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Gas Phase Ion Thermochemistry of Tetraaza Complexes Such as CyclamM^{2+} with H_2O, CH_3OH, NH_3, and Other Ligands, Where $M^{2+} = Mn^{2+}$, Ni^{2+}, Cu^{2+}, and Zn^{2+}

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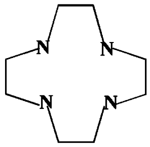
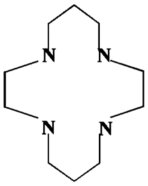
Tetraaza complexes with M^{2+} were produced in the gas phase by Electrospray (ESI) of solutions containing salts of M^{2+}dinitrates and a tetraaza compound such as cyclam. The complex CyclM^{2+} formed in solution and transferred to the gas phase via ESI was introduced into a reaction chamber containing known partial pressures of a ligand L. Equilibria between CyclM^{2+} and L establish $\mathrm{CyclML_n}^{2+} = \mathrm{CyclML}_{n-1}{}^{2+} + \mathrm{L}$ and the equilibrium constants $K_{n,n-1}$ are determined with a mass spectrometer. Determinations at different temperatures lead to not only the $\Delta G^0_{n,n-1}$ values but also the $\Delta H^0_{n,n-1}$ and $\Delta S^0_{n,n-1}$ values. Data for $n = 1$, 2, and 3 were obtained for L = H_2O and CH_3OH. The $\Delta G^0_{1,0}$, $\Delta H^0_{1,0}$ as well as $\Delta G^0_{2,1}$, $\Delta H^0_{2,1}$ values, when $M^{2+} = Mn^{2+}$ and Zn^{2+}, were larger than those for Ni^{2+} and Cu^{2+}. The ligand field theory and the Irvine−Williams series predict a reverse order, i.e., stronger bonding with Ni^{2+} and Cu^{2+} for simple ligand reactions with M^{2+}. An examination of the differences of the reactions in solution and gas phase provides a rationale for the observed reverse order for the CyclM^{2+} + L reactions. Differences between gas phase and solution are found also when $M^{2+} = Cu^{2+}$, but the tetraaza macrocycle is changed from, 12-ane to 14-ane to 15-ane. The strongest bonding in solution is with the 14-ane while in the gas phase it is with the 15-ane. Bond free energies, $\Delta G^0_{1,0}$, for CyclCu^{2+} with L = H_2O, CH_3OH, NH_3, C_2H_5OH, C_3H_7OH, $(C_2H_5)_2O$, and CH_3COCH_3, are found to increase in the above order. The order and magnitude of the $\Delta G^0_{1,0}$ values is close to $\Delta G^0_{1,0}$ values observed with potassium K^+ and the same ligands. These results show that the cyclam in CyclCu^{2+} leads to an extensive shielding of the +2 charge of Cu^{2+}. Ligands with gas phase basicities that are relatively high, lead to deprotonation of CyclM^{2+}. The deprotonation varies with the nature of M^{2+} and provides information on the extent of electron transfer from the N atoms of the cyclam, to the M^{2+} ions.

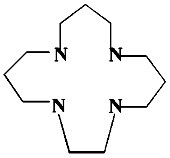
1. Introduction

Macrocyclic polyamines such as cyclam, (1,4,8,11-tetraazacyclotetradecane, generally abbreviated as 14-ane N_4) see structure **II** below, and substituted cyclams, form strongly bonded complexes with doubly charged transition metal ions. Cyclams and related macrocycles, see for example **I** and **III**, have generated continuous interest right from the time of their synthesis[1] (for convenience the notation for the macrocycles **I**−**III** is used without the N_4 in the subsequent discussion). This is due in part to their partial structural and functional resemblance to naturally occurring macrocyclic ligands, such as the porphyrin ring of the heme proteins and the related natural macrocyclic complexes of magnesium in chlorophyll and its derivatives. Therefore, it is not surprising that complexes involving cyclam derivatives also have important applications in medicine.[2] The interactions of macrocyclic polyamines with metal ions represent also an important part of modern coordination chemistry [1]. Yet, essentially no gas-phase ion chemistry determinations have been made for this class of compounds. There have been physical measurements such as the determinations of the photoelectron spectra of cyclam and three substituted cyclams.[3] These led to measurements of the ionization energies of the valence shells which provided some insights into the complexation tendencies of the differently substituted cyclams.[3]

Doubly charged metal ions M^{2+}ions and their complexes were very difficult or impossible to produce in the gas phase before it was shown[4] that the M^{2+} ions and complexes can be readily obtained by electrospray of water or methanol solutions containing a soluble salt of the M^{2+} ion and the given ligand. The complexes were observed by mass spectrometry. The use of electrospray for studies of metal ion complexes in the gas phase was followed by numerous studies from this and other laboratories; see refs 5−7 and references therein.


I


II


III

I = 12-ane N_4 II = 14-ane N_4 III = 15-ane N_4

In the present work, solutions of salts where the cations, $M^{2+} = Mn^{2+}$, Ni^{2+}, Cu^{2+}, and Zn^{2+}, are complexed to tetraaza coordination compounds, such as cyclam, were used to obtain the cyclam−metal complexes in the gas phase and then study some of their reactions with ligands such as H_2O in a gas-phase reaction chamber. Thus, stepwise hydration energies

$$\mathrm{CyclM(H_2O)}_n{}^{2+} = \mathrm{CyclM(H_2O)}_{n-1}{}^{2+} + \mathrm{H_2O}\ (n,n-1) \quad (1)$$

were obtained by determination of the equilibrium constants $K_{n,n-1}$, see eq 2a, where $P(H_2O)$ stands for the partial pressure of H_2O, at a constant temperature T. The standard free energy, $\Delta G^0_{n,n-1}$, was obtained with eq 2b, while the enthalpy and entropy changes were obtained from van't Hoff plots of the

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equilibrium constants, based on eq 2c.

$$K_{n,n-1} = P(\mathrm{CyclM(H_2O)}_{n-1}{}^{2+}) \times P(\mathrm{H_2O})/P(\mathrm{CyclM(H_2O)}_n{}^{2+}) \quad (2a)$$

$$\Delta G^0{}_{n,n-1} = -RT \ln K_{n,n-1} \quad (2b)$$

$$\Delta G^0{}_{n,n-1} = \Delta H^0{}_{n-1,n} - T\,\Delta S^0{}_{n,n-1} \text{ (at constant } T) \quad (2c)$$

A more detailed description of the method and experimental conditions is given in the Experimental Section. Determinations were made not only with H_2O as a ligand L but also for L = CH_3OH, C_2H_5OH, n-C_3H_7OH, n-C_4H_9OH, NH_3, and n-C_3H_9-NH_2.

The hydration or more generally the ligation energies of the macrocyclic complexes with $M^{2+}$and particularly the data for the ligation by one and two ligand molecules, i.e., the (1,0) and the (2,1) values, obtained in the present work are of interest for several reasons.

In aqueous solution, the $CyclM^{2+}$ is expected to be present largely as axially distorted octahedral compound where the approximately square and planar $CyclM^{2+}$ has added two water molecules. The resulting structure will be axially distorted because the water molecules are weak ligands compared to the secondary amine nitrogens of the cyclam.

