

Intraionic, Interligand Proton Transfer in Collision-activated Macrocyclic Complex Ions of Nickel and Copper

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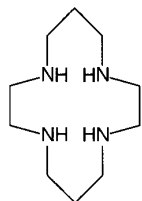
Intraionic, interligand proton transfer in collision-activated macrocyclic complex ions of nickel and copper has been observed. The macrocyclic ligand 1,4,8,11-tetraazacyclotetradecane (cyclam) or tris(2-aminoethyl)amine (tren) can transfer, after collision activation, one of its amino protons to an anion, but not to a solvent molecule, adducted to the complex; the neutral, protonated anion then leaves the complex. Proton transfer from the macrocycle to an adducted neutral, aromatic nitrogen base is also possible provided that the proton affinity of the base is sufficiently high. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: proton transfer; collision activation; macrocyclic complex metal ions; nickel complexes; copper complexes

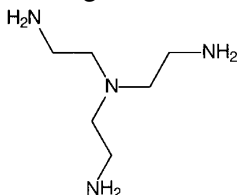
INTRODUCTION

Nickel and copper macrocyclic complexes play important roles in biological systems.¹ The solution chemistry of model complexes, such as $[M^II L]^{2+}$, where M = Ni or Cu, L = cyclam (1,4,8,11-tetraazacyclotetradecane) or tren (tris(2-aminoethyl)amine), has been extensively studied.^{2–5}

Cyclam stabilizes high oxidation states, e.g. Cu^{III} and Ni^{III}, that are not typically attainable using linear polydentate amine ligands.^{4–6} Complexes of cyclam have been used as model systems for metalloproteins that contain macrocyclic ligands, such as heme, chlorophyll and corrinoids;^{1,6} similarly to the biological macrocyclic ligands, cyclam contains four donor nitrogen atoms confined to a plane, thus leaving two axial sites



Cyclam, C₁₀H₂₄N₄



Tren, C₆H₁₈N₄

available for interaction with substrates or other ligands. $[Ni(cyclam)]^{2+}$ has been used as a specific chemical probe for guanine in nucleic acids.⁵ Likewise, tren also contains four donor nitrogen atoms, but they occupy three equatorial and one axial position in binding with the central metal ion, thus forcing subsequent ligands to bind *cis* to each other.⁷

Electrospray mass spectrometry is becoming extensively applied to the study of inorganic and organometallic complexes.^{8,9} One of the earliest examples was Co^{III} sepulchrate.^{10,11} Complexes of alkali metal cations with crown ethers have been examined.^{12–14} Ternary complexes of amino acids or dipeptides and 2,2'-bipyridyl with Cu^{II} have been systematically investigated.^{15–19} Other mixed ligand complexes, such as those of Ru^{II}, Rh^{III} and Co^{III}, have also been studied.²⁰

We are interested in Ni^{II} and Cu^{II} complexes of cyclam and tren because of their potential as templates for subsequent *trans* and *cis* additions of different ligands to these metal ions. Our plan is to study these complexes using electrospray mass spectrometry. As it turns out, the electrospray mass spectrometry of these complexes themselves is interesting. This paper describes our findings.

EXPERIMENTAL

Most experiments were performed on a PE-SCIEX API 300 triple-quadrupole mass spectrometer. Samples, typically 50 μM in acetonitrile, acetone, dimethyl sulfoxide (DMSO), methanol, water–methanol (50:50) or methylene chloride, were infused into the electrospray probe at a typical rate of 2 μl min^{–1} by means of a

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syringe pump (Harvard Apparatus, Model 22). Fragmentation in the lens region was effected by selecting the appropriate orifice potential; since the skimmer in the API 300 is permanently grounded, the potential drop across the orifice-skimmer (related to the collision energy) is numerically equal to the orifice potential (OR). Tandem mass spectrometry (MS/MS) was performed with a nitrogen pressure of 2–4 mTorr (1 Torr = 133.3 Pa) in q_2 . Some MS/MS experiments were also conducted on a SCIEX TAGA 6000E triple-quadrupole mass spectrometer at a collision gas thickness of 1×10^{14} atoms cm^{-2} (an equivalent pressure of 9×10^{-5} Torr²¹) with argon as target gas.

All metal salts, macrocycles and aromatic nitrogen bases were commercially available (Aldrich) and were used as received. Solvents were of HPLC grade (Anachemia). The macrocyclic complexes were synthesized using methods similar to a published method.²² The following is the procedure for the preparation of $[\text{Ni}(\text{cyclam})](\text{PF}_6)_2$; procedures for that of other complexes were very similar. A 100 mg amount of cyclam was dissolved in 5 ml of methanol–water (1:1, v/v); 165 mg of $\text{Ni}(\text{NO}_3)_2$ was then added and the solution was stirred. To the ice-chilled solution, 1.5 equiv. of NH_4PF_6 was added in 4 ml of water. The precipitate, $[\text{Ni}(\text{cyclam})](\text{PF}_6)_2$, was collected by filtration, washed with chilled water, methanol–water (1:1, v/v) and diethyl ether, and then dried in air.

