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Relative metal-ion affinities of alkylamines in the gas-phase

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Abstract

The relative metal ion (Ni^+, Co^+, $CoCl^+$) affinities of twelve alkylamines have been estimated using Cooks' kinetic method in a FAB mass spectrometer. The results are compared with proton affinities and with two-ligand dissociation enthalpies. An approximate ordering for the relative metal ion affinities of the amines is given and discussed. The RNH_2–Ni^+ bond is found to be slightly weaker than RNH_2–$CoCl^+$ but stronger than RNH_2–Co^+. The effective temperature (T) of the metal-bound dimer ions may fall in the range $298\ K \leq T < 400\ K$.

There has been considerable interest in gas-phase metal ion chemistry during the last decade [1]. The gas-phase is an ideal environment for the study of the intrinsic properties of metal ions in the absence of any complicating solvent effects. Complexation, binding and reactions of the metal ions with molecules and related thermochemistry are the most important aspects. Thermochemical studies can provide metal ion–ligand bond energies. These data are useful in approaching the energetics of reaction mechanisms, catalytic processes, and bonding modes.

We have recently obtained relative metal-ion affinities of a series of nitriles [2] using Cooks' kinetic method [3]. Those results were compared with corresponding proton affinities (PA), two-ligand dissociation energies, affinities for other metal ions, and dipole moments of the nitriles. It was shown that Cooks' kinetic method could give semi-quantitative data even when using an analytical mass spectrometer rather than an instrument designed for physical chemistry studies. In this paper, we report a study of relative amine–Ni^+, amine–Co^+, and amine–$CoCl^+$ bond energies using Cooks' kinetic metastable ion (MI) method [3]. The amines used in this work are given below.

NH_3 **(1)**

CH_3NH_2 **(2)**

$CH_3CH_2NH_2$ **(3)**

$CH_3(CH_2)_2NH_2$ **(4)**

$(CH_3)_2CHNH_2$ **(5)**

$CH_3(CH_2)_3NH_3$ **(6)**

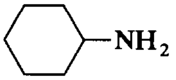
$(CH_3)_2CHCH_2NH_2$ **(7)**

$CH_3CH_2CH(CH_3)NH_2$ **(8)**

$(CH_3)_3CNH_2$ **(9)**

$CH_3(CH_2)_4NH_2$ **(10)**

$CH_3(CH_2)_5NH_2$ **(11)**



(12)

It should be emphasized that Cooks' method should be used with great care, because it involves extreme assumptions regarding the factors controlling dissociation kinetics [3]. Applications are thus limited to weakly bound cluster ions which undergo simple dissociation

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kinetics. Furthermore, without confirmation or support from other appropriate measurements such as equilibrium measurements and/or by theoretical calculations, it is best to treat the results from Cooks' method qualitatively or semi-quantitatively rather than quantitatively. Despite this, a number of successful applications of Cooks' method have been reported [3,4].

1. Experimental section

A Kratos Concept IS double-focusing mass spectrometer of E/B configuration (Kratos Analytical, Urmstom, Manchester, UK) was used in this work. The instrument was controlled by a Kratos DS 90 Data General Eclipse based computer system. The Kratos Mach 3 data system running on a SUN SPARC station was used for further data workup. The normal fast-atom bombardment (FAB) source was modified so that it could accept a reservoir probe, via the electron ionization/chemical ionization probe lock, as the source of gaseous molecules. The source was also modified to operate at higher pressure than the conventional FAB source. Detailed descriptions of the modified instrument and operating conditions are given elsewhere [5]. Briefly, the instrument was fitted with an Ion Tech saddle field atom gun. Xenon was used as the fast-atom source. The fast-atom beam energy was 8 keV with a density corresponding to an emission current of about 1 mA. The source was operated at a temperature of 25°C, a pressure of about 10^{-5} Torr (measured in the source housing not in the reaction region) and an accelerating voltage of 6 kV. Normal mass spectra were recorded at a resolving power of ~ 1000. Metastable ion fragmentations of the dimers in the first field-free region were monitored by B/E linked scans. Peak height ratios of the product ions in the MI spectra were reproducible within ±15–20% and the logarithm of the ratios within ±0.10–0.15. Since there was some diffusion of the FAB gun xenon from the source into the collision chamber region, metastable ions for recording the MI spectra might have been partially activated. The use of a FAB source produces metastable ions with lower internal energies than obtained in conventional EI sources.

