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An Unusual Elimination of NH_3 from Cobalt-Bound Alkylamine Dimer Ions

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Reactions of naked or ligated transition-metal ions with ammonia and organic amines have been investigated for several years.[1] Earlier studies of the metal ions with primary amines, in particular $CH_3CH_2NH_2$,[2] demonstrated some reactions such as dehydrogenation, demethanation, hydride abstraction, and loss of other hydrocarbon neutrals.[3] The relative extent of these reactions depends on both the metal ions and the amines. Moreover, Fe^+ was found to be the only first-row transition-metal ion that inserted into the C–N bond of *n*-$C_3H_7NH_2$.[3c] The observed reactivity was described in terms of promotion energies required to achieve a configuration conducive to the formation of two σ-bonds. Recent studies employing ^2H-labeled propylamines suggested that a remote functionalization was involved in the elimination of H_2 for Fe^+ and Co^+ and of C_2H_4 for Ni^+ and Co^+.[4] In contrast, for Fe^+, the α- and β-methylene groups are completely equilibrated via an ethylene complex before C_2H_4 and probably C_3H_6 as well as NH_3 are formed. Parallel results were observed for some other alkylamines.

In our recent study of relative metal cation–nitrile[5] and metal cation–alkylamine[6] bond energies using Cooks' kinetic method,[7] we found an intense loss of NH_3 from the cobalt-bound alkylamine dimer ions. This is surprising because the corresponding alkylamine–Co^+ complexes and nickel-bound alkylamine dimer ions do not yield NH_3.[2–4] We report the following results from our preliminary studies.

Experiments were done with a Kratos Concept IS double-focusing mass spectrometer of E/B configuration. The instrument was controlled by a Kratos DS 90 Data General Eclipse based computer system. A Kratos Mach3 data system running on a SUN SPARCstation was used for further data workup. The original FAB source was modified with a small hole to accept the ligand vapor from a heated reservoir probe inserted via the EI/CI probe lock.[8] The instrument was fitted with an Ion Tech saddle field atom gun, and 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, and an accelerating voltage of 6 kV. A resolving power of 1000 was used for recording normal mass spectra. Naked metal ions were generated by sputtering from the solid salts $FeSO_4{\cdot}7H_2O$, $CoCl_2{\cdot}6H_2O$, and $NiCl_2{\cdot}6H_2O$, which had been deposited by evaporation onto the FAB probe tip. A 3-μL sample of the liquid reagent was typically injected into the reservoir probe. Complexation of naked metal ions and Co^+Cl with the amines yielded monoadducts, RNH_2–M^+ (R = alkyl; M = Ni, Co) and RNH_2–Co^+Cl, metal-bound dimer ions, $(RNH_2)_2M^+$, and three-ligand complexes, $(RNH_2)_2Co^+Cl$. Unsymmetrical metal-bound dimer ions, RNH_2–M^+–$R'NH_2$ and RNH_2–M^+–NCR', were formed by simultaneously introducing the two different amines RNH_2 and $R'NH_2$ or $R'CN$. Metastable ion (MI) fragmentations in the first field-free region behind the source slit were monitored by B/E-linked scans.

For the sake of simplicity and clarity, we will first consider a less complicated $(C_2H_5NH_2)_2Co^+$ complex and the corresponding monoadduct, $C_2H_5NH_2$–Co^+. Metastable dissociation of $C_2H_5NH_2$–Co^+ (*m/z* 104) produces the neutrals H_2 (corresponding ionic fragment at *m/z* 102), C_2H_4 (ion at *m/z* 76), and CoH (ion at *m/z* 44) (Figure 1a). The results are somewhat different from those of an ICR study where Radecki and Allison observed the loss of CH_4 instead of C_2H_4 using EI at 70 eV.[2] Both the CH_4 and the C_2H_4 losses are estimated to be exothermic.[2] The absence of the C_2H_4 loss led Radecki and Allison to suggest that the Co^+–NH_2 bond energy of the C_2H_5–Co^+–NH_2 intermediate was less than 18.7 kcal/mol.[2] However, it was recently reported that the Co^+–NH_2 bond energy is as high as about 62 kcal/mol,[9] indicating the formation of the intermediate for the C_2H_4 loss is also exothermic. We are thus not surprised to observe the C_2H_4 loss. Similarly, Schwarz and co-workers[4] could not observe the CH_4 loss from *n*-$C_3H_7NH_2$–Fe^+, using a sector spectrometer, while Fe^+ reacting with *n*-$C_3H_7NH_2$ in ICR instruments generated CH_4.[3] The reason for the difference between the results from this work and those of Radecki and Allison is not clear at this time. One can suggest that different methods used in the studies account for the differences in reactions. Despite the differences, however, the loss of NH_3 has not been observed, in either case, from $C_2H_5NH_2$–Co^+. We also synthesized other alkylamine–Co^+ complexes (see below) and could not observe the NH_3 loss. In fact, previous studies show that only *n*-$C_3H_7NH_2$–Fe^+ affords NH_3 but it is not found for any other alkylamine–M^+ complexes.[2–4] In sharp contrast to that of $C_2H_5NH_2$–Co^+, the MI spectrum of $(C_2H_5NH_2)_2Co^+$ (*m/z* 149) demonstrates two reactions, elimination of 17 amu, yielding an ion at *m/z* 132, and $C_2H_5NH_2$ (ion at *m/z* 104) (Figure 1b). Due to the weak bonding of $C_2H_5NH_2$ to Co^+, $(C_2H_5NH_2)_2Co^+$ prefers to lose one $C_2H_5NH_2$ ligand. Most interesting is the unusual loss of 17 amu that corresponds to an intensity of 33% relative to the sum of all fragmentations.