RESULTS AND DISCUSSION

Figure 1 shows a typical electrospray mass spectrum of $[\text{Ni}(\text{cyclam})](\text{PF}_6)_2$ with an OR = 35 V, a condition

typical for efficient ion transmission. The base peak is the $[\text{Ni}(\text{cyclam})]^{2+}$ ion at m/z 129; m/z 130 is almost exclusively $[\text{Ni}(\text{cyclam})]^{2+}$. The ratio of the two ions is approximately 2.3, which reflects the natural abundance ratio of ^{58}Ni to ^{60}Ni . The peaks at m/z 257 and 259 are due to $[\text{Ni}(\text{cyclam}-\text{H})]^+$. The relative abundance of the $[\text{Ni}(\text{cyclam}-\text{H})]^+$ and the $[\text{Ni}(\text{cyclam})]^{2+}$ cluster was a function of OR. This is illustrated in Fig. 2, in which a near exponential increase of the relative abundance with increasing OR is apparent. This trend is in accordance with an interpretation of collision-induced dissociation of $[\text{Ni}(\text{cyclam})]^{2+}$ and/or its solvated clusters to $[\text{Ni}(\text{cyclam}-\text{H})]^+$. Similar charge reduction has been reported for Co^{III} sepulchrate, whose ligand is a cage-like amino macrocycle.^{10,11}

Since Fig. 2 shows that a small but significant peak of $[\text{Ni}(\text{cyclam}-\text{H})]^+$ persisting down to OR = 0 V, some efforts were spent on investigating if some of the $[\text{Ni}(\text{cyclam}-\text{H})]^+$ ions observed could be formed in solution. The ability of Ni^{II} and Cu^{II} to promote deprotonation of an amide proton on a chelating amino acid or oligopeptide in solution is well known.^{23,24} Electrochemical oxidation of $[\text{Ni}^{\text{II}}(\text{cyclam})]^{2+}$ to $[\text{Ni}^{\text{III}}(\text{cyclam})]^{3+}$ with subsequent deprotonation of the cyclam to $[\text{Ni}^{\text{III}}(\text{cyclam}-\text{H})]^{2+}$ has been observed.³ The $[\text{Ni}^{\text{III}}(\text{cyclam})]^{3+}$ ion is known to be unstable in alkaline solution.⁴ In a series of experiments in which the solution pH was varied from 3 to 10, the $[\text{Ni}(\text{cyclam}-\text{H})]^+$ ion abundance was found to be independent of pH, and its abundance grew with increasing OR; this apparently eliminates $[\text{Ni}^{\text{III}}(\text{cyclam})]^{3+}$ as a possible intermediate. From an acid–base chemistry point of view, the $\text{p}K_a$ of

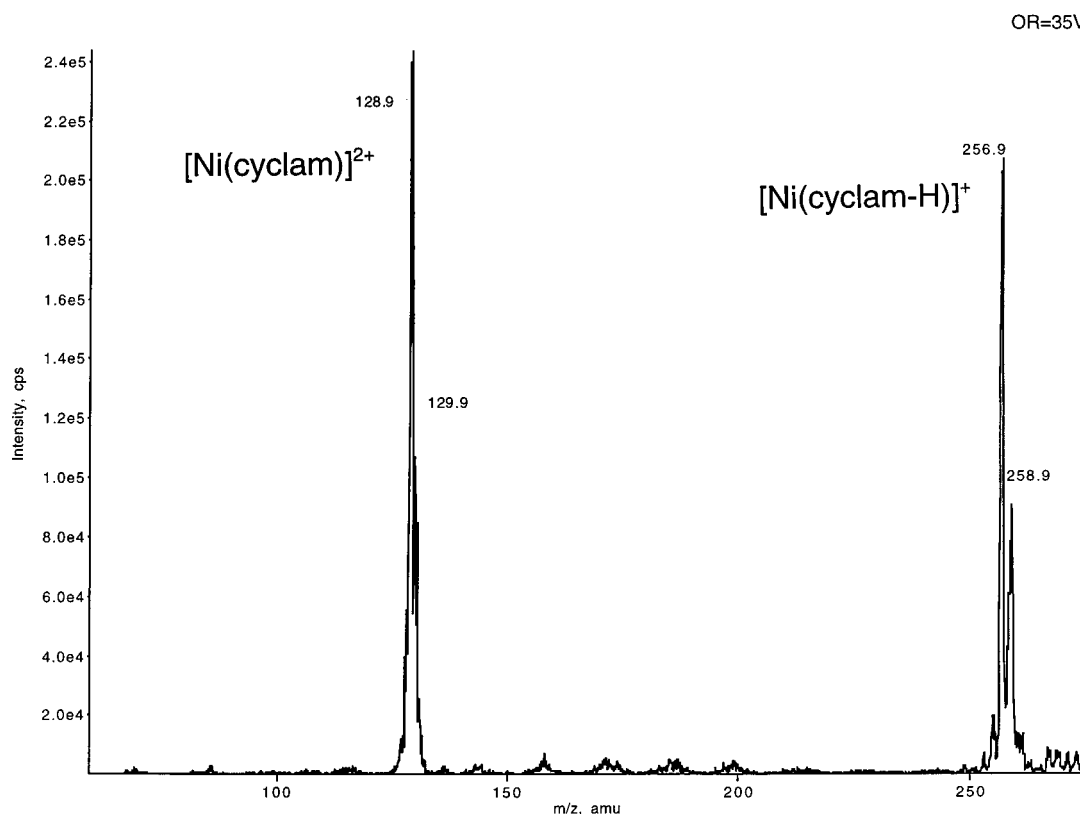


Figure 1. Electrospray mass spectrum of 50 μM $[\text{Ni}(\text{cyclam})](\text{PF}_6)_2$ in acetonitrile. OR = 35 V.