It should be noted that the B/E linked scans may not result in accurate relative intensities of product ions when the product ion formation is accompanied with considerable kinetic energy release, because the peak height in the B/E linked scan spectrum corresponds only to the central part of the peak. However, for our systems, the metal-bound dimer ions are loosely bonded and expected to generate monoadducts without significant kinetic energy release. We thus consider that the B/E linked scans give reasonably accurate ion intensities. In fact, consistent values of $\ln(k_n/k_1)$ can be readily derived from different stair-steps (see Results section).

"Naked" metal ions were generated from $FeSO_4 \cdot 7H_2O$, $CoCl_2 \cdot 6H_2O$, and $NiCl_2 \cdot 6H_2O$ which had been dissolved in water and deposited by evaporation onto the FAB probe tip. We used $FeSO_4 \cdot 7H_2O$ rather than $FeCl_3 \cdot 6H_2O$ because the latter gave lower intensities of Fe^+. Other metal salts which might also generate high-intensity naked metal ions were not studied further. The amines were introduced into the source using the reservoir probe. To obtain an asymmetric dimer ion, $R'NH_2–M^+–NH_2R''$ ($M = Ni^+$ or Co^+), the amines $R'NH_2$ and $R''NH_2$ (~ 3 μl of each) were injected simultaneously into the heated reservoir probe. All samples were commercially available and used without further purification.

2. Results

Under the FAB source conditions, the metal salts themselves give primarily naked metal ions after ionization. For $CoCl_2 \cdot 6H_2O$, $CoCl^+$ is also formed. These ions react with an amine in the source to generate monoadducts and metal-bound dimer ions, $RNH_2–M^+(Cl)$ and $R'NH_2–M^+(Cl)–NH_2R''$. Under our FAB source conditions, Fe^+ does not form any dimer ions.

Previous studies using FTMS [6] and ion-beam instruments [7] have shown that ligated or naked transition-metal ions reacting with ammonia generated MH^+ and MNH_2^+ ions. The $M^+–N$ bond energies for these ions are stronger than for the corresponding isoelectronic carbon analogs, MCH_2^+ and MCH_3^+. This enhancement is attributed to the significant interaction between the lone pair of electrons on nitrogen and the empty 3d orbitals on metal ions. These results suggest that bond insertion structures such as $H–M^+–NH_2$ are involved in the reactions. Furthermore, the bond inserting abilities are different from metal to metal. For instance, ligated Fe^+ (LFe^+) reacting with ammonia gives higher yields of bond insertion products than LCo^+, whereas LNi^+ and LRu^+ exclusively undergo attachment and ligand displacement [6a]. It is expected that the bond insertion complex greatly reduces the ability of the metal ions to insert further into and/or attach the second ammonia or amine. This may explain why no $(RNH_2)_2Fe^+$ dimer ions are formed in our FAB source. In fact, normal mass spectra recorded for Fe^+ reacting with amines in the FAB source show that the $[RNH_2–H_2]Fe^+$ ions are the most important products. In contrast, the intensity of analogous $[RNH_2–H_2]Co^+$ ions is reduced when Co^+ is the reacting metal ion. For the reactions of Ni^+, the monoadduct ions, RNH_2Ni^+, become the most important product.