In order to identify this neutral species of 17 amu, D-labeled *i*-$C_3H_7ND_2$ and *i*-$C_3D_7NH_2$ were employed as ligands. Under the MI conditions, shifts of 17 amu to 19 amu and to 18 amu are observed for $(i\text{-}C_3H_7ND_2)_2Co^+$ and $(i\text{-}C_3D_7NH_2)_2Co^+$, respectively. We thus conclude that 17 amu corresponds to NH_3, which is formed by addition to the NH_2 group of a hydrogen from either of the two ligand molecules.

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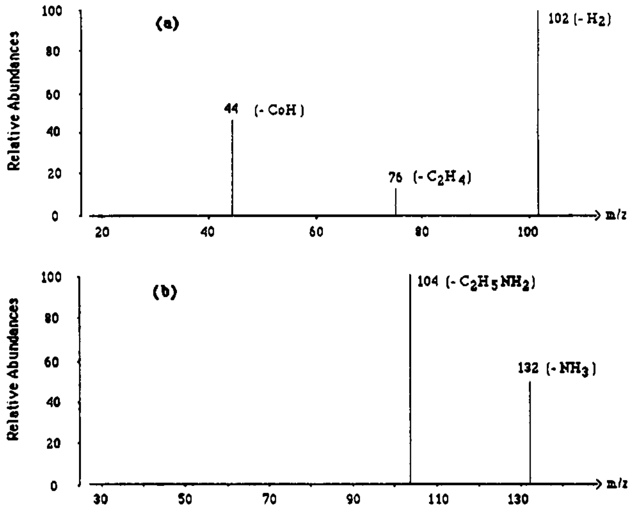


Figure 1. MI spectra of $C_2H_5NH_2$–Co^+ at m/z 104 (a) and $(C_2H_5NH_2)_2Co^+$ at m/z 149 (b).

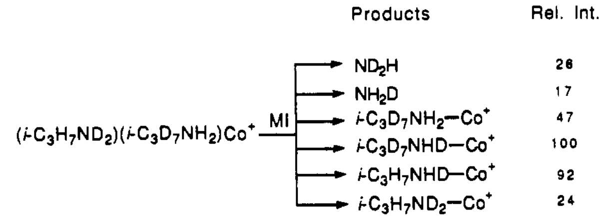
Table I. Loss of NH_3 from Metastable Two- and Three-Ligand Complexes of Co^+

R	R′	loss of NH_3[a]	R	R′	loss of NH_3[a]
		$(RNH_2)(R'NH_2)Co^+$			
H	H	b	n-C_3H_7	s-C_4H_9	20
H	CH_3	b	n-C_3H_7	n-C_5H_{11}	16[c,d]
CH_3	CH_3	e	i-C_3H_7	i-C_4H_9	33[c]
CH_3	C_2H_5	18	i-C_3H_7	s-C_4H_9	29[c]
CH_3	n-C_3H_7	20	i-C_3H_7	n-C_5H_{11}	18[c,d]
C_2H_5	C_2H_5	33	n-C_4H_9	n-C_4H_9	29[c]
C_2H_5	n-C_3H_7	17	n-C_4H_9	n-C_5H_{11}	19[c,d]
C_2H_5	i-C_3H_7	27	i-C_4H_9	n-C_5H_{11}	16[c,d]
n-C_3H_7	n-C_3H_7	27	i-C_4H_9	n-C_6H_{13}	6[c,d]
n-C_3H_7	n-C_4H_9	34	c-C_6H_{11}	n-C_6H_{13}	10[c,d]
n-C_3H_7	i-C_4H_9	30			
		$(RNH_2)(R'CN)Co^+$			
C_2H_5	C_2H_5	40	i-C_3H_7	n-C_3H_7	25
C_2H_5	n-C_3H_7	29	i-C_3H_7	i-C_3H_7	28

[a] Data given as the intensities of NH_3 in percent of the sum of ligand molecules and NH_3. [b] NH_3 loss is observed, but it is due to a direct ligand detachment. [c] The complexes also afford H_2 loss. [d] The complexes also afford minor alkene loss. [e] No NH_3 is observed.

