. 5, R. J. H. Clark and R. E. Hester, Ed., Heyden, London, 1978 p 217.

(14) B. M. Craven and D. Hall, *Acta Crystallogr.*, **21**, 177 (1966).

(15) L. V. Interrante, K. W. Browall, and F. P. Bundy, *Inorg. Chem.*, **13**, 1158 (1974).

(16) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", Van Nostrand, Princeton, N.J., 1945, p 105.

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

Metal Complexes of Cyclic Triamines. 2. Stability and Electronic Spectra of Nickel(II), Copper(II), and Zinc(II) Complexes Containing Nine- through Twelve-Membered Cyclic Triamine Ligands

LEVERETT J. ZOMPA

Received February 6, 1978

The acidity constants of three cyclic triamines, 1,4,7-triazacyclodecane ([10]aneN_3), 1,4,8-triazacycloundecane ([11]aneN_3), and 1,5,9-triazacyclododecane ([12]aneN_3), were measured at 25 °C in aqueous 0.1 F KNO_3. The formation constants of each of these amines with Ni(II), Cu(II), and Zn(II) were obtained as well as the hydrolysis equilibrium constants for several of the complexes. The results indicate that these complexes are generally more stable than those with the corresponding linear or branched triamine ligands. The stability of the cyclic triamines varies inversely with ligand ring size. The electronic spectra of Ni[x]aneN_3^{2+} (x = 9, 10, 11, 12) are presented and trends in the ligand field parameter (Dq) and nephelauxetic ratio (β) for these complexes are discussed. The compounds [Ni[12]ane$N_3(OH)(H_2O)_2$]ClO_4 and [Cu([11]ane$N_3)_2$]$(NO_3)_2 \cdot H_2O$ were synthesized and isolated. Electronic and infrared spectra are presented along with magnetic susceptibility data.

Introduction

The series of cyclic triamines shown in Figure 1 presents a nearly ideal system to study the properties of metal complexes which contain ligands with similar coordinative tendencies yet which progressively distort the stereochemical environment of the metal. Although the synthesis of [12]aneN_3 was published in 1966,[1] few studies of metal complexes containing cyclic triamines were reported prior to 1972.[2] Since that time, several investigations of metal complexes of cyclic triamines have appeared in the literature[3-12] and it is likely that interest in these and similar cyclic compounds where one or more nitrogens are replaced by other heteroatoms will continue to grow.

The extra stability of [9]aneN_3 complexes has been well documented[4-6] and our preliminary work[5] with the remaining congeners suggested that these cyclic amines behave similarly. In this work the preliminary study has been refined and considerably extended, and we show that this entire series of cyclic amines forms complexes which are generally several orders of magnitude more stable than those which contain corresponding linear and branched triamines. Trends in acid dissociation among the ligands as well as complex stability in relation to ligand ring size are also presented and discussed.

Another interesting aspect of cyclic triamine chemistry is the spectroscopic behavior of the complexes. In particular, the bis nickel(II) complexes show a wide range of values for the ligand field parameter (Dq). As with the macrocyclic complexes of saturated tetraamines,[13] those complexes containing the smaller ring ligands have the largest values of Dq. On the basis of an octahedral model, the values of Dq for Ni([9]ane$N_3)_2^{2+}$ and Ni([10]ane$N_3)_2^{2+}$ are among the largest reported for any alkylamines.[6,7] We now report the electronic spectra of the mono nickel(II) complexes of the triamines. Both Dq and β (the nephelauxetic ratio) are calculated for these complexes and based upon these values certain aspects of their structure and bonding are discussed.

The synthesis and characterization of two new complexes, [Ni[12]ane$N_3(OH)(H_2O)_2$]ClO_4 and [Cu([11]ane$N_3)_2$]$(NO_3)_2 \cdot H_2O$ are also described.

Experimental Section

Materials. All reagents and solvents used were reagent grade and were used without further purification. Solutions of nickel(II), copper(II), and zinc(II) as the nitrates were standardized by complexometric techniques.[14] The cyclic triamines were all synthesized using Richmann's modification[15] of the method of Koyama and Yoshino.[3] The trihydrochloride salts of the amines were prepared in nearly quantitative yield from the trihydrobromide salts.[6] Analyses, NMR spectral data, and melting points of these salts are given in Table I.

Metal Complexes. The complexes of [9]aneN_3 and [10]aneN_3 were prepared as the nitrate and/or perchlorate salts by methods previously described.[6,7]

[Cu([11]ane$N_3)_2$]$(NO_3)_2 \cdot H_2O$. To an ethanolic (15 mL) slurry of 120 mg of [11]ane$N_3 \cdot$3HCl(0.450 mmol) was added 76 mg of KOH (1.4 mmol), and the solution was then heated at 60 °C for 15–20 min. After being cooled, the solution was filtered into 10 mL of an ethanolic solution containing 54.4 mg of $Cu(NO_3)_2 \cdot 3H_2O$ (0.225 mmol). Blue

Table I

		% C		% H		% N		% Cl		
compd	mp, °C	calcd	found	calcd	found	calcd	found	calcd	found	NMR $\delta(Me_4Si)$ D_2O
[10]aneN_3·3HCl ($C_7H_{20}N_3Cl_3$)	239 dec	32.32	33.12	7.99	7.80	16.65	16.19	42.04	41.41	3.90 (t, 4H, H_α(trimethylene)) 3.85 (s, 8H, H(ethylene) 2.60 (m, 2H, H_β(trimethylene)
[11]aneN_3·3HCl ($C_8H_{22}N_3Cl_3$)	243 dec	36.03	36.02	8.32	8.51	15.76	15.46	39.89	39.56	3.94 (s, 4H, H(ethylene) 3.88 (t, 8H, H_α(trimethylene)) 2.66 (m, 4H, H_β(trimethylene))
[12]aneN_3·3HCl ($C_9H_{24}N_3Cl_3$)	260 dec	38.51	38.41	8.62	8.95	14.97	14.89	37.90	38.01	3.89 (t, 12H, H_α(trimethylene)) 2.75 (m, 6H, H_β(trimethylene))

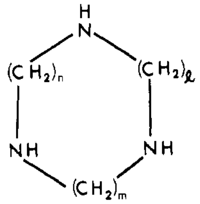


Figure 1. Cyclic triamine structures: $l = m = n = 2$, 1,4,7-triazacyclononane ([9]aneN_3); $l = m = 2$ and $n = 3$, 1,4,7-triazacyclodecane ([10]aneN_3); $l = 2$ and $m = n = 3$, 1,4,8-triazacyclodecane ([11]aneN_3); $l = m = n = 3$, 1,5,9-triazacyclododecane ([12]aneN_3).

crystals of the complex formed after partial evaporation of the solvent.