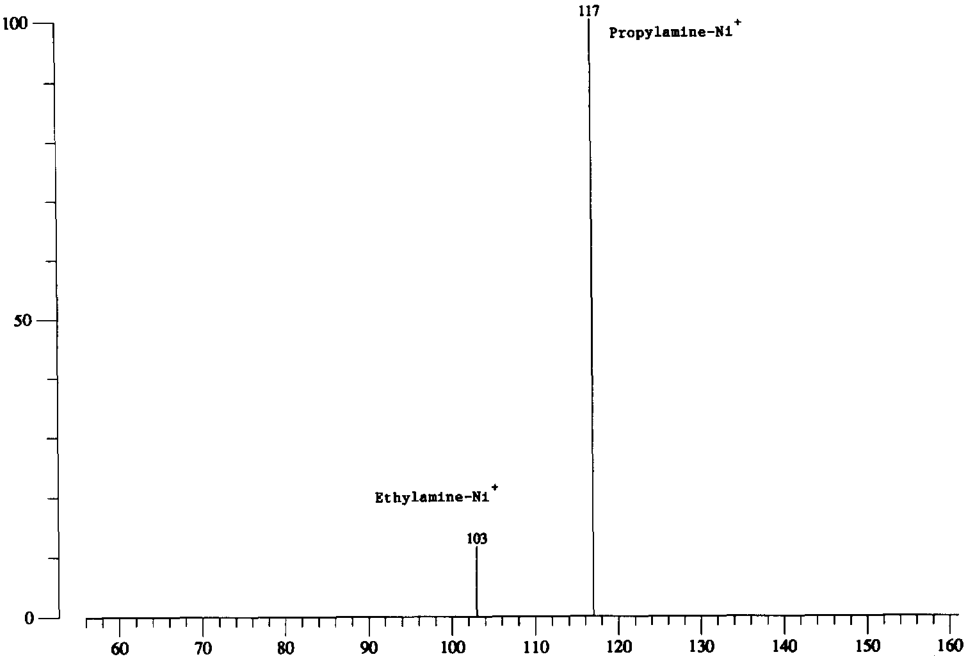

Fig. 1. MI spectrum of propylamine-Ni^+-ethylamine dimer ion.

The MI spectra of the asymmetric nickel-bound dimer ions ($R'NH_2$-Ni^+-NH_2R'') give two peaks corresponding to $R'NH_2M^+$ and $R''NH_2M^+$ ions. Figure 1 shows a typical MI spectrum of n-$C_3H_7NH_2$-Ni^+-$NH_2C_2H_5$. The higher intensity of the n-$C_3H_7NH_2$-Ni^+ ion at m/z 117 than that of $C_2H_5NH_2$-Ni^+ indicates that n-$C_3H_7NH_2$ has a greater affinity for Ni^+ than $C_2H_5NH_2$. Minor H_2 loss may also be observed for large amines such as hexylamine and cyclohexylamine. More significant H_2 loss occurs for the cobalt-bound dimer ions. Moreover, the cobalt-bound dimer ions eliminate NH_3 [8]. The dehydrogenation and the NH_3 elimination are essentially absent for $R'NH_2$-$CoCl^+$-NH_2R'' ions. The fragmentations in addition to the ligand loss may indicate the contributions from covalently bonded structures which involve metal ion insertion [6,7,9]. The more intense additional fragmentations for the complexes of Co^+ may then be attributed to the higher inserting ability of Co^+ than Ni^+ [6,7]. The insertion structures and the additional reactions are likely to affect the application of Cooks' method. Despite this, however, we believe that Cooks' method is still applicable to the present case for a semi-quantitative or qualitative study.

In order to measure accurately the abundance ratios of [$R'NH_2$-M^+]/[$R''NH_2$-M^+] in the MI spectra, the dimer ions must be formed with high enough intensities in the FAB source to give good S/N. Furthermore, the dimer ions should be chosen to consist of a pair of amines which have similar metal ion affinities and give comparable RNH_2-M^+ ion abundances in the MI spectra, because larger differences between the two RNH_2-M^+ ion abundances result in less accurate measurements. In fact, we found that a pair of amines with a difference in PA less than 3 kcal/mol can form metal-bound dimer ions in detectable intensities which then give comparable RNH_2-M^+ abundances in the MI spectra. As shown in Figs. 2 and 3, 22 Ni^+(Co^+)-bound and 26 $CoCl^+$-bound dimer ions of different amines have been investigated. Since NH_3-$CoCl^+$ is absent in the MI spectra of NH_3-$CoCl^+$-NH_2R, the relative bonding energy of NH_3-$CoCl^+$ is not mea-

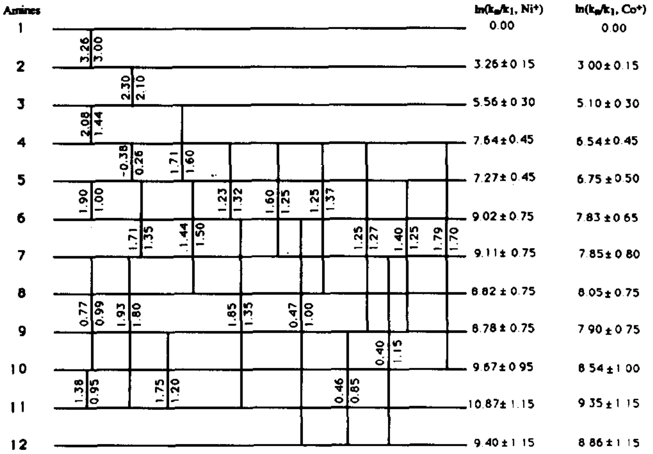

Fig. 2. Measured ln(k_n / k_1, Ni^+) and ln(k_n / k_1, Co^+) for amine-Ni^+ and amine-Co^+, respectively. Data on the left side of the vertical lines correspond to amine-Ni^+ and on the right side to amine-Co^+.