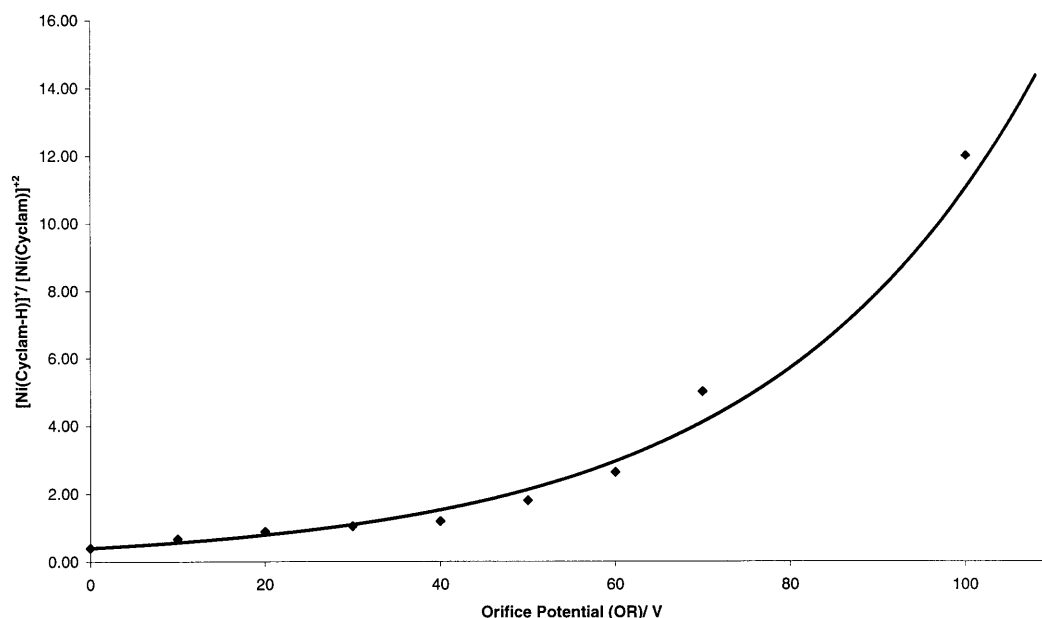


Figure 2. Relative abundance of $[\text{Ni}(\text{cyclam} - \text{H})]^+$ and $[\text{Ni}(\text{cyclam})]^{2+}$ versus OR.

$[\text{Ni}(\text{cyclam})]^{2+}$ is expected to be >14 ,²⁵ therefore deprotonation to form $[\text{Ni}(\text{cyclam} - \text{H})]^+$ is insignificant under our experimental conditions. These observations appear to rule out both electrochemical and solution contributions to the generation of the $[\text{Ni}(\text{cyclam} - \text{H})]^+$ ions.

To confirm the gas-phase origin of the $[\text{Ni}(\text{cyclam} - \text{H})]^+$ ion, MS/MS was performed. Figure 3 shows the product ion spectrum of $[\text{Ni}(\text{cyclam})(\text{CH}_3\text{CN})_2]^{2+}$, which was produced in

abundance after the curtain-gas flow was reduced. It is evident that $[\text{Ni}(\text{cyclam})(\text{CH}_3\text{CN})_2]^{2+}$ fragments to $[\text{Ni}(\text{cyclam})(\text{CH}_3\text{CN})]^{2+}$ and $[\text{Ni}(\text{cyclam})]^{2+}$, and on comparatively higher collision energy to smaller fragment ions, including Ni^+ (data not shown). However, the $[\text{Ni}(\text{cyclam} - \text{H})]^+$ ion is *not* one of the product ions seen. This observation, or the lack of it, has been confirmed with a number of $[\text{Ni}(\text{cyclam})(\text{solvent})_2]^{2+}$ precursor ions where solvent = acetone, dimethyl sulphoxide and acetonitrile. Figure 1 is a relatively clean