Dihydration leading to octahedral $CyclM(H_2O)_2{}^{2+}$ complexes is observed in X-ray crystal structures.[8a,b] The exact bond distances of the water molecules obtained from X-ray crystal structures are not very significant because they depend also on the nature and location of the counterions, i.e., the anions. More interesting are results[8c] obtained with X-ray diffraction of aqueous solutions of $CyclNi^{2+}$ containing also ammonia. These indicated a regular octahedral complex in which the Ni $-NH_3$ nitrogen distance was approximately equal to the Ni $-$ N distances involving the cyclam N atoms, i.e., presumably nearly equally strong interaction of the NH_3 and cylcam nitrogens with Ni.

Bonding in transition metal complexes does not depend only on the ligand but also on the d electron configuration of the metal ion and on other factors. For the transition metal series Mn^{2+} d^5, Fe^{2+} d^6, Co^{2+} d^7, Ni^{2+} d^8, Cu^{2+} d^9, and Zn^{2+} d^{10}, experimental determinations in solution of the structure, formation constants, reactivity, etc. exhibit the same trends for a great variety of different ligands, which depend on the number of d electrons of M^{2+}. These observations are often referred to as the "Irving−Williams" series. The crystal and ligand field theory (LFT) together with the Jahn−Teller effect have been successfully used to provide an explanation and prediction of the observed trends.[9] Notable also are theoretical ab initio studies such as the calculations of Akesson and co-workers[10] of the hexahydrates $M(H_2O)_6{}^{2+}$ in the gas phase where M^{2+} are transition metals of the Irving−Williams series. These results reproduce the predictions of the ligand field theory. It is of interest to determine whether the LFT predictions can be used to rationalize also the present experimental results in the gas phase, such as the $\Delta G^0{}_{1,0}$ and $\Delta G^0{}_{2,1}$ and corresponding ΔH^0 values for the $CyclM^{2+}$ obtained with the same tetraaza compound complexed to one of the ions Mn^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}.

Another area that can be examined are changes of the gas-phase hydration energies where the ion M^{2+} is the same but the size of the tetraaza macrocycle is varied.

Because the octahedral configuration is especially stable, the third water molecule will probably go to an "outer" position where it hydrogen bonds to one of the inner water molecules. Therefore, it is interesting to find whether the hydrations of $CyclM^{2+}$ by a third and a fourth molecule are significantly weaker that that for the second.

The hydration and ligation energies in the gas phase should be relevant also to theoretical, i.e., ab initio calculations. There seems to be a great paucity[8b] of ab initio calculations of the bonding of tetraaza complexes with transition metal ions. This is not surprising because of difficulties when the d electron shell is incomplete and also due to difficulties with the geometry optimization of these large complexes. Yet such calculations could be very enlightening. Most of the interpretation of the relative stabilities of $CyclM^{2+}$ and M^{2+} complexes with other tetraaza macrocycles is based on stabilities observed in solution where it is often difficult to separate the intrinsic effects from effects due to the solvent. Such a separation becomes possible only if data obtained in the absence of the solvent, i.e., gas phase, are available. The present experimental gas-phase ligation data for the M−tetraaza complexes could stimulate ab initio calculations because the experimental data provide check points for the ab initio calculations. From this standpoint, it would have been most relevant to determine experimentaly the dissociation energies of the tetraaza M^{2+}complexes in the gas phase; see eq 3, where L stands for a tetraaza macrocycle.

$$LM^{2+} = L + M^{2+} \quad (3)$$

$$L_AM^{2+} + L_B = L_BM^{2+} + L_A \quad (4)$$

However, the binding energies are expected to be very large, in the hundreds of kcal/mol range (see data provided later such as in eqs 7 and 8), and this makes the determination via equilibria, eq 3, essentially impossible with conventional techniques. On the other hand, the determination of the ligand exchange equilibria, eq 4, which provide binding energy differences of ligand L_A and L_B, might be possible and may be attempted in future work.

2. Experimental Section

The apparatus used has been described in detail.[11] In the present work, an equimolar, 4×10^{-4} M, solution of the M^{2+} salt (generally the nitrates were used) and of the tetraaza macrocycle in methanol is continuously injected with a motor driven syringe, at a rate of 1 μL/min, into the electrospray capillary, which is at +3500 V. The capillary emits a plume of very small droplets into the atmospheric air. The droplets are charged by an excess of positive ions. Evaporation of the droplets in the plume of the spray leads to gas-phase positive ions. The plume impinges on a stainless steel sampling capillary (+25 V) that leads to a fore-chamber. A countercurrent of nitrogen gas around the entrance of the sampling capillary inhibits the entrance of methanol vapor into the sampling capillary while the ions guided by the potential drop enter the capillary. A weak electric field is used to drift the ions from the fore chamber to the reaction chamber whose temperature is maintained to ±0.2 °C. Both chambers are supplied with nitrogen gas at 10 Torr containing known partial pressures of the reagent gas H_2O (or other ligand) in the 1−100 mTorr range. A very weak electric field drifts the ions through the reaction chamber. At the end of the chamber some of the gas and ions effuse through a small orifice into the vacuum of the mass spectrometer (a quadrupole mass analyzer). Both fore and reaction chamber are maintained at the same temperature. The solvation (ligation) equilibria establish in the reaction chamber. The ratio of the ion intensities, I_n/I_{n-1}, detected with the mass

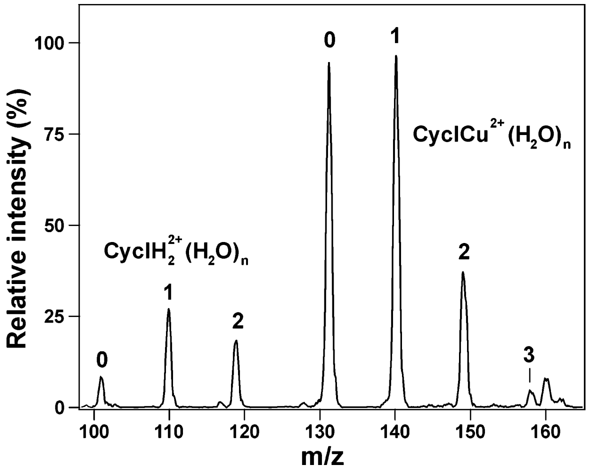

Figure 1. Mass spectrum of gas-phase ions obtained from electrospray ionization(ESI) of solution containing cyclam and monoisotopic ^{63}Cu-$(NO_3)_2$. Ions react with H_2O vapor 60 mTorr in 10 Torr bath gas (N_2) at 80° C. Observed hydrates $CyclCu(H_2O)_n^{2+}$ with $n = 0-3$ are at equilibrium. Hydrates of diprotonated cyclam, which is also present in the sprayed solution, are also observed (*m*/*z* resolution better than 0.5 *m*/*z* units).

spectrometer is assumed to be equal to the concentration ratio of the ions in the reaction chamber:

$$I_n/I_{n-1} = [CyclM(H_2O)_n{}^{2+}]/[CyclM\ (H_2O)_{n-1}{}^{2+}] \qquad (5)$$

Monoisotopic ^{63}Cu and ^{64}Zn salts were used for those elements because that led to less complicated spectra and "concentrated" the ion intensity into one peak.

No reliable data could be collected for the first hydration of $CyclZn^{2+}$ as the equilibrium appeared slow to establish. The reason for this behavior was not determined.