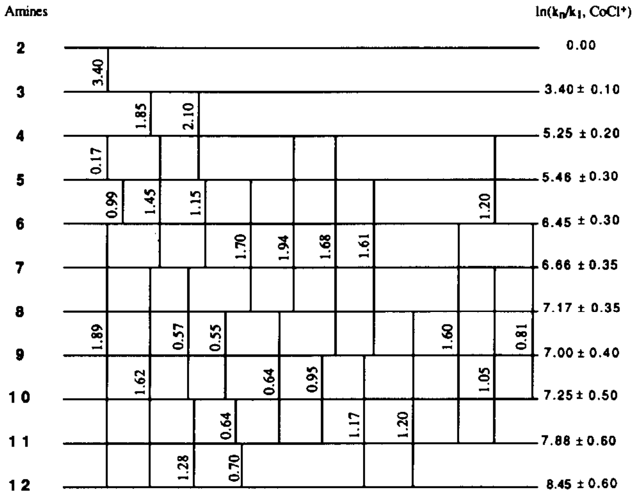

Fig. 3. Measured $\ln(k_n/k_1$, $CoCl^+)$ for amines.

sured. The ordering of $\ln(k_n/k_1)$ given in the ladder diagram is derived using the B/E linked metastable ion scan technique. The zero points of the scales are chosen arbitrarily by setting the values of NH_3 and CH_3NH_2 equal to zero for Ni^+ and Co^+ as well as for $CoCl^+$, respectively.

For some amines, two or more $\ln(k_n/k_1)$ values are obtained from different steps. For example, the relative $\ln(k_n/k_1)$ of n-butylamine (**6**) is derived either from n-butylamine dimer or from i-propylamine–M^+–n-butylamine dimer. In these cases, the relative $\ln(k_n/k_1)$ values given in Figs. 2 and 3 are the averages. The errors given along with the $\ln(k_n/k_1)$ values correspond to both the peak-intensity-ratio measurements and the averages.

3. Discussion

According to Cooks' method, the experimentally determined $\ln(k_n/k_1)$ values are connected with the relative metal ion affinities (ΔMIA) for the amines, provided the entropic effects are negligible:

$$\Delta\text{MIA} \cong RT\ \ln(k_n/k_1) \qquad (1)$$

Significant contributions to the entropic changes for the metal-bound dimer ion fragmentation are due to the changes in symmetry numbers and moment of inertia [10]. Since the geometry for the dimer ions is not available, calculations for the entropic effects are impossible. Fortunately, the amines investigated in this work do not involve symmetry number changes during the course of the fragmentation. The moment of intertia changes are important when metal–ligand bonding distance and ligand mass are significantly different for the two ligands [11]. This effect is probably unimportant in the present work since the ligands studied with the metal ions are closer in mass and are similarly bonded. It is thus acceptable to neglect the entropic effects for a semi-quantitative or qualitative study.

At a given temperature (T), ΔMIA can be calculated from eqn. (1). Note that the temperature is not the temperature of the dimer ions in the source but the effective temperature of the reactive dimer ions which undergo unimolecular dissociation in the first field-free region [3]. In the CID experiments for measuring the relative proton affinities [3,12], the effective temperature of ions is much higher than the source temperature because of the high energy collisions between the ions and inert gas. In contrast, in our high pressure

TABLE 1. Proton affinities (PA), metal ion affinities (ΔMIA) and two-ligand dissociation enthalpies ($\delta D(Ni^+–2L)$) of amines