Anal. Calcd for $C_{16}H_{40}N_8O_7Cu$: C, 36.95; H, 7.75; N, 21.55. Found: C, 37.16; H, 7.39; N, 21.73. Magnetic moment: $\mu_{eff} = 1.75$ μ_B at 20 °C.

[Ni[12]aneN_3(OH)(H_2O)$_2$]ClO_4. The free amine [12]aneN_3 employed for this synthesis was prepared by neutralization of an aqueous solution of [12]aneN_3·3HCl with sodium hydroxide solution followed by extraction of the amine with ether, drying of the solution (Na_2SO_4), and evaporation of the solvent. To a solution containing 1.000 g (5.78 mmol) of [12]aneN_3 in 20 mL of ethanol was added an ethanolic solution (20 mL) containing 0.705 g (1.93 mmol) of nickel(II) perchlorate hexahydrate. The solution was refluxed for 15 min and then filtered while hot to remove a blue-green powder. The filtrate was cooled and upon standing several days in a sealed flask, blue crystals were formed. Filtration yielded 0.35 g of the blue solid which was dried in vacuo at 60 °C. Analysis consistently indicated an approximate composition of [Ni([12]aneN_3)$_2$]·xH_2O (x = 2–4) (see Results). This material was then dissolved in a minimum of hot water and the pH adjusted to ca. 8 by addition of sodium bicarbonate solution (1 F). Sodium perchlorate solution (1 F) was then added to the hot solution to produce a blue crystalline solid. Upon cooling the mixture, more crystals formed which were of suitable size for X-ray diffraction studies. The solid was then dried in vacuo at 60 °C.

Anal. Calcd for $C_9H_{26}N_3O_7ClNi$: C, 28.26; H, 6.85; N, 10.99; Cl, 9.27. Found: C, 28.00; H, 6.29; N, 10.22; Cl, 9.39. X-ray molecular weight: calcd, 383; found, 394. Magnetic moment: $\mu_{eff} = 3.20$ μ_B at 20 °C.

Spectroscopic and Magnetic Measurements. Spectra of solutions and solids were obtained with a Cary Model 14 recording spectrophotometer. Diffuse transmittance spectra were obtained on Nujol mulls of the solids. Infrared spectra were recorded on a Perkin-Elmer 137 spectrophotometer employing KBr disks and/or Nujol mulls containing the sample. The NMR spectra were recorded with a Varian A-60 or Perkin-Elmer R-24 spectrometer using D_2O solvent, and the chemical shifts are relative to Me_4Si (external capillary).

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. An Orion 801 pH meter was used in combination with Beckman glass and calomel electrodes. Calibration of the meter–electrode system was previously described.[6] The titrant was added by a Radiometer ABU12 Autoburet. All measurements were done at 25 °C in 0.1 F KNO_3.

Solutions of the ligands as the trihydrochloride salts ($H_3L^{3+} + 3Cl^-$) were prepared and standardized by titration with standard sodium hydroxide solution. In general, metal–ligand titrations were performed over a tenfold concentration range (1.0×10^{-3}–1.0×10^{-2} F) with equimolar quantities of metal and ligand although in some cases the metal–ligand ratio was varied. An "out-of-cell" titration procedure was used in the nickel(II)–ligand systems because of the slow establishment of equilibrium. Each titration point was obtained from a single solution which was prepared by adding equimolar amounts of metal and ligand, sufficient solid potassium nitrate for a 0.1 F solution, the amount of base required to achieve a specific a value (a equals the moles of base added per mole of ligand present), and water to the appropriate volume in a volumetric flask. These solutions were stored in sealed containers in a constant-temperature bath (25 °C) and their pH values were recorded at biweekly intervals until they remained constant. Solutions generally required 3–4 months to attain equilibrium and were monitored for up to 1 year in order to make certain that no further reaction had occurred.

Equilibrium constants were calculated from the titration data by means of the generalized program SCOGS[16] adapted for a time-sharing Control Data Corp. 6600 facility and modified as described previously.[17]

Because of the very high pK_{a3} value encountered with these amines, the usual technique of meter standardization that employs a buffer of known pH did not give good results. Further the nonlinear response of the glass electrode in very alkaline solutions precluded the usual data analysis. An alternative procedure was employed which essentially compared the amine titration with a second blank titration. First, the pH–volume data from the potentiometric titration of the amine salt with standard base were recorded in the interval from $a = 2$ to $a = 3$ (this corresponds to the reaction $HL^+ + OH^- \rightarrow L + H_2O$). A second "blank" solution which contained sodium, potassium, and nitrate ion concentrations identical with the ligand solution at $a = 2$ was also titrated with the same standard base. Plots of pH vs. volume were made, and from the two curves differences in volume at various increments of pH were determined. This volume difference corresponds exactly to the amount of HL^+ titrated. The concentrations of L and HL^+ were calculated at each increment from

$$\Delta(\text{vol}) \times C_{NaOH} = [L] \qquad (1)$$

$$[HL^+] = [L]_t - [L] \qquad (2)$$

From these the value of pK_a is determined. For example, the pK_{a3} of [12]aneN_3 was determined from 18 points taken from three separate titration pairs with solutions ranging in ligand concentrations from 6×10^{-3} to 1×10^{-2} F. The standard deviation of the acid dissociation constant was 0.05 and the data showed statistical scatter throughout the range (a = 2.1–2.9).