3. Results and Discussion

(a) Experimental Determination of $\Delta G^0_{n,n-1}$, $\Delta H^0_{n,n-1}$, and $\Delta S^0_{n,n-1}$. The mass spectrum, Figure 1, shows ions observed on sampling of the reaction chamber. The conditions used in the chamber lead to hydration reactions, eq 1, that have reached equilibrium. The electrosprayed solution contained Cu^{2+} dinitrate and cyclam. The major ion series observed is due to $CyclCu^{2+}(H_2O)_n$ ions, with $n = 0$, 1, 2, and 3. The series essentially terminates at $n = 3$. Higher water partial pressures in the reaction chamber, lead to a shift in the hydrate series to higher n. Raising the temperature leads to lower n. Ions other than those due to $CyclCu^{2+}(H_2O)_n$ are also seen. Most prominent are the $Cycl{\cdot}H_2^{2+}$ hydrates with $n = 0$, 1, 2, and 3. The $CyclH_2^{2+}$ must be due to reaction of Cyclam with H^+ ions in the methanol solution that was electro-sprayed. The properties of the $CyclH_2^{+}$ ions are also of interest and will be described in a separate publication. Ions due to impurities are also present, such as the ion at $m/z = 160$, Figure 1. The identity and origin of this ion is not known. In some of the determinations involving other transition metal ions or other ligands, impurity ions could be more abundant and interfere with the measurements when their *m*/*z* value happened to be the same as one of the ions involved in the equilibrium. In such cases, the measurements had to be abandoned.

Examples of experimental data used to determine equilibrium constants $K_{n.n-1}$ are shown in Figure 2. The plots are based on the ion intensities I_n and I_{n-1} of the $Cycl{\cdot}Cu(H_2O)_n^{2+}$ ions observed in mass spectra from separate runs at a given temperature and the partial pressure of water $p(H_2O)$, was changed from run to run. From the equilibrium expression, $K_{n,n-1} = I_n/I_{n-1} \times p(H_2O)$, one expects that the plots in Figure 2 will lead to straight lines that go through the origin. The plots are seen to obey quite well that requirement. Plots a−c illustrate that measurements at higher temperature require higher water pressures. Thus, at 38 °C, the highest pressure is $p(H_2O) = 8$ mTorr, while at 80 °C one needs to go up to $p(H_2O) = 90$ mTorr to cover the same range of I_n/I_{n-1} values. In general, the range of partial pressures of H_2O was kept between 1 and 200 mTorr and the I_n/I_{n-1} ratio was kept in the 0.1−1.5 range. Under these conditions, the slope is largely determined by points where were $I_n/I_{n-1} \approx 1$ and the error in the intensity measurements is the lowest. We have found that these conditions lead to the least scatter in the van't Hoff plots.

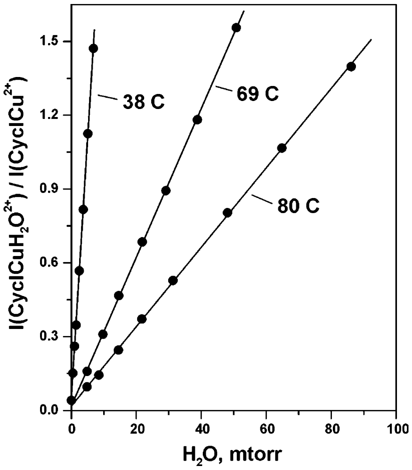

Figure 2. Plot of ion intensity ratio: $I(CyclCuH_2O)^{2+}/I(CyclCu^{2+})$ vs H_2O pressure, $P(H_2O)$, at constant temperature. Observed straight lines going through origin obey equilibrium constant relationship: $I(CyclCuH_2O)^{2+}/I(CyclCu^{2+}) = K_{0,1} \times P(H_2O)$. Results for three different constant temperatures, 38, 69, and 80 °C are shown.

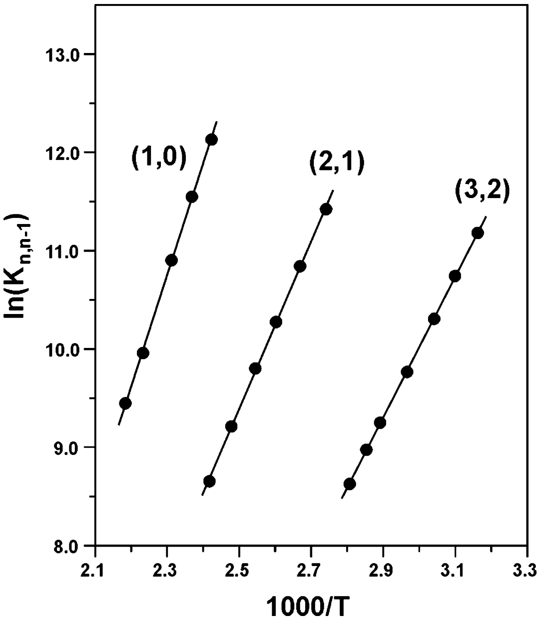

Figure 3. Van't Hoff plot of equilibrium constants $K_{n,n-1}$ for reaction $CyclMn(H_2O)_n^{2+} = CyclMn(H_2O)_{n-1}^{2+} + H_2O$, for $n = 1$, $n = 2$, and $n = 3$. The slope of plots is proportional to $\Delta H^0_{n,n-1}$.

The equilibrium constants $K_{n,n-1}$ obtained at different temperatures T are used in van't Hoff plots to obtain the enthalpy $\Delta H^0_{n,n-1}$ and entropy $\Delta S^0_{n,n-1}$ change. The van't Hoff plots for the hydration of $CyclMn^{2+}$ are shown in Figure 3 for the 1,0; 2,1, and 3,2 hydration steps and those for $CyclCu^{2+}$ are shown in Figure 4. The experimental scatter in the $\ln(K_{n,n-1})$ points is

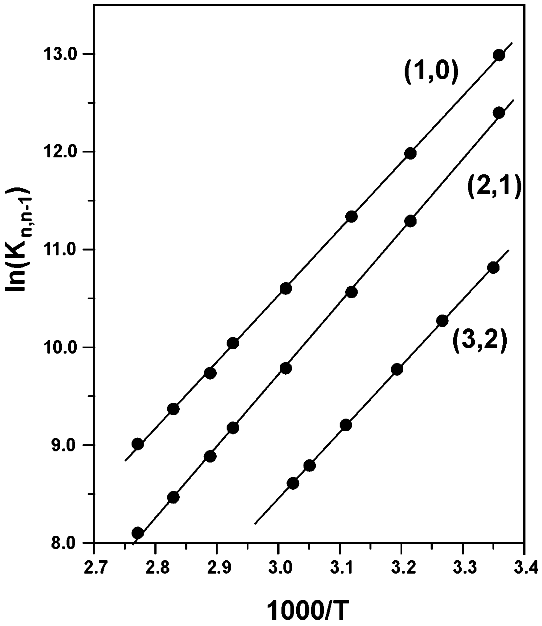

Figure 4. Van't Hoff plot of equilibrium constants $K_{n,n-1}$ for reaction $\text{CyclCu(H}_2\text{O)}_n^{2+} = \text{CyclCu(H}_2\text{O)}_{n-1}^{2+} + \text{H}_2\text{O}$, for $n = 1$, $n = 2$, and $n = 3$. The slope of plots is proportional to $\Delta H^0_{n,n-1}$.

seen to be very small. This is attributed to the accuracy of the determinations of the $I_{n/n-1}$ plots; see Figure 2. The van't Hoff plots were obtained over a relatively narrow temperature range of some 50−60 K; see Figures 3 and 4. However the low scatter in the $K_{n,n-1}$ values—see Figures 2−4—compensates for the relatively narrow temperature range used.