	RNH_2 R =	PA [a]	ΔMIA(Ni^+) [b]	ΔMIA(Co^+) [b]	ΔMIA($CoCl^+$) [b]	δD(Ni–2L) [c]
1	H	205.0	0	0		0
2	CH_3	214.1	1.93 ± 0.09	1.78 ± 0.09	0	5.31
3	C_2H_5	217.0	3.29 ± 0.18	3.02 ± 0.18	2.01 ± 0.06	7.82
4	n-C_3H_7	218.5	4.53 ± 0.27	3.87 ± 0.27	3.11 ± 0.12	
5	i-C_3H_7	219.4	4.31 ± 0.27	4.00 ± 0.30	3.23 ± 0.18	11.79
6	n-C_4H_9	219.0	5.34 ± 0.44	4.64 ± 0.39	3.82 ± 0.18	
7	i-C_4H_9	219.5	5.40 ± 0.44	4.65 ± 0.47	3.94 ± 0.21	
8	s-C_4H_9	220.5	5.23 ± 0.44	4.77 ± 0.44	4.25 ± 0.21	
9	t-C_4H_9	221.3	5.20 ± 0.44	4.68 ± 0.44	4.15 ± 0.24	
10	n-C_5H_{11}	219.6	5.73 ± 0.56	5.06 ± 0.59	4.29 ± 0.30	
11	n-C_6H_{13}	220.1	6.44 ± 0.68	5.54 ± 0.68	4.67 ± 0.36	
12		221.3	5.57 ± 0.68	5.25 ± 0.68	5.00 ± 0.36	

[a] Proton affinities in kcal/mol taken from ref. 23.

[b] Relative metal ion affinities in kcal/mol (ΔMIA(Ni^+), ΔMIA(Co^+) and ΔMIA($CoCl^+$)) at 298 K are obtained from this work.

[c] Relative two-ligand dissociation enthalpies taken from ref. 16.

FAB source, the dimer ions, once formed, collide with other species and become thermally stabilized. Our previous work showed that the effective temperature of the metal-bound dimers of nitriles in our FAB source fell in the range 298 K $< T <$ 400 K [2]. Assuming that the effective temperature of the dimer ions is about 298 K, the relative metal ion affinities can be estimated from eqn. (1). Table 1 lists the ΔMIA values for the amines. Note, because the real effective temperature is not known, the ΔMIA values given here should derive from the actual values (*vide infra*). However, we use the ΔMIA values only for the purpose of comparing with other available data of the amines.

In the studies of two or one ligand relative dissociation enthalpies for metal ions, it has been found that comparison of these enthalpies with those of reference Lewis acids could reveal some interesting features about the nature of the metal–ligand bonding interactions [2,11,13–19]. In the following, we will compare our ΔMIA values with other reference acids.

Figure 4 shows a plot of the relative Ni^+ affinities ($\Delta MIA(Ni^+)$) *vs.* available two-ligand dissociation enthalpies of four amines ($\delta D(Ni^+\text{-}2L)$) [18]. A least-squares fit to this scale is given by $\delta D(Ni^+\text{-}2L) = 2.63\Delta MIA(Ni^+) - 0.04$ kcal/mol, correlation coefficient $r^2 = 0.99$. If we simply assume that $\delta D(Ni^+\text{-}2L)$ is approximately twice the $\Delta MIA(Ni^+)$, the slope of $\delta D(Ni^+\text{-}2L)$ *vs.* $\Delta MIA(Ni^+)$ should be 2 which is smaller than 2.63 derived from Fig. 4. Comparing these two slopes, one can get an effective temperature of the metal-bound dimer ions as about 400 K. Note, however, that $\delta D(Ni^+\text{-}2L)$ should be less than twice ΔMIA, because interaction between the partial charges on the amines decreases the total bond energies of the dimer ions, compared with twice the bond energies of the single amine complexes [11,18,19]. The effective temperature is thus expected to be lower than 400 K, *i.e.*, 298 K $\leq T <$ 400 K. This is similar to our previous results from the metal–nitrile system [2]. Because of the higher internal temperature, the actual ΔMIA values may be greater than those estimated at 298 K in Table 1, *i.e.*, ΔMIA(298 K) ≤ ΔMIA(actual) < 1.3ΔMIA(298 K). The higher effective temperature of the dimer ions than 298 K is probably due, in part, to the high energy collision in the first field-free region of the mass spectrometer, between the dimer ions and the Xe gas which diffuses from the FAB source, and incomplete thermalization in the FAB source. Cooks *et al.* also reported that the effective temperature of proton-bound metastable dimer ions undergoing dissociations in the second field-free region was higher than the source temperature [3].