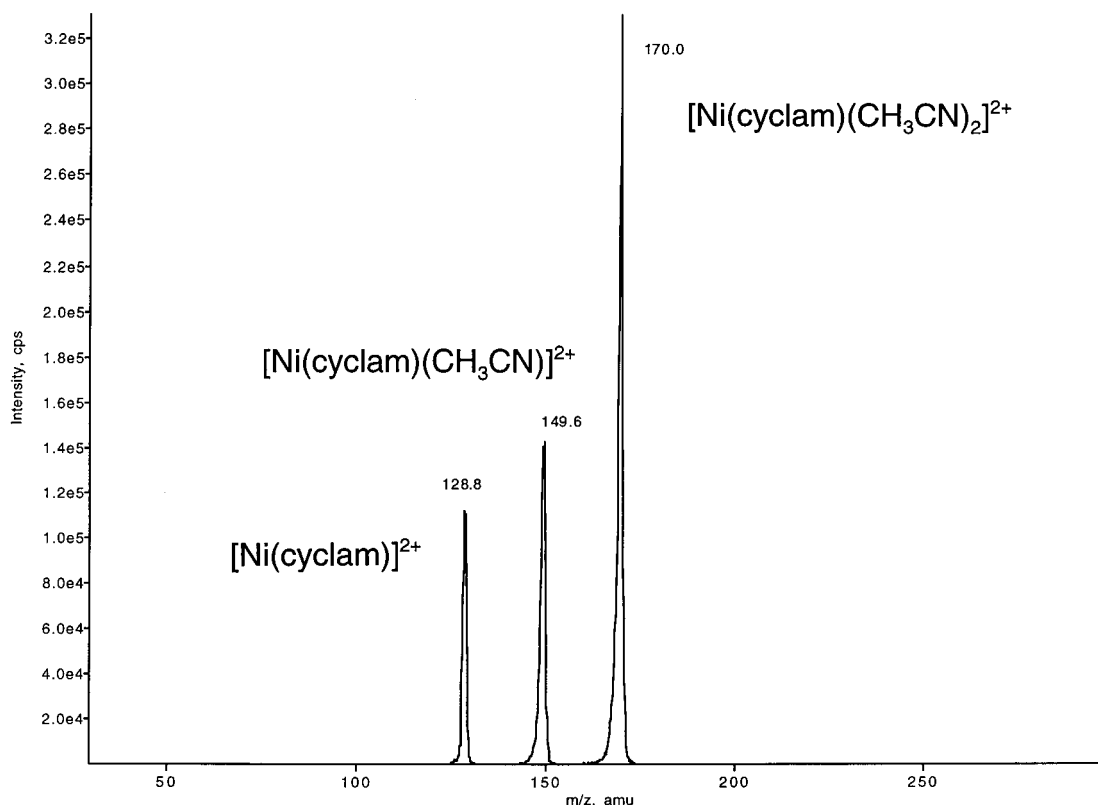


Figure 3. Product ion spectrum of $[\text{Ni}(\text{cyclam})(\text{CH}_3\text{CN})_2]^{2+}$. $E_{\text{lab}} = 40$ eV.

spectrum containing only two predominant ion clusters, $[\text{Ni}(\text{cyclam})]^{2+}$ and $[\text{Ni}(\text{cyclam} - \text{H})]^+$, which means that the precursor ion of $[\text{Ni}(\text{cyclam} - \text{H})]^+$ is likely to have an m/z value > 270 . Figure 4 shows electrospray mass spectra of $[\text{Ni}(\text{cyclam})](\text{PF}_6)_2$ with an upper m/z limit of 500 collected under different orifice potentials. Figure 4(b) shows the results for an OR of 35 V, identical with that used to collect the mass spectrum shown in Fig. 1. The ion cluster at m/z 403 and 405 has been identified as $[\text{Ni}(\text{cyclam})(\text{PF}_6)]^+$. It is evident that the abundance of that cluster increases with OR < 35 V [Fig. 4(a)] and decreases with OR > 35 V [Fig. 4(c)], an indication that the $[\text{Ni}(\text{cyclam})(\text{PF}_6)]^+$ ion is collisionally dissociated on increasing OR.

Tandem mass spectrometry was then performed to identify the product ions of $[\text{Ni}(\text{cyclam})(\text{PF}_6)]^+$ dissociation; these are shown in Fig. 5. It is apparent that at a relatively low collision energy [$E_{\text{lab}} = 14.6$ eV, Fig. 5(a)], the product ions are $[\text{Ni}(\text{cyclam})\text{F}]^+$ and $[\text{Ni}(\text{cyclam} - \text{H})]^+$; at a comparatively high collision energy [$E_{\text{lab}} = 20.4$ eV, Fig. 5(b)], the only predominant product ion is $[\text{Ni}(\text{cyclam} - \text{H})]^+$. That $[\text{Ni}(\text{cyclam})(\text{PF}_6)]^+$ and $[\text{Ni}(\text{cyclam})\text{F}]^+$ are the only precursor ions was ascertained in a precursor ion scan of $[\text{Ni}(\text{cyclam} - \text{H})]^+$; in that experiment the only precursor ions observed were $[\text{Ni}(\text{cyclam})(\text{PF}_6)]^+$ and $[\text{Ni}(\text{cyclam})\text{F}]^+$.

Thus far only the results for $[\text{Ni}(\text{cyclam})](\text{PF}_6)_2$ have been discussed. The results for $[\text{Ni}(\text{cyclam})](\text{CH}_3\text{COO})_2$, $[\text{Ni}(\text{cyclam})](\text{NO}_3)_2$, $[\text{Ni}(\text{tren})](\text{PF}_6)_2$, $[\text{Cu}(\text{cyclam})](\text{PF}_6)_2$ and $[\text{Cu}(\text{tren})](\text{CH}_3\text{COO})_2$ are all similar. As an illustration, Fig. 6 shows the product ion spectrum of $[\text{Cu}(\text{tren})(\text{CH}_3\text{COO})]^+$; it is apparent

that $[\text{Cu}(\text{tren} - \text{H})]^+$ is the only prominent product ion.