Results obtained from such plots are given in Tables 1 and 2.

(b) Sequential Hydration Energies of Tetraaza Macrocycles Complexed to Mn^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}. The hydration energies obtained with cyclam are given in Table 1. The metal ions, Mn^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2} were selected because this set is just sufficient to provide examples of the different types of behavior in the transition metal series: Mn^{2+} d^5, Co^{2+} d^6, Fe^{2+} d^7, Ni^{2+} d^8, Cu^{2+} d^9, Zn^{2+} d^{10}. The equilibrium constants K_F for the formation of the CyclM^{2+} in aqueous solution[13] are also given in Table 1. The $\log K_\text{F}$ values for CyclM^{2+} complexes are known to follow the Irving−Williams series,[9] where the $\log K_\text{F}$ values for the same ligand and different M^{2+} have the following relative magnitudes: $\text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}$. The $\log K_\text{F}$ values given in Table 1, where the values are relatively low for Mn^{2+} and Zn^{2+} and high for Ni^{2+} and Cu^{2+}, provide an example of the Irving−Williams order. Essentially the same order is predicted by the ligand field theory (LFT).[9] The cause for the low values observed for Mn^{2+}d^5 and $\text{Zn}^{2+}\text{d}^{10}$ is that the high spin Mn^{2+} and the Zn^{2+} ions have the same number of electrons in each of the five d orbitals such that the LFT interactions cancel.

Examining the experimental gas-phase hydration free energies $\Delta G^0_{1,0}$ and $\Delta G^0_{2,1}$ as well as the corresponding $\Delta H°$ values in Table 1, one finds that the values for Mn^{2+} and Zn^{2+} are of similar magnitude and that the corresponding values for Ni^{2+} and Cu^{2+} are also similar. Thus, $\Delta G^0_{2,1} = 9.8$ kcal/mol (Mn^{2+}) and 9.9 kcal/mol (Zn) and similarly, $\Delta H^0_{2,1} = 16.9$ kcal/mol (Mn^{2+}) and 16.9 kcal/mol (Zn^{2+}). For Ni^{2+} and Cu^{2+} the $\Delta G^0_{2,1}$ values are 6.7 and 7.3 kcal/ mol and the $\Delta H^0_{2,1}$ values are 12.8 and 14.6 kcal/mol. Notably the values for Mn^{2+} and Zn^{2+} are significantly higher than those for Ni^{2+} and Cu^{2+}. The same holds also for the $\Delta G^0_{2,0} = \Delta G^0_{1,0} + \Delta G^0_{2,1}$ and corresponding $\Delta H^0_{2,0}$ values. Thus, $G^0_{2,0} = 23.3$ (Mn), 14.3 (Ni), and 15.0 (Cu), and $\Delta H^0_{2,0} = 39.5$ (Mn), 26.1 (Ni), and 28.1 (Cu), with all values in kcal/mol.

There are also indications in the hydration data that the bonding of the first two water molecules to the CyclM^{2+} is entirely classical electrostatic for Mn^{2+} and probably also Zn^{2+}, while for Ni^{2+} and Cu^{2+} there is also a ligand field component. Thus, for Mn^{2+} the values for $\Delta G^0_{1,0}$ and $\Delta H^0_{1,0}$ are consider-

TABLE 1: Sequential Hydration Energies of in Tetraaza Macrocycle Complexes with M^{2+} Ions (Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+})[a,b]

	(n, n − 1)									
	(1,0)			(2,1)			(3,2)			
	ΔG°	ΔH°	ΔS°	ΔG°	ΔH°	ΔS°	ΔG°	ΔH°	ΔS°	log K_F [c]
Mn^{2+} 14 ane	13.5	22.6	30.6	9.8	16.9	23.7	7.3	14.2	22.8	*e*
Ni^{2+} 14 ane	7.6	13.3	19.0	6.7	12.8	20.4	5.9			22.2
Cu^{2+} 14 ane	7.7	13.5	19.5	7.3	14.6	24.4	6.5	13.5	23.6	27.2
Zn^{2+} 14 ane	*d*	*d*	*d*	9.9	16.9	23.6	7.4	14.1	22.4	15.5
Ni^{2+} 15 ane	7.9	13.4	18.7	6.7	12.6	19.7	5.9			18.4
Cu^{2+} 15 ane	7.5	12.9	18.3	6.8	13.1	21.3	6.2			24.4

[a] Experimental data from determinations of equilibrium constants of dehydration reactions: $\text{M}^{2+}\text{14 ane(H}_2\text{O)}_n = \text{M}^{2+}\text{14 ane(H}_2\text{O)}_{n-1} + \text{H}_2\text{O}$. [b] $\Delta H°_{n,n-1}$ and $\Delta G°_{n,n-1}$ values in kcal/mol, $\Delta S°_{n,n-1}$ values in cal/degree.mole $\Delta G°_{n,n-1}$ value given is for 298 K. $\Delta H°_{n,n-1}$ and $\Delta S°_{n,n-1}$ are approximately independent of temperature. Standard state 1 atm. The estimated absolute errors are ± 0.5 kcal/mol for $\Delta G^0{}_{n,n-1}$, ± 1 kcal/mol for $\Delta H^0_{n.n-1}$, and ± 4 cal/deg•mol for $\Delta S^0_{n,n-1}$. The relative errors are significantly smaller than the absolute errors. [c] Formation constants for reaction: $\text{M}^{2+} + \text{14-ane} = \text{M.14 ane}^{2+}$ in aqueous solution with some values also for 15-ane. From the compilation by Martel.[12] [d] Good values could not be obtained. See Experimental Section. [e] Not available in Martel.[12] Expected on the basis of the Irving−Williams plots to be much lower than K_F values for Ni^{2+}, Cu^{2+}, and lower than Zn^{2+}.

TABLE 2: Sequential Hydration Energies of Cu^{2+} Complexes with Tetraaza Macrocycles with Increasing Size[a,b]

	(n, n − 1)									
	(1,0)			(2,1)			(3,2)			
	ΔG°	ΔH°	ΔS°	ΔG°	ΔH°	ΔS°	ΔG°	ΔH°	ΔS°	log K_f [c]
Cu^{2+} 12 ane	10.6	16.8	22.8	8.6	14.9	21.3				24.6
Cu^{2+} 14 ane	7.7	13.5	19.5	7.3	14.6	24.4	6.5	13.5	23.6	27.2
Cu^{2+} 15 ane	7.5	12.9	18.3	6.8	13.1	21.3	6.2			24.4