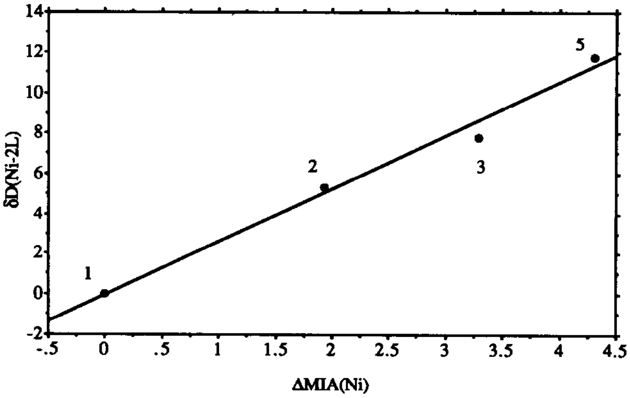

Fig. 4. Comparison of relative nickel ion affinities ($\Delta MIA(Ni^+)$) with relative two-ligand dissociation enthalpies $\delta D(Ni^+\text{-}2L)$. A least-squares fit of parameters is: $\delta D(Ni^+\text{-}2L) = 2.63\Delta MIA(Ni^+) - 0.04$ kcal/mol, $r^2 = 0.99$. Values of $\delta D(Ni^+\text{-}2L)$ are obtained form ref. 18. Both $\Delta MIA(Ni^+)$ and $\delta D(Ni^+\text{-}2L)$ of NH_3 are set as zero.

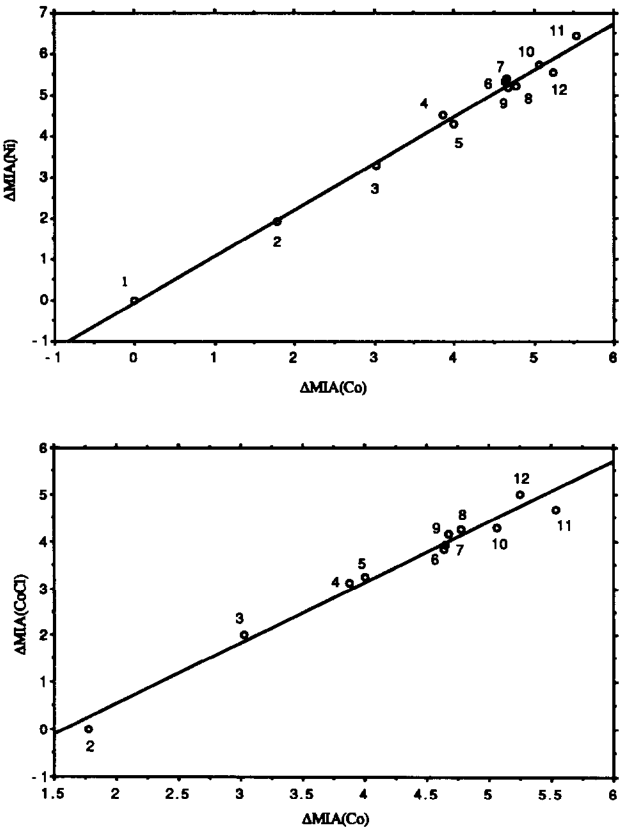

Fig. 5. Comparison of $\Delta MIA(Ni^+)$ and $\Delta MIA(CoCl^+)$ with $\Delta MIA(Co^+)$. Least-squares fit for the upper line: $\Delta MIA(Ni^+) = 1.132\Delta MIA(Co^+) - 0.045$ kcal/mol ($r^2 = 0.992$); and for the bottom line: $\Delta MIA(CoCl^+) = 1.289\Delta MIA(Co^+) - 2.039$ kcal/mol ($r^2 = 0.976$).

Figure 5 shows slopes of $\Delta MIA(Ni^+)$ *vs.* $\Delta MIA(Co^+)$ and $\Delta MIA(CoCl^+)$ *vs.* $\Delta MIA(Co^+)$. The amines fall on the lines given by $\Delta MIA(Ni^+) = 1.132$ $\Delta MIA(Co^+) - 0.045$ kcal/mol ($r^2 = 0.99$), and $\Delta MIA(CoCl^+) = 1.289\delta MIA(Co^+) - 2.039$ kcal/mol ($r^2 =$

0.98). The slope of the correlation line has been shown to reflect the relative metal–ligand bond strength [2,11,13–19]. The greater the bond strength, the greater the alkyl substituent effects, since the substituent is closer to the charge centre [18,19]. The slope (1.132) of ΔMIA(Ni^+) *vs.* ΔMIA(Co^+) and the slope (1.289) of ΔMIA($CoCl^+$) *vs.* ΔMIA(Co^+) thus may indicate a bond strength order: $CoCl^+$–amine > Ni^+–amine > Co^+–amine. Considering the differences in these slopes are not large, it is expected that relative bonding energies of the amines to these three ions should be very close. Previous workers have found that Ni^+ binds slightly more strongly towards oxygen bases than does Co^+ [18]. It should be noted, however, that experiments show that Co^+–NH_3 is slightly stronger than Ni^+–NH_3 [20], although high-level theoretical calculations demonstrate that $r(Ni^+\text{–}NH_3) = 3.783\ a_0$ is shorter than $r(Co^+\text{–}NH_3) = 3.817\ a_0$ [21].