The above results are in accordance with an interpretation that PF_6^- (more likely F^-), CH_3COO^- and NO_3^- act as the acceptor (base) for the proton lost from the macrocyclic ligand, whereas adducted solvent molecules, such as acetonitrile, acetone and dimethyl sulphoxide, do not. This interpretation is based on a consideration of the proton affinities of the various potential bases. Table 1 lists the relevant proton affinities (PAs) of the bases²⁶ and the $\Delta H_{\text{acid}}^\circ$ values²⁷ of the acids involved. The most acidic protons on cyclam and tren are the amino protons (product ion spectra of d_4 - $[\text{Ni}(\text{cyclam})(\text{PF}_6)]^+$ and d_6 - $[\text{Cu}(\text{tren})(\text{PF}_6)]^+$, the fully deuterated complexes being produced by dissolving $[\text{Ni}(\text{cyclam})](\text{PF}_6)_2$ and $[\text{Cu}(\text{tren})](\text{PF}_6)_2$ in $\text{CH}_3\text{OD}/\text{D}_2\text{O}$, showed d_3 - $[\text{Ni}(\text{cyclam} - \text{D})]^+$ and d_5 - $[\text{Cu}(\text{tren} - \text{D})]^+$, respectively, as the only H/D abstraction products, thus proving that the proton lost

Table 1. Proton affinities²⁶ and $\Delta H_{\text{acid}}^\circ$ values²⁷

Species	PA (kcal mol ⁻¹)	$\Delta H_{\text{acid}}^\circ$ (kcal mol ⁻¹)
Acetonitrile	186.2	
Acetone	194.1	
Dimethyl sulphoxide	211.4	
Dimethylamine		396.5
HPF ₆		85.0
HF		371.3
CH ₃ COOH		348.5
HNO ₃		326.7

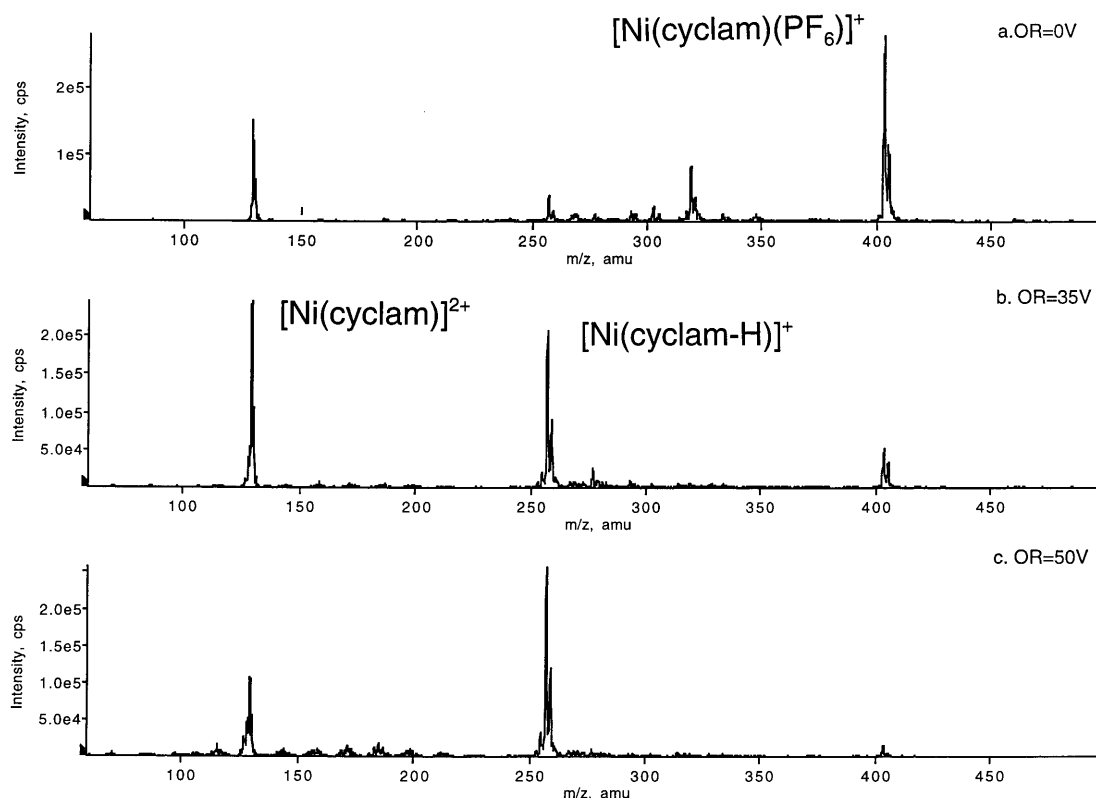


Figure 4. Electrospray mass spectrum of 50 μM $[\text{Ni}(\text{cyclam})](\text{PF}_6)_2$ in acetonitrile. OR = (a) 0, (b) 35 and (c) 50 V. Peak at m/z 317, $[\text{Ni}(\text{cyclam})(\text{CH}_3\text{COO})]^+$ (acetate being an impurity); m/z 277, $[\text{Ni}(\text{cyclam})\text{F}]^+$.