Results

Potentiometric Titrations. The neutralization titration curves of the [x]aneN_3·3HCl (x = 10, 11, 12), as with that of the [9]aneN_3·3HCl,[6] all show two steep inflections at a = 1 and 2 corresponding to the loss of two acidic protons from the amine salts. The third proton is too weakly acidic for an inflection to be observed. With the exception of [12]aneN_3·3HCl the first acid dissociations are those of a strong acid. The acid dissociation constants are given in Table II.

The copper(II)–ligand 1:1 titration curves are shown in Figure 2. For [10]aneN_3, like [9]aneN_3, the complex formation is measurable throughout the a = 0–3 range. The larger ring ligands do not appear to measurably react with copper(II) until the concentration of HL^+ is appreciable (a > 1). For example, in the copper(II)–[12]aneN_3 equilibrium system there is no appreciable reaction between the metal ion and H_2L^{2+}. Within experimental uncertainty the only complex

Table II. Acidity Constants of the Cyclic Amines in 0.1 F KNO_3 at 25.0 °C

reaction	[9]aneN_3[a]	[10]aneN_3	[11]aneN_3	[12]aneN_3
$H_3L^{3+} \rightleftharpoons H_2L^{2+} + H^+$	strong	strong	strong	2.41 ± 0.03
$H_2L^{2+} \rightleftharpoons HL^+ + H^+$	6.82 ± 0.02	6.59 ± 0.02	7.61 ± 0.02	7.57 ± 0.02
$HL^+ \rightleftharpoons L + H^+$	10.42 ± 0.02	12.02 ± 0.02	11.96 ± 0.02	12.60 ± 0.05

[a] From ref 6.

Table III. Metal Complex Formation Constants in 0.1 F KNO_3 at 25.0 °C

reaction	[9]aneN_3[a]	[10]aneN_3	[11]aneN_3	[12]aneN_3
$Cu^{2+} + L \rightleftharpoons CuL^{2+}$	15.52[b]	15.48	14.44	12.63
$Cu^{2+} + L + OH^- \rightleftharpoons CuLOH^+$	23.77			18.27
$Zn^{2+} + L \rightleftharpoons ZnL^{2+}$	11.62	11.28	10.41	8.75
$Zn^{2+} + L + OH^- \rightleftharpoons ZnLOH^+$			16.01	15.04
$Ni^{2+} + L \rightleftharpoons NiL^{2+}$	16.24	14.58	12.88	10.93

[a] From ref 6. [b] Standard deviations in calculated constants are ±0.08 for Ni complexes and ±0.05 or less for all other complexes.

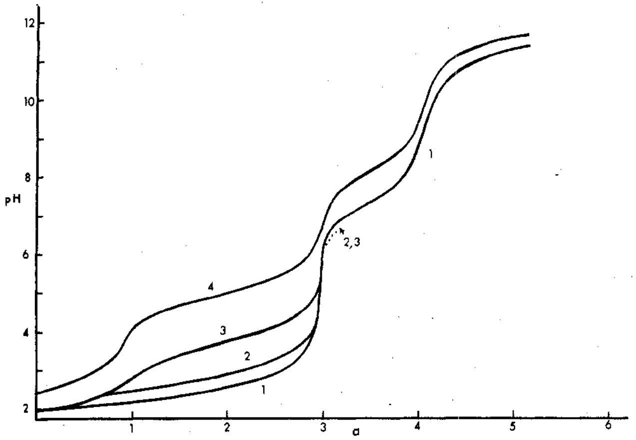


Figure 2. Titration curves for copper(II)–ligand (1:1) systems: curve 1, [9]aneN_3; curve 2, [10]aneN_3; curve 3, [11]aneN_3; curve 4, [12]aneN_3. Concentration 7 × 10^{-3} F. The arrow indicates precipitate formation.

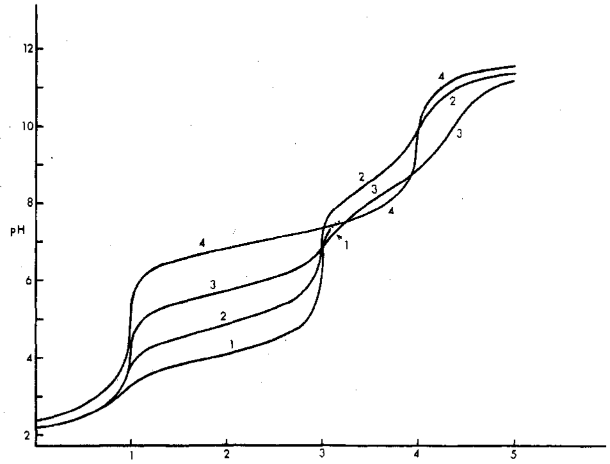


Figure 3. Titration curves for zinc(II)–ligand (1:1) systems: curve 1, [9]aneN_3; curve 2, [10]aneN_3; curve 3, [11]aneN_3; curve 4, [12]aneN_3. Concentration 7 × 10^{-3} F. The arrow indicates precipitate formation.

species detectable in the region a = 0–3 is CuL^{2+}. At $a > 3$ hydrolysis of the complexes leads to precipitate formation ([x]aneN_3 (x = 10, 11)). For the [12]aneN_3 titration it was possible to make equilibrium pH measurements. The pK_a calculated for the complex Cu[12]aneN_3^{2+} ($CuL(H_2O)_x^{2+} \rightleftharpoons CuLOH(H_2O)_{x-1}^+ + H^+$) is 8.14.