[a] Experimental data from equilibrium determinations of dehydration reaction: $\text{Cu}^{2+}\text{ ane (H}_2\text{O)}_n = \text{Cu}^{2+}\text{ ane (H}_2\text{O)}_{n-1} + \text{H}_2\text{O}$, in the gas phase, leading to equilibrium constants $K_{n,n-1}$at different temperatures. [b] $\Delta G°_{n,n-1}$ in kcal/mol at 298°K standard state 1 atm, $\Delta H°_{n,n-1}$ values in kcal/mol, approximately independent of temperature, $\Delta S°_{n,n-1}$ values in cal/deg•mol. Standard state, 1 atm. The estimated errors are ±0.5 kcal/mol for $\Delta G^0{}_{n,n-1}$, ±1 kcal/mol for $\Delta H^0_{n.n-1}$, and ±4 cal/deg•mol for $\Delta S^0_{n,n-1}$. [c] Formation constants for reaction $\text{Cu}^{2+} + \text{L} = \text{Cu}^{2+}\text{L}$, where L are the tetraaza macrocycles, determined in aqueous solution. From the compilation by Martel.[12]

ably larger than the second hydration values, $\Delta G^0_{2,1}$ and $\Delta H^0_{2,1}$ while for Cu^{2+} and Ni^{2+} these values are close to equal, see Table 1. Thus, for Mn^{2+}, $\Delta G^0_{1,0} = 13.5$ while $\Delta G^0_{2,1} = 7.7$ kcal/mol and $\Delta H^0_{1,0} = 22.6$ kcal/mol while $\Delta H^0_{2,1} = 16.9$ kcal/mol. On the other hand, for Cu^{2+}, $\Delta G^0_{1,0} = 7.7$ and $\Delta G^0_{2,1} = 7.3$ and $\Delta H^0_{1,0} = 13.5$ kcal/mol and $\Delta H^0_{2,1} = 14.6$ kcal/mol. The large decrease observed for Mn^{2+} is typical for systems where the interactions are purely electrostatic. Such decreases are observed for the singly charged ions Li, Na, K, etc., which have complete electron shells.[14]

The result obtained for Cu^{2+} where $\Delta H^0_{2,1}$ is larger than $\Delta H^0_{1,0}$ represents a first observation in ion ligand reactions, of a $\Delta H^0_{n,n-1}$ value that increases with n. It is very unlikely that this result is due to an error. Even a simple visual observation of the plots in Figure 4 reveals that the slope of the $\ln K_{2,1}$ plot is larger than that for the $\ln K_{1,0}$ plot and the slopes of the plots are proportional to the $\Delta H^0_{n,n-1}$values. Also, because the $\Delta G^0_{1,0}$ and $\Delta G^0_{2,1}$ values are close, the measurements of the equilibria were made simultanously, i.e., under identical conditions, which provides a high precision for the relative values of $K_{1,0}$ and $K_{2,1}$.Furthermore, a similar $\Delta H^0_{1,0} < \Delta H^0_{2,1}$ result was obtained also for $CyCu^{2+}$ and MeOH; see Table 3 in section d. The authors are unable to rationalize this unusual result.

The higher hydration values for $CyclMn^{2+}$ and $CyclZn^{2+}$ relative to $CyclNi^{2+}$ and $CyclCu^{2+}$ show a trend that is the opposite to that observed for the formation constants of the $CyclM(H_2O)_2{}^{2+}$ in aqueous solution and expected also from simple LFT. It is close to certain that the energy changes for the formation of the $CyclM^{2+}$complexes from Cyclam and M^{2+} in the gas phase will follow trends with M^{2+} similar to those given by the log K_F values in solution. This is expected even though the reaction in aqueous solution involves not only the complexation with cyclam but also with two water molecules. The reaction with cyclam will be decisive because the free energy change for it will be at least 1 order of magnitude larger than that for the hydration by the two axial water molecules. We have not been able to find experimental information in the literature whether the axial water molecules are more strongly bonded to $CyclM^{2+}$ complexes when M^{2+} represents the LFT active Ni^{2+} and Cu^{2+} or the inactive Mn^{2+} and Zn^{2+}.

Before discussing the present experimental results in more detail, it will be useful to consider the relative contributions to the ion−ligand bonding by the electrostatic energy component and by the ligand field interactions and how these differ in the gas phase relative to aqueous solution. From the values for $\log K_F$, Table 1, one can evaluate the free energy, $\Delta G^0_F = -RT \ln K_F$, for the formation of the complex from the reactants in their standard states (unit activity in aqueous solution). The values at $T = 298$ K are given in eq 6a,b:

$$-\Delta G^0{}_F(CyclZn^{2+}) = -\Delta G^0{}_F(esCyclZn^{2+}) = 21.1 \text{ kcal/mol} \quad (6a)$$

$$-\Delta G^0{}_F(CyclCu^{2+}) = -(\Delta G^0{}_F(esCyclCu^{2+}) + (\Delta G^0{}_F(\text{d el}CyclCu^{2+})) = 37.1 \text{ kcal/mol} \quad (6b)$$

$$\Delta G^0{}_F(esCyclCu^{2+}) \approx 24 \text{ kcal/mol} \text{ -}\Delta G^0{}_F(\text{d el}CyclCu^{2+}) \approx 13 \text{ kcal/mol} \quad (6c)$$

The bonding of Cycl with Zn^{2+} d^{10} is dependent mostly on electrostatic forces between the positive charge on M^{2+} and the polar secondary amino groups of the cyclam. This is expressed in eq 6a where (es) stands for electrostatic interaction. The bonding with Cu^{2+} d^9 involves a favorable interaction of the ligand field with the d electrons of M^{2+}, (which we call (d el)) and an electrostatic interaction (es),see eq 6b. The electrostatic interaction with Cu^{2+} should be close to but somewhat stronger than that with Zn^{2+} because the (d el) interaction helps bring the reactants closer together, which leads to an increase of the electrostatic bonding. Thus, one expects, $-\Delta G^0{}_F(esCyclCu^{2+}) > 21.1$ kcal/mol, see eq 6a. Assuming arbitrarily a value, $-\Delta G^0{}_F(esCyclCu^{2+}) \approx 24$ kcal/mol leads to $-\Delta G^0{}_F(\text{d el}CyclCu^{2+}) \approx 13.1$ kcal/mol. These rough estimates are given in eq 6c. However, the actual (d el) interaction will be somewhat stronger when account is taken also for the partial dehydration of M^{2+} which must occur on formation of the complex $CyclM^{2+}$ from M^{2+} and Cycl. The dehydration energy for Cu^{2+} is larger than that for Zn^{2+} due to the d electron interactions with the water molecules. A rough estimate based on the absolute hydration energies of the ions[13] (see Appendix) indicates that for $CyclCu^{2+}$ the total (d el) term is still smaller than the (es) term but the values are closer, i.e., for $CyclCu^{2+}$, the d el and es terms are of similar magnitudes. It will be seen that in the gas phase the situation is drastically different.

TABLE 3: Comparison of the Sequential Ligation Energies of Cylam Complexes $CyCu^{2+}$ with H_2O and MeOH[a]

	$\Delta G°$		$\Delta H°$		$\Delta S°$	
$n, n-1$	H_2O	MeOH	H_2O	MeOH	H_2O	MeOH
1, 0	7.7	9.6	13.5	15.6	19.5	20.1
2, 1	7.3	8.8	14.6	16.3	24.4	25.0
3, 2	6.5	7.7	13.5	15.0	23.6	24.6
4, 3		6.7				
5, 4		6.0				

[a] $\Delta G°_{n,n-1}$ and $\Delta H°_{n,n-1}$ values in kcal/mol. $\Delta G°_{n,n-1}$ at 298 K. $\Delta S°_{n,n-1}$ values in cal/deg·mol. Standard state 1 atm.