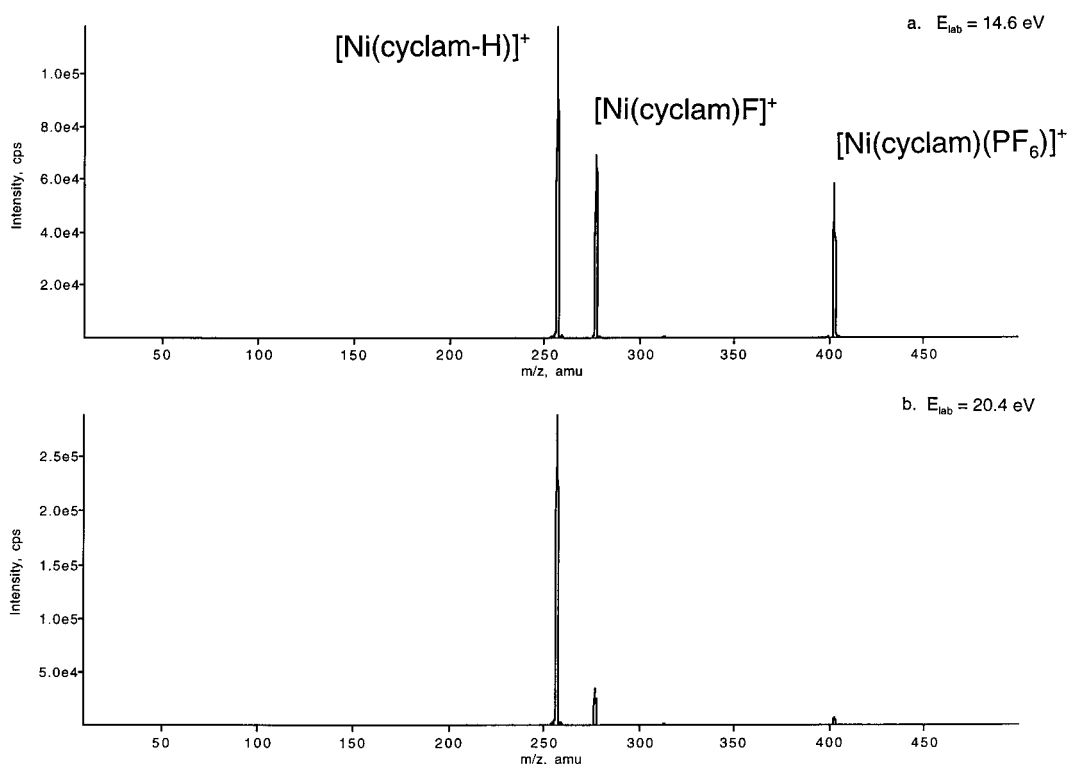


Figure 5. Product ion spectrum of $[\text{Ni}(\text{cyclam})(\text{PF}_6)]^+$. $E_{\text{lab}} =$ (a) 14.6 and (b) 20.4 eV.

is an exchangeable, i.e. amino, proton); dimethylamine is used to model the acidity of cyclam as well as tren. The intraionic, interligand proton transfer from cyclam or tren to a base can be viewed as a competition

between the conjugated base of the macrocycle and the base. Although the energetics of proton transfer involving Ni- and Cu-bound macrocycle and base are unknown, qualitative or semi-quantitative trends may

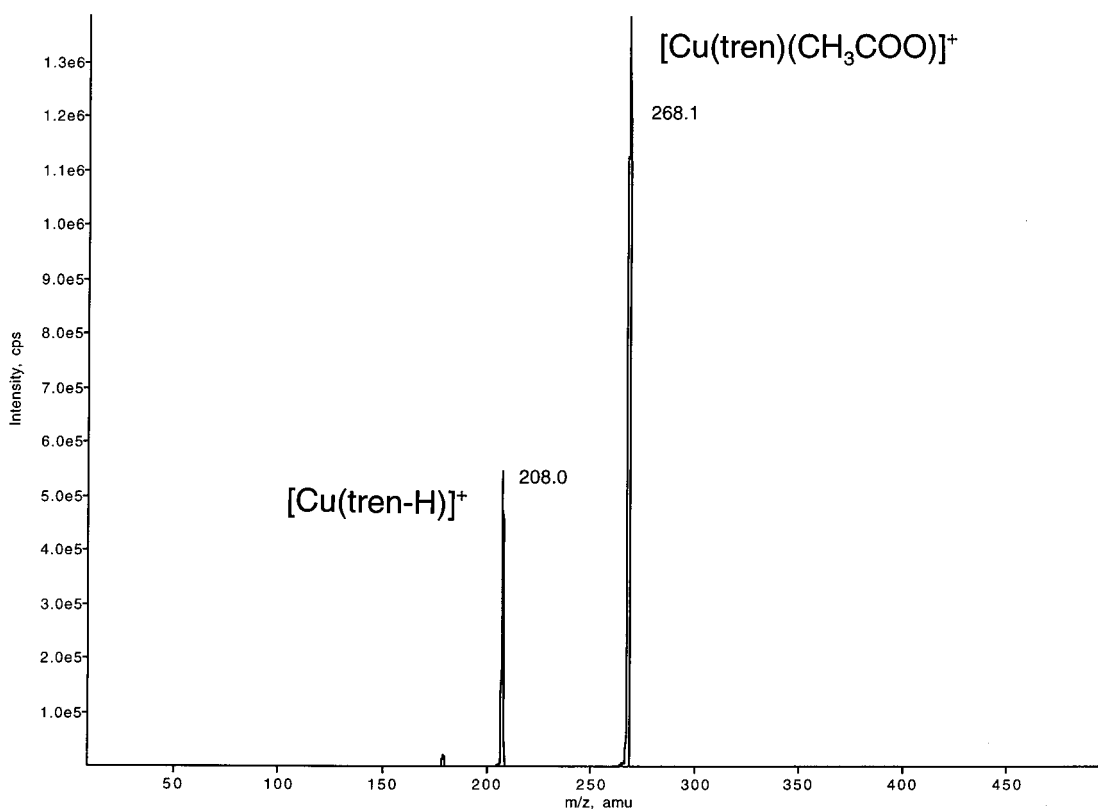
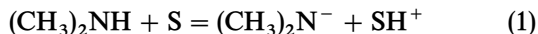