The M^+–ligand bonding is usually considered to involve both covalent and ionic characteristics although the latter is expected to be dominant [11,13–19]. The covalent bonding may occur in two ways. First, electrons from occupied ligand orbitals donate to the empty 4s and/or 4p orbitals of the metals. This delocalization is limited by repulsion by the electrons in the filled 3d and core orbitals on the metals. Secondly, 3d electrons of the metals can delocalize into the unoccupied ligand orbitals, forming a π back-bond. This occurs only for molecules with suitable empty orbitals such as π^* orbitals for accepting the 3d electrons. Both of the covalent contributions, in particular the π back-bonding, seem unimportant in the metal–amine system. If we assume that the covalent contributions to the metal–ligand bonding are negligible, the bonding energies will be determined by the electrostatic interactions which include ion-permanent dipole, ion-induced dipole, polarization, dispersion, and repulsive interactions [22].

Simple electrostatic calculations for amine–Li^+ complexes suggest that the polarizability interaction is the dominant term [10]. Moreover, a large electrostatic repulsion is expected between Li^+ and the methyl groups of Me_3N. The repulsion accounts for an irregular ordering of the binding energies, $D(Li^+\text{–}NH_3) < D(Li^+\text{–}MeNH_2) < D(Li^+\text{–}Me_3N) < D(Li^+\text{–}Me_2NH)$. A similar, slightly weaker repulsive term has also been suggested for Ni^+–amine [18] and $CpNi^+$–amine complexes [15]. If analogous repulsion operates between Ni^+ and the methyl groups at the α-position of the amines, it may explain the results obtained in this work. As shown in Table 1, the Ni^+ affinities of the amines decrease as the α-position becomes more branched, *i.e.*, i-$C_3H_7NH_2$ < n-$C_3H_7NH_2$, t-$C_4H_9NH_2$ < s-$C_4H_9NH_2$ < n-$C_4H_9NH_2$, and c-$C_6H_{11}NH_2$ < n-$C_6H_{13}NH_2$. Although the tendency becomes less significant when considering the possible measurement errors, it is still valid. This repulsion significantly decreases, however, for the Co^+ and $CoCl^+$ affinities. Only a much weaker repulsion is observed for t-$C_4H_9NH_2$–Co^+ and t-$C_4H_9NH_2$–$CoCl^+$ compared with s-$C_4H_9NH_2$–Co^+ and s-$C_4H_9NH_2$–$CoCl^+$, respectively, and for c-$C_6H_{11}NH_2$–Co^+ compared with n-$C_6H_{13}NH_2$–Co^+. The decreasing repulsion from Ni^+–amine to Co^+–amine is probably due to the longer distance between the methyl groups and Co^+ than that between the methyl groups and Ni^+. Although the reasons for the lesser repulsion and the stronger bonding between amine and $CoCl^+$ are not clear at this time, it is likely due to the ligand effects from Cl. The ligand effects are usually complicated and have not been fully understood [23]. The ligand may affect the electronic structure of the metal ion and make the bonding different from naked metal ion toward molecules. $CrCl^+$ has been found to be different in electronic structure from naked Cr^+ as well as from $MnCl^+$ and $FeCl^+$ [24].