In the gas phase, due to the absence of the high dielectric constant of water, the stabilization due to pure electrostatic interactions will be very much higher than in solution. Unfortunately, ab initio evaluated dissociation energies for $CyclM^{2+}$ complexes in the gas phase are not available. However available ab initio calculations for the hexahydrates, $M(H_2O)_6{}^{2+}$ provide very useful insights. The dissociation energies ΔE for the octahedral hydrates, eq 7

$$M(H_2O)_6{}^{2+} = M^{2+} + 6H_2O \ \Delta E(M^{2+}\cdot 6H_2O) \quad (7)$$

were evaluated by Akesson et al.,[10a] for the first row transition metals. An Irving−Williams plot was obtained for reaction eq 7 (see Figure 3 in ref 10a). From this plot one can estimate the bonding contributions due to electrostatic interaction $\Delta E(es,M^{2+}\cdot 6H_2O))$ and those due to stabilization from d electron configuration, $\Delta E(\text{d el},M^{2+}\cdot 6H_2O)$. The values for Cu^{2+} are

$$\Delta E(es,Cu^{2+}\cdot 6H_2O) \approx 308 \text{ kcal/mol}; \quad \Delta E(\text{d el},Cu^{2+}\cdot 6H_2O) \approx 13 \text{ kcal/mol} \quad (8)$$

The values in eq 8 are approximate but the message is clear. In the gas phase, the electrostatic interactions are dominant over the d electron configuration ligand field interactions. Thus, the ΔE(d el) is only 4% while the ΔE(es) is 96% of the total interaction. Considering that cyclam is expected to be a more strongly bonding ligand compared to the combined six water molecules, one expects larger values for $\Delta E(es, CyclCu^{2+})$. and for $\Delta E(\text{d el}, Cycl\ Cu^{2+})$, but probably, the ratio, $\Delta E(es)/\Delta E(\text{d el})$, will not be too different from that observed for the hexahydrates.

Results from theoretical calculations[10c] for the Zn^{2+} hexahydrates, providing values for the sequential hydration energies $\Delta E_{n,n-1}$ of M^{2+} ions are also of interest because they illustrate the rapid decrease of the energies with n. Thus, for $Zn(H_2O)_6{}^{2+}$: $\Delta E_{1,0} = 102$ kcal/mol; $\Delta E_{2,1} = 87$ kcal/mol, $\Delta E_{5,4} = 24$ kcal/

TABLE 4: Approximate $\Delta G^\circ_{1,0}$ Values for the Following Reactions: $CyCuL^{2+} = CuCy^{2+} + L$ and $KL^+ = K^+ + L$[a]

$CyclCu^{2+}$

L	H_2O	CH_3OH	C_2H_5OH	n-C_3H_7OH	$(C_2H_5)_2O$	n-C_4H_9OH	$(CH_3)_2CO$	NH_3
$\Delta G^\circ_{1,0}$	6.7	8.5	9.9	11.0	11.0	11.9	16.9	8.0

K^+

L	H_2O	CH_3OCH_3	$(C_2H_5)_2O$	NH_3
$\Delta G^\circ_{1,0}$	9.9	12.1	13.6	10.8

[a] $\Delta G^\circ_{1,0}$ values in kcal/mol. Standard state 1 atm. $T \approx 350$ K. Values for K^+ from Davidson and Kebarle.[15]

mol, $\Delta E_{6,5} = 22$ kcal/mol. The sequential energies add up too: $\Delta E_{6,0} = 329$ kcal/mol.[10d]

The $\Delta E_{6,5} = 22$ kcal/mol, can be compared with $\Delta H^0_{2,1} = 16.9$ kcal/mol for $CyclZn(H_2O)_2{}^{2+}$, Table 1, since in both cases it is the sixth interacting group that is lost. The value for the hydrated cyclam is lower as should be expected because the secondary amines are very much stronger electron donors than the four water molecules and therefore are expected to lead to a stronger attenuation of the sequential energies.

With the above information on the dominance of electrostatic interaction in the gas phase, we examine the finding that the hydration energies of $CyclMn^{2+}$ and $CyclZn^{2+}$ are considerably larger than those for $CyclNi^{2+}$ and $CyclCu^{2+}$, Table 1, and that the difference is in the opposite direction from that predicted by the Irving–Williams series These phenomena must be in some way connected to the presence of d electron effects for Ni^{2+} and Cu^{2+}. The observed magnitude of the differences, Table 1, is too large to be attributed to direct d electron effects on the bonding of the H_2O ligands. Thus, the theoretical results for the hexahydrates[10a] indicated that the ΔE(d el) was only some 4% of the total bonding while the differences, Table 1, are in the 15% range. To account for these results the following scheme is proposed. The differences observed in the hydration energies must be caused by d electron effects involved in the bonding not of $CyclM^{2+}$ to H_2O but of M^{2+} to the cyclam. The bonding of the cyclam to M^{2+} is vastly stronger and differences due to d electrons will be also numerically much more substantial. The stronger bonding of Ni^{2+} and Cu^{2+} due to d electrons will enhance the electron shifts from the nitrogens of the secondary amines of the cyclam, to the Ni^{2+} and Cu^{2+} ions. The resulting enhanced shielding of the positive charge of the ions will decrease the electrostatic bonding of the water molecules to the $CyclNi^{2+}$ and $CyclCu^{2+}$ and thus lead to the observed lower hydration energies of the $CyclNi^{2+}$ and $CyclCu^{2+}$. Additional evidence for a larger electron shift from the cyclam to Ni^{2+} and Cu^{2+} ions is given is section d. This evidence is based on observed deprotonation reactions of $CyclM^{2+}$ by ligands of high gas-phase basicities.

It is interesting to compare the values for the third hydration, $\Delta G^0_{3,2}$ and $\Delta H^0_{3,2}$ of the $CyclM^{2+}$ complex with those for the first two hydrations. The $\Delta G^0_{3,2}$ and $\Delta H^0_{3,2}$ values, see Table 1 are smaller than the$\Delta G^0_{2,1}$ and $\Delta H^0_{2,1}$ values for all M^{2+} ions. However the decreases are not large. A large discontinuity between (3,2) and (2,1) values is not indicated. The bonding of the third water molecule could occur at two possible sites: (a) The water molecule is hydrogen bonded to one of the two water molecules of the $CyclM(H_2O)_2{}^{2+}$ complex. These hydrogen bonds will still be quite strong due to partial positive character of the H atoms of the inner water molecules induced by the polarizing effect of the M^{2+}ion. (b) Other likely H_2O bonding sites are the four H atoms on the four secondary amino groups of the cyclam. Electron donation from the nitrogen to the M^{2+}-ions, will lead to a positive character of the amino hydrogens. These interactions could be stronger than those described in part a.

In conclusion, the data and discussion in this section show that while specific d electron configuration effects can be deduced from the differences between the data for the Mn^{2+} and Zn^{2+} relative to the Ni^{2+} and Cu^+ complexes, the bonding is dominated by classical electrostatic effects of the M^{2+} charge.

(c) Sequential Hydration Energies of Cu^{2+} Complexes with Tetraaza Macrocycles of Increasing Size. Table 2 provides a summary of the hydration data obtained for Cu^{2+} ions complexed to the macrocycles: 12-ane N_4, 14-ane N_4 (cyclam), and 15-ane N_4; see structures **I**–**III** in the Introduction.

The $\Delta G^0_{1,0}$ and $\Delta G^0_{2,1}$ values are seen to decrease as one moves from the12-ane to the 14-ane and the 15-ane; see Table 2. The formation constants for the complexes in solution—see Table 2—show the highest value, $\log K_F = 27.2$ for the 14-ane complex, while the values for the 12-ane, $\log K_F = 24.6$, and 15-ane, $\log K_F = 24.4$, are considerably lower. These results can be interpreted that in solution the 12-ane is too small for the Cu^{2+} while the 14-ane is just right and the 15-ane is too large. If this is the case also in the gas-phase one would expect that the strongest interaction occurring with 14-ane will lead to the largest shielding of the positive charge of the Cu^{2+} ion and thus to the lowest hydration energies $\Delta G^0_{1,0}$ and $\Delta H^0_{1,0}$. But this is not the case; see Table 2. Therefore, we consider a different mechanism.