Figure 6. Product ion spectrum of $[\text{Cu}(\text{tren})(\text{CH}_3\text{COO})]^+$. $E_{\text{lab}} = 18 \text{ eV}$.

be established in an examination of transfers involving only the macrocycle and the base. That is, the energetics of the proton transfer may be compared using the enthalpy changes of the following two gas-phase reactions:

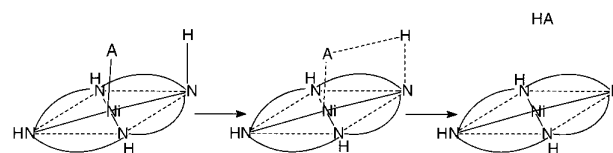


where S is a neutral base such as an adducted solvent molecule and A^- is a conjugated base such as F^- , PF_6^- , CH_3COO^- and NO_3^- . The enthalpy changes, ΔH_1 and ΔH_2 , are

$$\Delta H_1 = \Delta H_{\text{acid}}^\circ((\text{CH}_3)_2\text{NH}) - \text{PA}(\text{S}) \quad (3)$$

$$\Delta H_2 = \Delta H_{\text{acid}}^\circ((\text{CH}_3)_2\text{NH}) - \Delta H_{\text{acid}}^\circ(\text{HA}) \quad (4)$$

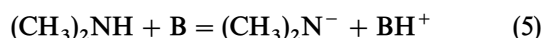
From Table 1, for $\text{S} = \text{CH}_3\text{CN}$, $\Delta H_1 = 210 \text{ kcal mol}^{-1}$ (1 kcal = 4.184 kJ); $\text{A}^- = \text{F}^-$, $\Delta H_2 = 25 \text{ kcal mol}^{-1}$. Since the entropy change (ΔS) in a proton transfer reaction, such as reaction (1) or (2), is typically close to zero, $\Delta G \approx \Delta H$. It is readily apparent that proton transfer to an adducted solvent molecule (S) from a macrocyclic ligand (represented by $(\text{CH}_3)_2\text{NH}$) is highly endoergic whereas that to a ligated anion (A^-) is much less so. Consequently, collision activation is able to overcome the endoergicity of the equivalent of reaction (2) for the metal complex but not that of reaction (1), which means that proton transfer to anions is observed with high OR or E_{lab} values, whereas that to adducted solvent is not. It should be noted that PF_6^- is not a likely proton acceptor because of the low acidity of its conjugated acid; however, its fragment ion, F^- , is, in accordance with results shown in Fig. 5. The proto-



Scheme 1.

nated acid anion can then leave the complex as a neutral molecule (see Scheme 1; charges and methylene groups are omitted for clarity; the middle structure may be regarded as the collision-activated transition complex).

Solvent molecules, such as acetonitrile and acetone, have relatively low proton affinities thus making reaction (1) highly endoergic. Other neutral bases, e.g. various amines, have higher proton affinities that may render the proton transfer reaction less endoergic and therefore observable after collision activation. That is,



where B is a nitrogen base. Figure 7 shows the product ion spectra of the $[\text{Ni}(\text{cyclam})\text{B}]^{2+}$ ions; B = benzylamine, $\text{PA} = 218.4 \text{ kcal mol}^{-1}$ [Fig. 7(a)]; and B = 1-methylimidazole, $\text{PA} = 229.3 \text{ kcal mol}^{-1}$ [Fig. 7(b)]; under single collision conditions at constant collision energy in the center-of-mass frame ($E_{\text{CM}} = 4 \text{ eV}$). It is apparent that fragmentation of $[\text{Ni}(\text{cyclam})\text{B}]^{2+}$ leads to $[\text{Ni}(\text{cyclam})]^{2+}$, BH^+ and $[\text{Ni}(\text{cyclam} - \text{H})]^+$ and that reaction (5) proceeds much more readily after collision activation of $[\text{Ni}(\text{cyclam})(1\text{-methylimidazole})]^{2+}$ than $[\text{Ni}(\text{cyclam})(\text{benzylamine})]^{2+}$. Figure 8 illustrates the relationship between the relative abundances of $[\text{Ni}(\text{cyclam} - \text{H})]^+$ versus