Examination of the data from the zinc(II)–[x]aneN_3 (x = 10, 11, 12) 1:1 titrations, Figure 3, shows that there is no measurable metal–ligand interaction in the a = 0–1 region and that between a = 1 and a = 3 the only detectable complex species is ZnL^{2+}. At $a > 3$ hydrolysis of the complexes occurs. Unlike the zinc(II)–[9]aneN_3 equilibrium system these hydrolysis reactions do not lead to the formation of insoluble products and pK_as were obtained for $ZnL(H_2O)_x^{2+}$ (pK_a = 8.20 and 7.51 for L = [11]aneN_3 and [12]aneN_3, respectively). In the case of the zinc(II)–[10]aneN_3 complex, the hydrolysis reaction likely involves polymeric species, and no attempt to study this equilibrium was made. A monoprotic hydrolysis reaction occurs in an overlapping equilibrium with complex formation in the zinc(II)–[12]aneN_3 1:1 system.

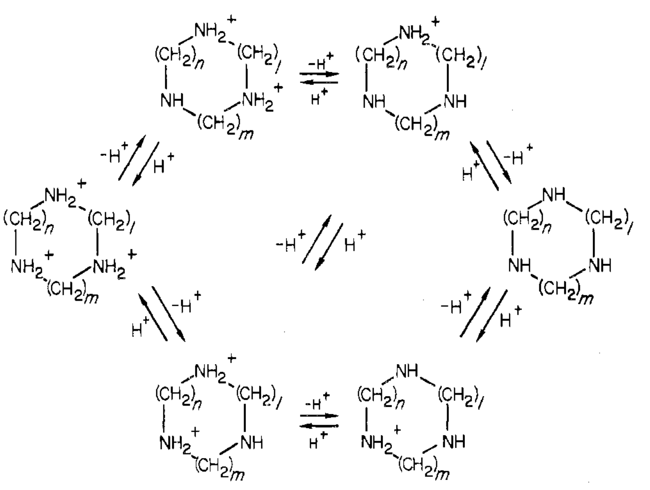
The 1:1 nickel(II)–[x]aneN_3 (x = 10, 11, 12) titration curves were examined between $a \approx 0.4$ and $a \approx 2.7$ using the out-of-cell technique. The curves appear quite similar to those of copper(II) and as with the copper(II) and zinc(II) systems, the only detectable complex species in solution at pH values where data were collected was NiL^{2+}.

The metal complex formation constants are given in Table III.

Synthesis and Electron Spectra of the Nickel(II) and Copper(II) Complexes. The nickel(II) bis complexes of the [10]- and [11]aneN_3 were synthesized as the perchlorate salts using the method of Nonayama[7] and as the nitrate salts using methods previously described for the syntheses of $[Ni([9]aneN_3)_2](NO_3)_2 \cdot H_2O$.[6,18] In our attempts to isolate the bis nickel(II) complex of [12]aneN_3 we obtained blue crystals of a compound whose elemental analysis and molecular weight agree with the composition $[Ni[12]aneN_3(OH)(H_2O)_2]ClO_4$.[19] Although elemental analyses of material isolated from the reaction of the amine with nickel(II) perchlorate in ethanol appeared to indicate that we had also isolated the bis complex, the electronic spectrum of the solid appears identical with the mono complex. In aqueous solution spectroscopic evidence obtained from Job's[20] plots of solutions containing varying amounts of nickel(II) and [12]aneN_3 indicates that only the 1:1 complex forms. The solutions used in the spectroscopic study were heated to 80 °C until no further change in the absorption spectrum occurred (approximately 15 min) before readings were recorded. This procedure was necessary because of the slow formation of complex at room temperature.

The compound $[Cu([11]aneN_3)_2](NO_3)_2 \cdot H_2O$ was also isolated and the electronic spectrum of the solid shows a single broad absorption maximum at 16.0 × 10^3 cm^{-1}. When the complex is dissolved in water, the absorption maximum shifts to that of the 1:1 compound (15.1 × 10^3 cm^{-1}). Analysis of potentiometric titration data in solutions with ligand-to-metal ratios as high as 4:1 shows no evidence of complexes with ligand-to-metal ratio greater than 1:1. The magnetic moment of the complex measured at 20 °C is 1.75 μ_B. Our attempts to synthesize the bis copper(II)–[12]aneN_3 complex as with that of nickel(II) has not met with success.

Scheme I. Microscopic Equilibria for $H_3[x]aneN_3^{3+}$ ($x = 10, l = 3, m = n = 2; x = 11, l = 2, m = n = 3$) Deprotonation



Discussion

Protonation of the Cyclic Amines. The triprotonated cyclic amines are strongly acidic, and only in the case of the $[12]aneN_3$ was it possible to determine the acidity constant for the loss of the first proton. The characteristic strong acid behavior of these triprotic amines may be explained on the basis of positive charge localization. The protonated amine functions are forced into close proximity by the cyclic nature of the compound and loss of a proton is facilitated. In the 12-membered ring the protonated amines are separated by the largest distance and therefore the $H_3[12]aneN_3^{3+}$ is least acidic. The trend in acidity among the H_2L^{2+} and HL^+ species is difficult to interpret. Not only are conformational effects important, but in the case of the [10]- and $[11]aneN_3$ several microscopic processes involving protonated intermediates of different tautometric forms are possible (see Scheme I). Thus the use of simple charge-repulsion arguments does not explain the reversal of the order of acidities (pK_{a2}) for the [9]- and $[10]aneN_3$ and the [11]- and $[12]aneN_3$ (Table II).

The loss of the last proton from these amines is worthy of comment. Linear and branched triamines (e.g., 2,2-tri, 2,3-tri, 3,3-tri, tame, ptn, and c-tach)[21] have pK_{a3} values in the 9.5–11.7 range[22] while the corresponding values for the [10]-, [11]-, and $[12]aneN_3$ show even weaker acidic behavior. We feel that the unusually weak acid properties of the monoprotonated [10]-, [11]-, and $[12]aneN_3$ are due to the trapping of H_3O^+ by an efficient hydrogen-bonded interaction. Both Dreiding and space-filling (CPK) models show that the cavity symmetry of $[12]aneN_3$, in particular, presents an ideal space for a hydrogen-bonded H_3O^+. As ring size decreases, this interaction diminishes and pK_{a3} of the $[9]aneN_3$ falls in the expected range for the monoprotic triamines. Arguments based upon favorable hydrogen-bonded interactions have been suggested to account for the extremely weak acid behavior of macrocyclic amines.[23] Recent work by Cram and co-workers[24] with Host–Guest alkylamines and macrocyclic polyethers also appears to support this hypothesis.