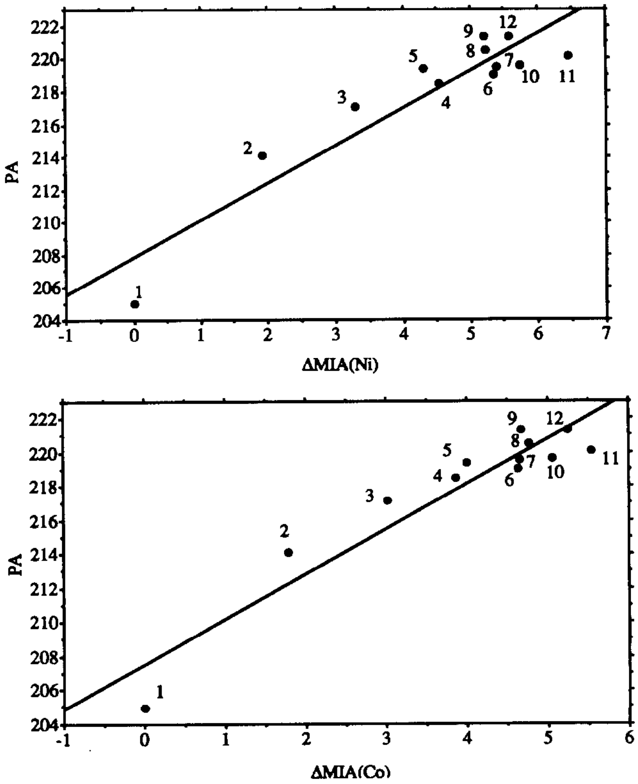

Fig. 6. Comparison of ΔMIA(Ni^+) and ΔMIA(Co^+) with PA. Least-squares fit for the upper line: PA = 2.289ΔMIA(Ni^+)+207.847 kcal/mol (r^2 = 0.865); and for the bottom line: PA = 2.648ΔMIA(Co^+)+207.521 kcal/mol (r^2 = 0.896). PA are taken from ref. 25.

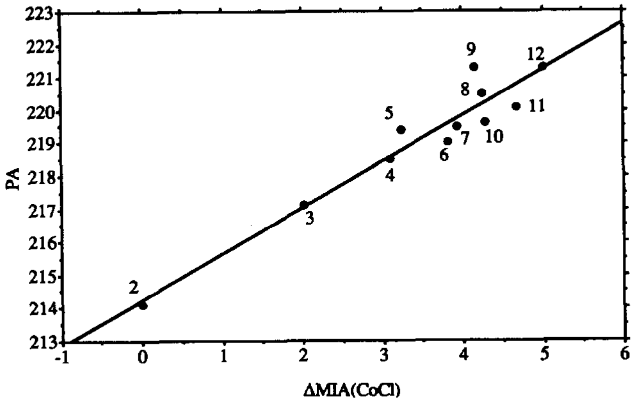

Fig. 7. Comparison of ΔMIA($CoCl^+$) with PA. A least-squares fit for the line: PA = 1.391ΔMIA($CoCl^+$)+214.263 kcal/mol (r^2 = 0.92). PA are taken from ref. 25.

Comparisons of the relative metal ion affinities with corresponding proton affinities [25] are shown in Figs. 6 and 7. Least-squares fits to these data give PA = 2.289ΔMIA(Ni^+) + 207.847 kcal/mol ($r^2 = 0.865$), PA = 2.648ΔMIA(Co^+) + 207.521 kcal/mol ($r^2 = 0.896$), and PA = 1.391ΔMIA($CoCl^+$) + 214.263 kcal/mol ($r^2 = 0.92$). Complications introduced into such comparisons have been discussed for neutral donor–acceptor adducts [26] and for gas-phase ion–molecule complexes [27]. The absolute metal ion affinities for organic molecules are, in general, much smaller than the corresponding proton affinities [28], due to a much smaller degree of covalency in the metal ion–ligand bond. Because H^+ does not have any core electrons, the larger repulsions associated with metal ions are not present in the protonated complexes. Therefore, the relative PA increase as the α-position of the amines becomes more branched.

4. Conclusion

Although Cooks' kinetic method involves assumptions and simplification, it can semi-quantitatively or at least qualitatively give relative metal ion affinities of amines. Comparison of these data with corresponding two-ligand dissociation enthalpies indicates that the metal-bound dimer ions undergoing metastable dissociations in the first field-free region probably contain slightly higher energies with an effective temperature of 298–400 K. The temperature range is the same as that of metal–nitrile systems. Further comparisons of the metal ion affinities with each other and with proton affinities may suggest a bond strength order, RNH_2–H^+> RNH_2–$CoCl^+$> RNH_2–Ni^+> RNH_2–Co^+. Our results also suggest that there is a significant repulsion between Ni^+ and the α-substituent of the amines, which decreases the bonding energies of RNH_2–Ni^+.

Although the measurements reported in this paper are approximate, they provide valuable insights into the relative metal ion affinities. This is particularly useful in the cases where no other data are available or other measurement techniques such as equilibrium measurements are not applicable. We have also shown that an "analytical" mass spectrometer is capable of producing some semi-quantitative or at least qualitative gas-phase metal-ion affinities, provided the effective temperature is known.

Acknowledgements

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