In the gas phase the binding energies of alkali ions such as potassium, K^+, with ligands such as H_2O, CH_3OCH_3, C_2H_2-OC_2H_5, NH_3, CH_3NH_2, and n-$C_3H_9NH_2$ are known to increase with alkyl substitution and with increasing length of the alkyl group[15](for numerical values of binding energies, see Table 4, section d). This effect can be attributed to a stabilization of the complex by the polarizability of the alkyl groups.[15] The effect is not seen in solution because the bulky alkyl groups interfere with the solvation of the ion. The stabilization by alkyl groups in the gas phase is expected to be much stronger for doubly charged M^{2+} ions. Considering now the macrocycles, we note that two of the alkyl groups of the 12-ane are shorter than those of the 14-ane and this means that the M^{2+} ion will be more strongly stabilized in the 14-ane. The M^{2+} in the 14-ane complex will have a lower net positive charge and therefore bind less strongly to the H_2O molecules. A similar but smaller decrease is expected for the 15-ane because only one alkyl group is lengthened. These predictions agree with the observed changes of the $\Delta G^0_{1,0}$ and $\Delta H^0_{1,0}$ in Table 2 for the 12-ane to 14-ane to 15-ane macrocycles. This simple reasoning does not consider that the increasing size of the macrocycles may lead to a loose fit with the 15-ane that could weaken the interaction with the M^{2+} ion. However this neglect is justified because in the gas phase, a “loose fit” does not lead necessarily to a weaker interaction. This is because the macrocycle can “pucker” around the ion. For example, the 12 crown-4 macrocycle which bonds most strongly with Na^+ in solution, bonds more strongly with Li^+ in the gas phase.[16] The preference for Na^+ in solution is due to its hydration energy being lower than that for Li^+.

(d) Bonding of $CyclCu^{2+}$ Complexes with Other, Stronger Ligands than H_2O and Deprotonation of the $CyclM^{2+}$ Complexes. Tables 3 and 4 provide data that quantify the observed stronger bonding when H_2O is replaced with other ligands such as the alkyl alcohols, acetone and ammonia. The data in Table 3 provide a comparison of the sequential ligation

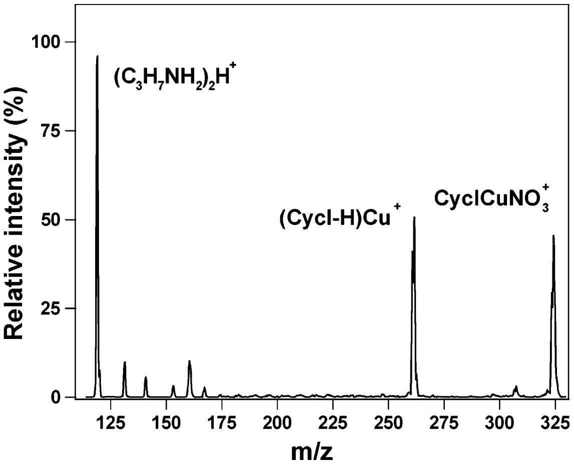

Figure 5. Mass spectrum of gas-phase ions obtained from ESI of solution containing cyclam and $^{63}Cu(NO_3)_2$. Reaction chamber at 100.5 °C. 10 Torr N_2 bath gas and 0.2 mTorr of *n*-propylamine reagent in reaction chamber. No n- propylamine adduct to $CyclCu^{2+}$ is observed. Instead, deprotonation of all of the $CyclCu^{2+}$ has occurred, leading to (CyclCu minus H)$^+$ and $n\text{-}C_3H_7NH_3^+$, which reacts with another propylamine leading to observed proton held dimer $(C_3H_7NH_2)_2H^+$.

energies of H_2O and CH_3OH with $CyclCu^{2+}$. It is seen that methanol is the stronger ligand. The $\Delta G^0_{n,n-1}$ values are larger by about 1.5 kcal/mol for methanol and similar differences are also observed for the enthalpy changes. The entropy changes are close to equal. The results for methanol exhibit very much the same trends as discussed for water in section b, except that the bonding enthalpies and free energies are somewhat higher.

Increasing the length of the alkyl chain of the alcohols leads to larger $\Delta G^0_{1,0}$ values as shown in Table 4. Acetone leads to the strongest interaction. Ammonia leads to $\Delta G^0_{1,0}$ which is only slightly larger than that for water. A priori, one might have expected a considerably larger value. However the results in Table 4 can be easily rationalized. As discussed in section b, the bonding interactions of M^{2+} with the four N atoms of the cyclam are expected to be very strong and add up to more than 350 kcal/mol. Because the binding energy decreases with each previous ligand interaction, see section b, the bonding with the fifth ligand will be much weaker. The positive charge of M^{2+} will be strongly shielded and possibly reduced to close to a single charge. Thus, one might expect that the ligand order will resemble that for a singly charged ion. Because the distance to the fifth ligand is expected to be not too close, the potassium ion, K^+, could be a suitable choice for comparison. Some values for the $\Delta G^0_{1,0}$ of different ligands bonding to K^+ are available[15] and are given in Table 4.

The interactions for K^+ are a little stronger but the trends with the type of ligand are similar. Thus, K^+ with NH_3 also leads to a $\Delta G^0_{1,0}$ that is only slightly higher than that for H_2O. NH_3 has a dipole moment (4.9×10^{-3} C•m) that is lower than the dipole moment (6.2×10^{-3} C•m) of H_2O, but a polarizability ($2.5 \times 10^{-40}\ J^{-1}\ C^2\ m^2$) that is higher than that for H_2O ($1.7 \times 10^{-40}\ J^{-1}\ C^2\ m^2$).[13] Therefore, NH_3 leads to stronger bonding when the charge on the ion is high and the distance to the ligand is short, while H_2O wins out at lower charge and larger distance. Apparently, for $CyclCu^{2+}$ and K^+ the net charge and the distance are similar so that, for both, the bond with NH_3 is slightly higher than that with H_2O.

When *n*-propylamine is used as a ligand, a new effect is observed. *n*-propylamine has a higher gas-phase basicity, GB = 211.3 kcal/mol, than NH_3, GB = 196, and all other bases used in Table 4 (GB values from Hunter and Lias[18] (see also ref 20)). The *n*-propylamine adds as a ligand to the $CyclMn^{2+}$ and $CyclZn^{2+}$ but deprotonates $CyclNi^{2+}$ and $CyclCu^{2+}$. This is illustrated by the mass spectra in Figures 5 and 6. A mass spectrum, not shown, obtained without any additive but otherwise under the same conditions as in Figure 5, demonstrated that the $CyclCu^{2+}$ species is stable under the conditions used. The major and essentially the only ions observed were $CyclCu^{2+}$ and with lower intensity, $CyclCuNO_3^+$. Addition of 0.2 mTorr of *n*-propylamine, see Figure 5, removes all of the $CyclCu^{2+}$ converting it into singly charged $CyclCu^+$ that has lost one hydrogen. This is obviously a deprotonation reaction:

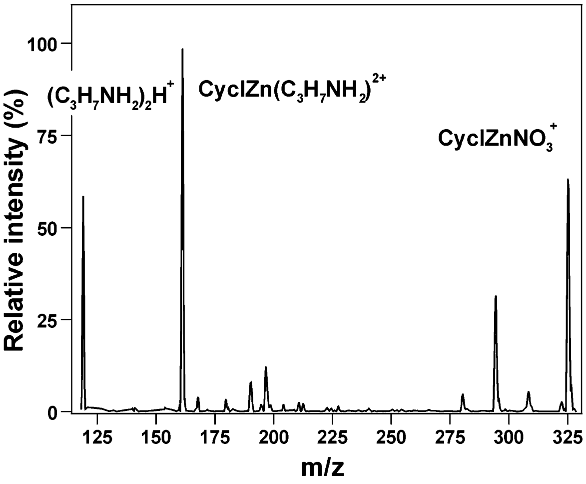

Figure 6. Same conditions as in Figure 5 but with $Zn(NO_3)_2$ salt, instead of $Cu(NO_3)_2$, in the solution. The $n\text{-}C_3H_7NH_2$ adduct to $CyclZn^{2+}$ is seen, while deprotonated (CyclZn minus H)$^+$ is absent.

$$CyclCu^{2+} + n\text{-}C_3H_7NH_2 = Cycl(\text{minus } H^+)Cu^{2+} + n\text{-}C_3H_7NH_3^+ \quad (9)$$

Some of the $n\text{-}C_3H_7NH_3^+$ reacts with $n\text{-}C_3H_7NH_2$, which leads to the proton held dimer $(C_3H_7NH_2)_2H^+$ that is also seen in the mass spectrum in Figure 5.

The same complete deprotonation reaction was also observed with $CyclNi^{2+}$. On the other hand, a deprotonation was not observed with $CyclMn^{2+}$ and $CyclZn^{2+}$. This is illustrated by the mass spectrum obtained with $CyclZn^{2+}$ and *n*-propylamine, see Figure 6. The result is not deprotonation but complex formation:

$$CyclZn^{2+} + n\text{-}C_3H_7NH_2 = (CyclZnC_3H_7NH_2)^{2+} \quad (10)$$

Thus, as already observed in section b, the cyclam complexes with $Cu^{2+}$and Ni^{2+} exhibit a chemistry that is different from that for the $Mn^{2+}$and Zn^{2+}.complexes. This difference can be rationalized on the basis of the considerations used in section b. The stronger bonding of the $CyclNi^{2+}$ and $CyclCu^{2+}$, due to the Ni^{2+} d^8 and Cu^{2+} d^9 electron configurations, leads to a larger electron shift from the cyclam N atoms to the metal ions. This shift results in a more positive character of the amino hydrogen of the $-CH_2-NH-CH_2-$ groups of the cyclam. The deprotonation most probably involves one of these hydrogens and is more facile with $CyclNi^{2+}$ and $CyclCu^{2+}$ because of the increased protic character of these hydrogens, see section b.

Reactions in the gas phase where a multiply charged ion−ligand complex is deprotonated by an additional ligand have been known for some time; see refs 4b and 19 and references therein for some examples. However, the present cases are especially interesting, because of their complexity and dependence on the d electron configuration of the transition metal ions.

Conclusions

(1) The d electron configuration of M^{2+} when these ions form complexes with ligands leads to more strongly bonded complexes with ions like Ni^{2+} d^8 and Cu^{2+} d^9 relative to Mn^{2+} d^5 and Zn^{2+} d^{10} This order is predicted by the ligand field theory and observed experimentally, see the Irving−Williams series. However, in the present work in the gas phase the observed order for the reactions of $CyclM^{2+}$ with ligands L such as H_2O and CH_3OH lead to a reversed order where the $CyclMn^{2+}$ and $CyclZn^{2+}$ lead to more strongly bonded $CyclM^{2+}L$ and $CyclM^{2+}L_2$ complexes.

(2) This reversed effect is attributed to the stronger bonding of the Cycl to Ni^{2+} and Cu^{2+} due to the d electron configuration of these ions. This stronger bonding leads to an increased shielding of the M^{2+} due to the electron shift from the N atoms of the Cycl to the M^{2+} ion. It is the lower effective charge that leads to the weaker bonding of $CyclNi^{2+}$ and $CyclCu^{2+}$ to the ligands L.

(3) Determinations of the bond free energy $\Delta G^0{}_{1,0}$ for the reaction: $CyclCuL^{2+} = CyclCu^{2+} + L$ showed that the energies increase in the order: $H_2O < CH_3OH \approx NH_3 < C_2H_5OH \ll (CH_3)_2CO$ etc. A very similar order is observed for $KL^+ = K^+ + L$. However the binding energy is somewhat higher for potassium. This result illustrates that the shielding of the Cu^{2+} charge by the Cyclam is very extensive.

(4). The observation that *n*-propylamine, a compound with relatively high gas-phase basicity, deprotonates $CyclNi^{2+}$ and $CyclCu^{2+}$ but forms a ligand complex with $CyclMn^{2+}$ and $CyclZn^{2+}$ demonstrates that $CyclNi^{2+}$ and $CyclCu^{2+}$ have more protic $-CH_2NHCH_2-$ amine hydrogens. This result supports the proposed larger shift of electrons from the N atoms of the $-CH_2NHCH_2-$ groups of the cyclam to the Ni^{2+} and Cu^{2+} ions, proposed in conclusion 2.

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Appendix. Relative Dehydration Energies Required in the Formation of the $CyclCu^{2+}$ and $CyclZn^{2+}$ in Aqueous Solution

The dehydration components can be estimated with use of the absolute hydration free energies for the following process: where M^{2+} is transferred from the gas phase to aqueous solution, eq 9a.

$$M^{2+}{}_{(g)} \rightarrow M^{2+}{}_{(aq)} \quad \Delta G^0{}_{abs,hyd}(M)^{2+} \tag{9a}$$

$$\Delta G^0{}_{abs,hyd}(Cu)^{2+} = -482.3 \text{ kcal/mol}; \quad \Delta G^0{}_{abs,hyd}(Zn)^{2+} = -469.6 \text{ kcal/mol} \tag{9b}$$

$$\Delta G^0{}_{abs,hyd}(Cu)^{2+} - \Delta G^0{}_{abs,hyd}(Zn)^{2+} = -12.7 \text{ kcal/mol} \tag{9c}$$

Values of $\Delta G^0{}_{abs,hyd}(M^{2+})$ for the transition metal ions are available, see Table 5.10 in Marcus.[13] As expected, the values follow the Irving−Williams order. The values for Cu^{2+} and Zn^{2+} are given in eq 9b. The difference between the hydration energies given in eq 9c is mainly due to the d electron bonding with the water molecules, present for Cu^{2+}. On formation of the $CyclCu^{2+}$ complex in water the required dehydration energy will be larger for Cu^{2+}. The difference, eq 9c. taken with an opposite sign to represent dehydration, provides the maximum of the dehydration difference between Cu^{2+} and Zn^{2+} that will be required for the formation of the $CyclCu^{2+}$ relative to the $CyclZn^{2+}$ complex. The actual value will be much smaller because the cyclam with its four secondary amino nitrogen atoms placed just at the right distance provides a very strong stabilization of the M^{2+} ion. This strong stabilization will reduce greatly the need for further stabilization of the complex by hydration. On that basis one could make the rough estimate that only about one-third of the hydration difference of 12.7 kcal/mol, eq 9c, needs to be considered.

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