Metal Complexes. The formation constants of the [9]–$[12]aneN_3$ series of ligands with nickel(II), copper(II), and zinc(II) are presented in Table III. For the [10]-, [11]-, and $[12]aneN_3$ complexes the normal (Irving–Williams)[25] order of stability $Cu^{2+} > Ni^{2+} > Zn^{2+}$ is observed. The reversal of this trend, $Ni^{2+} > Cu^{2+}$, for the complexes of $[9]aneN_3$ has already been discussed.[6] It is also shown that the magnitude of the formation constant decreases with incresing ligand ring size for all metals investigated to date. Stated in a different manner—the greater the number of five-membered chelate rings, the more stable the complex. This behavior is atypical for most metal complexes since it has been demonstrated that the replacement of one five-membered chelate ring by a six-membered ring in complexes containing a sequence of five-membered rings generally enhances the stability of the complex. Apparently the larger ring replacement does not relieve strain in the cyclic triamines as it does in other complexes (linear, branched, and macrocyclic) due to the coordinative environment of the triamines which resembles a puckered crown attached to the face of the coordination polyhedron of the metal ion. With the exception of the copper(II) complexes of 2,2-tri and 2,3-tri the cyclic ligands are more stable than saturated linear and branched triamines. The argument[6] based upon the weak axial bonding site in copper(II) which was used to explain the stability trend $Cu(2,2\text{-tri})^{2+} > Cu([9]aneN_3)^{2+}$ may readily be extended to include the results obtained from stability comparisons of the 2,3-tri and $[10]aneN_3$ copper(II) complexes.

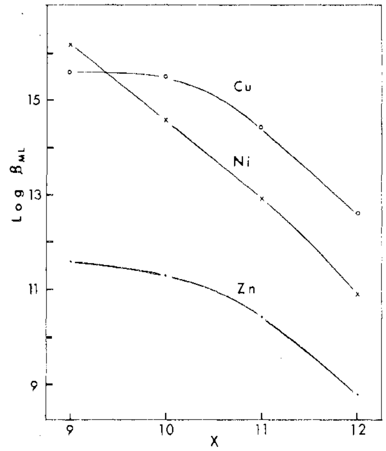


Figure 4. Trends in the stability of 1:1 Ni(II), Cu(II), and Zn(II) complexes of the cyclic amines. Plot of log β_{ML} vs. number of atoms in ring of ligand ($[x]aneN_3$, x = 9, 10, 11, 12): NiL (×), CuL (○), and ZnL (·).

The stability relationships for the systems studied are demonstrated by a plot of log β_{ML} vs. ligand (Figure 4). For those metals studied the greatest stability difference occurs between the [11]- and $[12]aneN_3$ complexes. The slope of the log β_{ML} curve is nearly constant in the case of the nickel(II) sequence and varies considerably in the copper(II) and zinc(II) series. These trends undoubtedly reflect the stereochemistry of the metal ions. In the case of the copper(II) 1:1 complexes similar trends are also observed spectrophotometrically by corresponding wavelength shifts of the absorption maxima. The 1:1 copper(II) complexes show little change in the absorption maximum with [9]- and $[10]aneN_3$ but the maximum shifts to progressively lower energy with larger ring ligands.[5]

If the stability constants of cyclic triamine complexes are compared with saturated amine complexes with similar coordinative environments and chelate ring size, the cyclic ligands always form more stable complexes. For example, $[12]aneN_3$, tame,[26] and c-tach[27] form 1:1 metal complexes with facial tridentate coordination and also form three six-membered chelate rings. The $[12]aneN_3$ complexes are more stable (Table IV). The greater solution stability of the cyclic complexes is further illustrated by comparison of log β_{ML} for complexes of ptn, a 5–5–6 chelate ring system with facial coordination, with those of $[10]aneN_3$, also a 5–5–6 facial system. The $[10]aneN_3$ complexes are more stable by several orders of magnitude. Although thermodynamic data (ΔH and ΔS) are not available for many of the compounds mentioned above, it appears that complexes containing cyclic ligands are more stable because these ligands are preoriented to their

Table IV. Comparison of Formation Constants for Some Tridentate Amines

	ligand									
complex	[9]aneN$_3$[a]	[10]aneN$_3$	[11]aneN$_3$	[12]aneN$_3$	2,2-tri[b]	2,3-tri[b]	3,3-tri[b]	tame[c]	c-tach[d]	ptn[e]
NiL^{2+}	16.2	14.6	12.9	10.9	10.6	11.2	9.2	10.1	9.9	10.1
CuL^{2+}	15.5	15.5	14.4	12.6	15.8	16.6	14.2	11.0	10.6	11.0
ZnL^{2+}	11.6	11.3	10.4	8.8	8.8	8.8	7.9	6.6	6.9	6.2

[a] R. Yang and L. J. Zompa, *Inorg. Chem.*, 15, 1499 (1976). [b] R. Barbucci, L. Fabbrizzi, and P. Paoletti, *Inorg. Chim. Acta*, 7, 157 (1973). [c] A. Sabatini and A. Vacca, *Coord. Chem. Rev.*, 16, 161 (1975). [d] R. F. Childers, R. A. D. Wentworth, and L. J. Zompa, *Inorg. Chem.*, 10, 302 (1971). [e] J. E. Prue and G. Schwarzenbach, *Helv. Chim. Acta*, 33, 995 (1950).