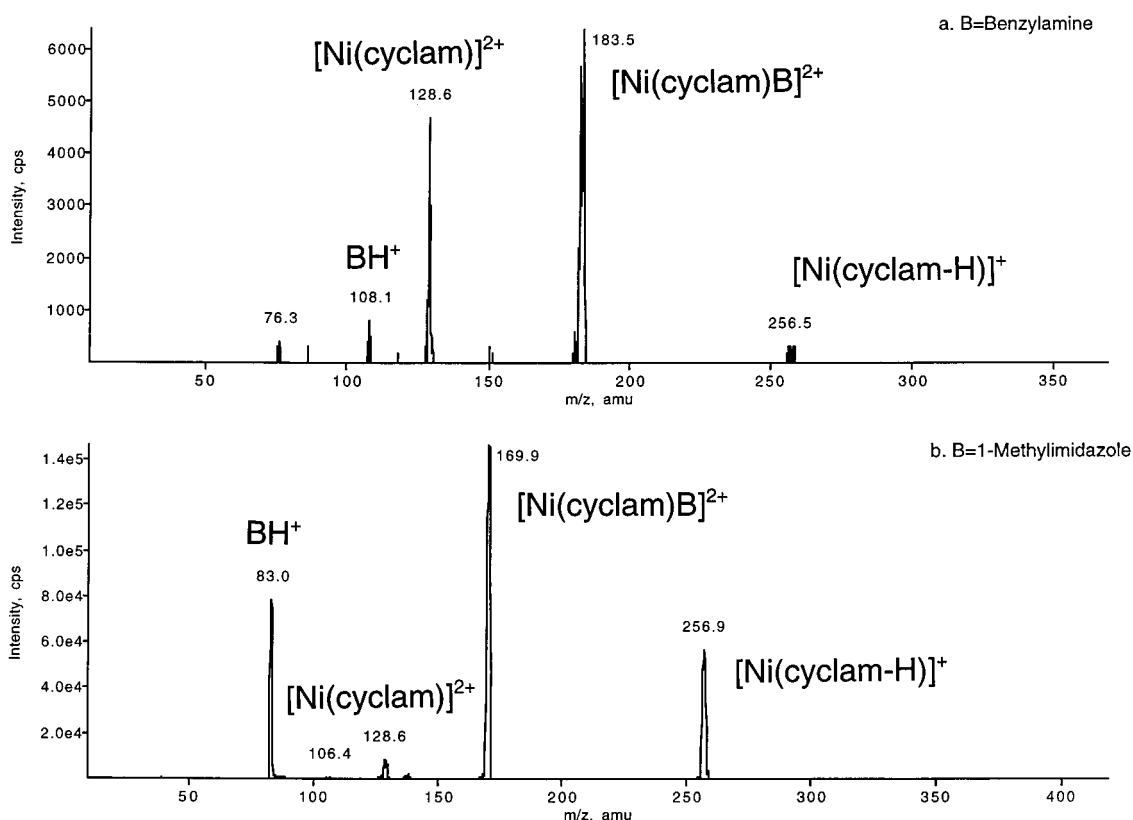


Figure 7. Product ion spectra of (a) $[\text{Ni}(\text{cyclam})(\text{benzylamine})]^{2+}$ and (b) $[\text{Ni}(\text{cyclam})(1\text{-methylimidazole})]^{2+}$. $E_{\text{CM}} = 4 \text{ eV}$.

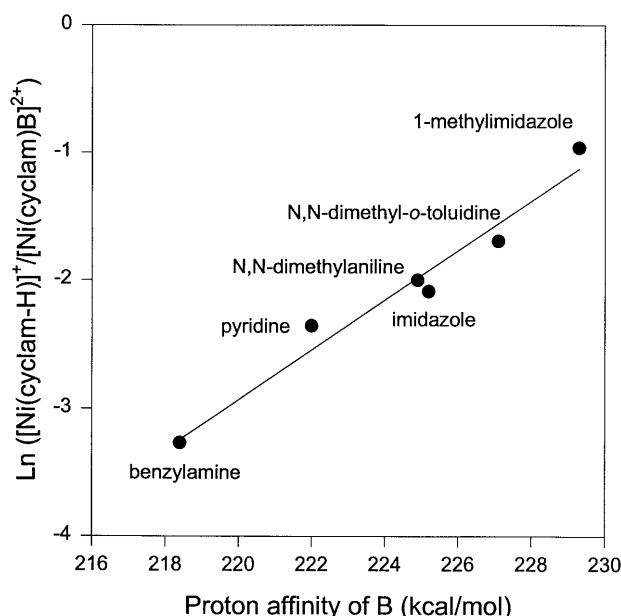


Figure 8. $\ln([Ni(cyclam-H)]^+ / [Ni(cyclam)B]^{2+})$ versus proton affinities of aromatic nitrogen bases (Bs). $E_{CM} = 4$ eV.

$[Ni(cyclam)B]^{2+}$ and the *PAs* of a number of aromatic nitrogen bases.²⁶ The relative abundance appears to increase exponentially with increasing proton affinity of B. Under our experimental conditions, the lowest proton affinity of B in which $[Ni(cyclam-H)]^+$ could be detected was ~ 213 kcal mol⁻¹ (pyrazole). Hence it appears that intraionic proton transfer from cyclam to an adducted neutral base can also occur as long as the endoergicity can be overcome with collision activation.

CONCLUSION

This study has shown that the charge-reduced, macrocyclic $[M(L-H)]^+$ complex ion of Ni^{II} and Cu^{II} (L is

the macrocycle) observed upon electrospraying a solution of $[ML]A_2$ (A = anion) is not produced from solvated $[ML]^{2+}$, but from $[MLA]^+$, after collision activation. $[M(L-H)]^+$ is also produced from $[MLB]^{2+}$ (B = neutral aromatic nitrogen base) provided that the *PA* of B is sufficiently high (> 213 kcal mol⁻¹ under our experimental conditions).

Acknowledgements

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