Table V. Electronic Absorption Spectra[a] and the Ligand Field Parameter for Ni([x]aneN$_3$)$_2$$^{2+}$ Based on an Octahedral Model ($\nu_1 = 10Dq$)

x	$\nu_1(^3A_{2g} \rightarrow {}^3T_{2g})$	$\nu_2(^3A_{2g} \rightarrow {}^3T_{1g})$	$\nu_3(^3A_{2g} \rightarrow {}^3T_{1g}(P))$[b]	Dq, cm^{-1}
9	12.5	19.8	30.8	1250
10	12.5	19.5	30.6	1250
11	11.2	18.0	28.6	1120

[a] Absorption maxima are reported in cm^{-1} × 10^3 and recorded in aqueous solution at 20 °C. [b] Since NO$_3^-$ absorbs in this region, the ν_3 band position is best determined from the perchlorate salts.

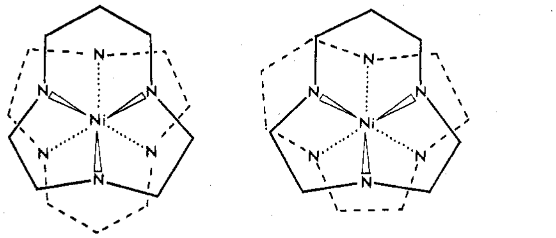


Figure 5. Geometrical isomers of NiL$_2^{2+}$, where L = [10]aneN$_3$. Similar structures can be drawn for L = [11]aneN$_3$ by replacing the ethylene bridging groups with trimethylene groups and the trimethylenes with ethylenes.

coordinative environment. It has already been demonstrated that a favorable entropy term is principally responsible for the exceptional stability of certain tetramine macrocycles[28] as well as Cu([9]aneN$_3$$^{2+}$.[11,12] Thus, a reduction in configurational entropy might account for the greater solution stability of complexes containing the cyclic triamines as ligands. If this argument is valid, rigid triamines which fix three nitrogens in triangular fashion with their nonbonded orbitals in a favorable orientation for tridentate coordination, i.e., *cis*-triazatris-σ-homobenzene,[29] should form metal complexes with stabilities of similar magnitude to the cyclic triamines and also should show extraordinarily large positive values for their entropy of complex formation.

The hydrolysis of the copper(II) and zinc(II) complexes in aqueous solution exhibit the expected behavior. In those cases where equilibrium constants were determined the magnitude of the hydrolysis constants fall into the usual range for loss of a proton from water coordinated to copper(II) and zinc(II).[22] For Cu([12]aneN$_3$)$^{2+}$ the hydrolysis involves the loss of one proton per molecule of complex to form Cu([12]aneN$_3$)OH$^+$ which may dimerize to a compound similar to that reported by Nonoyama.[7]

Several copper(II) and nickel(II) complexes of the cyclic triamines have been reported.[6,7] We have synthesized and characterized two additional complexes of importance, [Cu([11]aneN$_3$)$_2$](NO$_3$)$_2$·H$_2$O and [Ni([12]aneN$_3$)(OH)(H$_2$O)$_2$]ClO$_4$, and some spectroscopic properties of these and other complexes of the cyclic amines are now discussed.

The bis nickel(II) complexes exhibit a wide range of Dq with the [9]- and [10]aneN$_3$ having the largest reported values of any aliphatic triamines (Table V). Examination of the near-infrared (O_h, ν_1, $^3A_{2g} \rightarrow {}^3T_{2g}$) and visible ($O_h$, ν_2, $^3A_{2g} \rightarrow {}^3T_{1g}$ (F)) bands in the spectra obtained from Ni([x]ane)$_2$$^{2+}$ (x = 9, 10, 11) shows that they consist of at least two components. This band splitting likely arises from a trigonal distortion from octahedral symmetry in the case of the Ni([9]aneN$_3$)$_2$$^{2+}$,[30] but in the cases of Ni([x]aneN$_3$)$_2$$^{2+}$ (x = 10, 11) a more complicated perturbation of the octahedral field may result. Because of the inertness of the nickel(II) cyclic triamines,[31] the existence of two kinetically stable geometrical isomers for Ni([x]aneN$_3$)$_2$$^{2+}$ (x = 10, 11) is possible (Figure 5). The solution spectra of these complexes therefore would likely consist of an average spectrum of the two isomers. Although the spectra of the solids Ni([x]aneN$_3$)$_2$Y$_2$ (x = 10, 11; Y = NO$_3^-$, ClO$_4^-$) do not differ significantly from their solution spectra, it is not clear at this time if the solids isolated contain either one or both isomers.

Further complicating the interpretation of the spectra of the Ni([x]aneN$_3$)$_2$$^{2+}$ (x = 9, 10, 11) is the ^1E_g level crossing in the region of the low-energy spin-allowed band. For nickel(II) complexes with $Dq \approx 1200$ cm^{-1} it has been suggested that interaction of the low-energy spin-allowed term, $^3T_{2g}$, with the spin-forbidden term, ^1E_g, gives rise to intermediate coupling and the exact position of the pure $^3A_{2g} \rightarrow {}^3T_{2g}$ transition does not appear at the band maximum.[32] Thus a meaningful spectral interpretation of the bis nickel(II) complexes must await structural determinations so that the type and degree of distortion from octahedral symmetry can be assessed.

The solution spectra of the mono nickel(II) complexes Ni[x]aneN$_3$$^{2+}$ (x = 9, 10, 11, 12) shown in Table VI allow computation of Dq and B (Racah parameter) based upon the octahedral model. Values of Dq and B were calculated by a best-fit method[33] from the visible absorption bands. Although these values vary somewhat from those calculated from the equations given in Table VI, the general trends are maintained. In the case of the mono complexes the ^1E_g transition is sufficiently removed from the spin-allowed bands ($^3A_{2g} \rightarrow {}^1E_g$

Table VI. Electronic Absorption Spectra and Ligand Field Parameters for Ni[x]aneN$_3$$^{2+}$ in Aqueous Solution at 25 °C[a]

x	$\nu_1(^3A_{2g} \rightarrow {}^3T_{2g})$	$\nu_2(^3A_{2g} \rightarrow {}^3T_{1g})$	$\nu_3(^3A_{2g} \rightarrow {}^3T_{1g}(P))$	Dq, cm^{-1}	B(rms)[b]	B[c]	B[d]
9	10.4	17.4	29.9	1040	1061 (0.204)	1073	1057
10	10.4	17.4	28.4	1040	949 (0.266)	973	926
11	10.3	16.9	27.5	1030	887 (0.144)	900	882
12	10.0	16.3	26.7	1000	860 (0.079)	867	856

[a] Energy of the band positions reported in cm^{-1} × 10^3. [b] The values of B are obtained by a nonlinear regression method attributable to Gauss.[33] The column labeled rms represents the root-mean-square deviation of absorption maxima calculated from the best parameter given in the table and the experimental peak positions. [c] The values of B are calculated from the equation $(\nu_2 + \nu_3 - 3\nu_1)/15$.[34] [d] The values of B are obtained by interpolation of the data given in tables of ref 37.

occurs at $(12.7 \pm 0.1) \times 10^3$ cm^{-1}) and intermediate coupling is not important. As with the bis nickel(II) complexes, the order of Dq varies inversely with ligand ring size ([10] ~ [9] > [11] > [12]). The calculated values of B also vary inversely with ring size and therefore the nephelauxetic ratio (β)[34] shows the same trend.

The inverse relationship between ligand ring size and Dq likely reflects the degree of distortion from octahedral symmetry, the Ni[12]aneN$_3$ fitting nearly perfectly the octahedral model (Table VI). Although there are several contributing factors to β, it is generally agreed that a decrease in size indicates a greater covalency of the metal–ligand bond. This would indicate that covalency of the metal–ligand bond increases as ligand size increases for these complexes. Although our initial experiments[5] with copper(II) and zinc(II) led us to believe that orbital overlap might be more efficient with the smaller ring ligands, it now appears that, at least in the case of nickel(II), the larger ring amines allow more efficient overlap. Steric effects caused by the constraining nature of the smaller ring ligands cause the direction of the nitrogen lone-pair orbitals to be shifted away from the metal orbitals. This argument would effectively account for the observed trends in both Dq and β, that is, more distortion and poorer orbital overlap in the complexes containing the smaller ring ligands. Another way to describe this situation is to have the metal being squeezed from a position in the cavity of the ligand as ring size decreases.

Two types of copper(II) complexes of cyclic triamines have been reported: (1) bis complexes which likely contain the CuN$_6$ chromophore with tetragonally distorted octahedral stereochemistry[6,7] and (2) dimeric species containing chloro and/or hydroxy bridges.[7] The larger ring ligands apparently have a propensity toward the formation of the chloro- and hydroxy-bridged dimers.[7] We have isolated a copper(II) complex of the [11]aneN$_3$, [Cu([11]aneN$_3$)$_2$](NO$_3$)$_2$·H$_2$O, and we have studied its infrared and electronic spectra and magnetic susceptibility. The infrared spectrum indicates that nitrate is present as the free ion[35] with bands observed at 825 (m, sp), 1370 (vs, br), and 707 cm^{-1} (w, sp). The electronic spectum of the solid is similar to the spectra of the bis copper(II) complexes of [9]- and [10]aneN$_3$ containing a single absorption maximum at 16.0×10^3. The room-temperature magnetic moment of the compound (1.75 μ_B) is slightly low for copper(II) complexes but apparently does not possess the anomalously low moment which has been attributed to copper–copper magnetic exchange interaction in the case of the dimers. These results combined with the elemental analysis indicate unequivocally that this complex is of the type 1 class mentioned above.

In aqueous solution the bis complex dissociates to the mono complex. The cyclic triamines as well as c-tach[27] show this behavior. The above ligands all form stable complexes when bonded in a tridentate fashion, but our studies have found no evidence of either bidentate or unidentate coordination. The uni- and bicoordinated species are apparently substantially unstable with respect to the tricoordinated species under all pH conditions. Therefore the cyclic triamines and c-tach are either coordinated to their full potential (tridentate) or not coordinated to the metal at all. Since addition of a fifth and sixth nitrogen to the coordination sphere of copper(II) in aqueous solution is not thermodynamically favorable,[36] the equilibrium $CuL_2^{2+} \rightleftarrows CuL^{2+} + L$ lies far to the right and dissociation occurs.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research and the University of Massachusetts at Boston for a Faculty Research Grant. We also thank Professors Robert Gelb and Lowell Schwartz of this department for many helpful discussions.

Registry No. [10]aneN$_3$·3HCl, 67162-90-7; [11]aneN$_3$·3HCl, 67162-91-8; [12]aneN$_3$·3HCl, 67162-92-9; Cu[10]aneN$_3^{2+}$, 67163-01-3; Cu[11]aneN$_3^{2+}$, 67163-02-4; Cu[12]aneN$_3^{2+}$, 67163-03-5; Zn[10]aneN$_3^{2+}$, 67194-35-8; Zn[11]aneN$_3^{2+}$, 67163-04-6; Zn[12]aneN$_3^{2+}$, 67163-05-7; Ni[10]aneN$_3^{2+}$, 67163-06-8; Ni[11]aneN$_3^{2+}$, 67163-07-9; Ni[12]aneN$_3^{2+}$, 67163-08-0; Ni[9]aneN$_3^{2+}$, 67163-09-1; Ni([9]aneN$_3$)$_2^{2+}$, 59034-11-6; Ni([10]aneN$_3$)$_2^{2+}$, 60296-45-9; Ni([11]aneN$_3$)$_2^{2+}$, 60296-47-1; Cu[12]aneN$_3$(OH)$^+$, 67163-10-4; Zn[11]aneN$_3$(OH)$^+$, 67163-11-5; Zn[12]aneN$_3$(OH)$^+$, 67163-12-6; [Cu([11]aneN$_3$)$_2$](NO$_3$)$_2$, 67163-14-8; [Ni[12]aneN$_3$(OH)(H$_2$O)$_2$]ClO$_4$, 67163-16-0.

References and Notes

(1) J. L. van Winkle, J. D. McClure, and P. H. Williams, *J. Org. Chem.*, **31**, 3300 (1966).

(2) An exception involves the unsaturated ligand tribenzo[β,*f*,*j*][1,5,9]triazacyclododecine (TRI) which has been studied extensively by Busch and co-workers: (a) G. A. Melson and D. H. Busch, *J. Am. Chem. Soc.*, **87**, 1706 (1964); (b) S. C. Cummings and D. H. Busch, *Inorg. Chem.*, **10**, 1220 (1971), and references therein.

(3) H. Koyama and T. Yoshino, *Bull. Chem. Soc. Jpn.*, **45**, 481 (1972).

(4) T. Arishima, K. Hamada, and S. Takamoto, *Nippon Kagoku Kaishi*, 1119 (1973).

(5) M. DeRonde, D. Driscoll, R. Yang, and L. J. Zompa, *Inorg. Nucl. Chem. Lett.*, **11**, 521 (1975).

(6) R. Yang and L. J. Zompa, *Inorg. Chem.*, **15**, 1499 (1976).

(7) M. Nonoyama, *Transition Met. Chem.*, **1**, 70 (1976).

(8) S. F. Mason and R. D. Peacock, *Inorg. Chim. Acta*, **19**, 75 (1976).

(9) (a) M. Nonoyama, *Inorg. Chim. Acta*, **20**, 53 (1976); (b) *J. Inorg. Nucl. Chem.*, **39**, 550 (1977).

(10) M. S. Okamoto and E. K. Barefield, *Inorg. Chim. Acta*, **17**, 91 (1976).

(11) L. Fabbrizzi and L. J. Zompa, *Inorg. Nucl. Chem. Lett.*, **13**, 287 (1977).

(12) M. Kodama and E. Kimura, *J. Chem. Soc., Dalton Trans.*, 1473 (1977).

(13) L. Y. Martin, L. J. DeHayes, L. J. Zompa, and D. H. Busch, *J. Am. Chem. Soc.*, **96**, 4046 (1974).

(14) H. A. Flashka, "EDTA Titrations", 2nd ed, Pergamon Press, Oxford, 1964.

(15) J. E. Richmann and T. J. Atkins, *J. Am. Chem. Soc.*, **96**, 2268 (1974).

(16) I. G. Sayce, *Talanta*, **15**, 1397 (1968).

(17) L. J. Zompa, *Inorg. Chem.*, **10**, 2648 (1971).

(18) The nitrate salts were prepared by adding an ethanolic solution containing a stoichiometric amount of ligand to a solution of nickel(II) nitrate hexahydrate in ethanol. Partial evaporation of solvent produced violet crystals of the bis nickel(II) complexes. Satisfactory analyses were obtained for these materials.

(19) Because the IR spectrum of this compound appears to indicate the presence of ionic perchlorate, 1100–1085 (vs, b) and 924 cm^{-1} (w, sp) (K. Nakamoto, "Infrared Spectra of Inorganic Coordination Compounds", 2nd ed, Wiley, New York, N.Y., 1970, pp 175–176) and the electronic spectrum is typical of an octahedral complex, the formula is written in this fashion.

(20) M. M. Jones, "Elementary Coordination Chemistry", Prentice-Hall, Englewood Cliffs, N.J., 1964, p 282.

(21) Abbreviations: diethylenetriamine, 2,2-tri; 1,4,8-triazaoctane, 2,3-tri; 1,5,9-triazanonane, 3,3-tri; 1,1,1-tris(aminomethyl)ethane, tame; 1,2,3-triaminopropane, ptn; *cis,cis*-1,3,5-triaminocyclohexane, c-tach.

(22) L. G. Sillen and A. E. Martell, *Chem. Soc., Spec. Publ.*, **No. 17** (1964); **No. 25** (1971), and references given in Table IV.

(23) B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, **4**, 1102 (1965).

(24) R. C. Helgeson, T. L. Tarnowski, J. M. Tinker, and D. J. Cram, *J. Am. Chem. Soc.*, **99**, 6411 (1977), and references therein.

(25) H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 3192 (1953).

(26) A. Sabatini and A. Vacca, *Coord. Chem. Rev.*, **16**, 161 (1975).

(27) R. F. Childers, R. A. D. Wentworth, and L. J. Zompa, *Inorg. Chem.*, **10**, 302 (1971).

(28) (a) M. Kodama and E. Kimura, *J. Chem. Soc., Dalton Trans.*, 2341 (1976), and references therein; (b) A. Anichini, L. Fabbrizzi, and P. Paoletti, *Inorg. Chim. Acta*, **22**, L25 (1977).

(29) H. Prinzbach, R. Schuesinger, M. Breuninger, B. Gallenkamp, and D. Hunkler, *Angew. Chem., Int. Ed. Engl.*, **14**, 347 (1975).

(30) The symmetry of the NiN$_6$ chromophore in Ni([9]aneN$_3$)$_2^{2+}$ as determined by X-ray crystallography is a trigonally distorted octahedron: T. N. Margulis and L. J. Zompa, *Inorg. Chim. Acta*, **28**, L157 (1978).

(31) (a) L. T. Taylor and D. H. Busch, *J. Am. Chem. Soc.*, **89**, 5732 (1967); (b) L. Murphy and L. J. Zompa, to be submitted for publication.

(32) (a) R. D. Hancock and G. J. McDougall, *J. Chem. Soc., Dalton Trans.*, 67 (1977); (b) C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 1362 (1955).

(33) Y. Bard, "Nonlinear Parameter Estimation", Academic Press, New York, N.Y., 1974, Chapter 5.

(34) (a) A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1968; (b) C. K. Jørgensen, "Modern Aspects of Ligand Field Theory", Elsevier, Amsterdam, 1971.

(35) N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, **4**, 804 (1965).

(36) V. Romano and J. Bjerrum, *Acta Chem. Scand.*, **24**, 1551 (1970), and references therin.

(37) A. B. P. Lever, *J. Chem. Educ.*, **45**, 711 (1968).