For the purpose of comparison, analogous $(C_2H_5NH_2)_2Ni^+$ and $(C_2H_5NH_2)_2Fe^+$ ions were investigated. Although low intensities of $(C_2H_5NH_2)_2Fe^+$ precluded further studies, the MI spectrum of $(C_2H_5NH_2)_2Ni^+$ was readily recorded. Surprisingly, the reactions of $(C_2H_5NH_2)_2Ni^+$ are exclusively due to detachment of one $C_2H_5NH_2$. This implies that NH_3 loss is the specific reaction for $(C_2H_5NH_2)_2Co^+$. To extend this specificity, other two- and three-ligand complexes of Co^+ and Ni^+ have also been studied. These complexes consist of four systems, $(RNH_2)(R'NH_2)M^+$, $(RNH_2)(R'CN)M^+$, $(RNH_2)(R'NH_2)Co^+Cl$, and $(RCN)(R'CN)M^+$ (Table I). The experiments provide the following results. (i) For all the systems containing Ni^+ ($R \neq H$), no NH_3 loss is observed. These complexes exclusively undergo detachment of one ligand, except for some $(RNH_2)(R'NH_2)Ni^+$ ions consisting of longer-chain amines, such as n-$C_6H_{13}NH_2$, which also eliminate H_2. This "unreactivity" permits the application of Cooks' kinetic method for measuring the relative ligand–Ni^+ bond dissociation energies. (ii) Except for $(CH_3NH_2)_2Co^+$, where only the detachment of CH_3NH_2 occurs, all of the other $(RNH_2)(R'NH_2)Co^+$ dimer ions undergo NH_3 loss. Intensities of about 30% for the NH_3 loss relative to the sum of NH_3 and ligand loss are found for the symmetrical $(RNH_2)_2Co^+$ systems and of 15–30% for most of the unsymmetrical $(RNH_2)(R'NH_2)Co^+$ ions. In addition, some less important fragmentations such as H_2 loss are also observed for larger alkylamines. Note that the NH_3 loss from $(NH_3)_2M^+$ as well as $(NH_3)(CH_3NH_2)M^+$ ($M = Ni^+, Co^+$) seems to be a direct ligand detachment and does not involve hydrogen migration. (iii) Similar to $(RCN)(R'CN)Ni^+$,[10] $(RCN)(R'CN)Co^+$ ions solely lose either of the ligands.[5] However, the mixed $(RNH_2)(R'CN)Co^+$ complexes produce NH_3. Thus, not only the alkylamines but also the alkylnitriles as the second ligand introduced into RNH_2–Co^+ lead to the formation of NH_3. (iv) Introduction of a third ligand, Cl, into $(RNH_2)(R'NH_2)Co^+$ completely prevents the elimination of NH_3. Instead, the main reactions are detachment of one RNH_2 ligand and, in some cases, the loss of H_2. However, these reactions are explicable. Since the Co^+–Cl bond (70 ± 3 kcal/mol[11]) has more covalent properties than the approximately electrostatic Co^+–NH_2R bond ($D(Co^+–NH_3)$ = 58.8 kcal/mol[12]), elimination of RNH_2 occurs most easily than that of Cl.

Scheme I. MI Dissociations of the $(i\text{-}C_3D_7NH_2)(i\text{-}C_3H_7ND_2)Co^+$ Complex Ion[a]



[a] The intensities of the products are given relative to that of i-C_3D_7NHD–Co^+.

There are two possibilities that NH_3 is formed by the NH_2 group of one ligand incorporating a hydrogen from either the same or the other ligand. The latter involves a ligand–ligand coupling process.[13] In attempt to distinguish between these possibilities, we have investigated the metastable dissociations of a D-labeled $(i\text{-}C_3D_7NH_2)(i\text{-}C_3H_7ND_2)Co^+$ complex ion. If NH_3 originates from the same ligand, only NH_2D and ND_2H will be observed; otherwise, only NH_3 and ND_3 will be observed if NH_3 originates by NH_2 incorporating a hydrogen from a different ligand. Unfortunately, a fast H/D exchange between the two $NH(D)_2$ entities occurs, as indicated by the formation of i-C_3D_7NHD–Co^+ and i-C_3H_7NHD–Co^+ ions (Scheme I). Despite this, NH_2D and ND_2H but not NH_3 and ND_3 are produced. The results imply that the amino group and the hydrogen forming ammonia originate from the same ligand. This is further supported by the MI dissociations of D-labeled $(i\text{-}C_3D_7NH_2)(i\text{-}C_3H_7CN)Co^+$ and $(i\text{-}C_3H_7ND_2)(i\text{-}C_3H_7CN)Co^+$ ions. The two ions produce NH_2D and ND_2H, respectively, revealing that the ammonia originates from the amine ligand only and does not involve any elements from the RCN ligand. The mechanism for the NH_3 loss is suggested in Scheme II.

This is a general mechanism established for the reactions of transition-metal ions with polar organic compounds.[14] The complexed Co^+ initially inserts into a C–N bond, forming the intermediate **2**, followed by a β-H transfer and eventual elimination of NH_3. An isotopic effect of $k_H/k_D = 1.91$ is observed for the ammonia loss from the $(i\text{-}C_3D_7NH_2)(i\text{-}C_3H_7NH_2)Co^+$ ion. This mechanism is supported by the fact that the metastable ion **4** formed after the NH_3 loss exclusively generates $C_3H_7NH_2$–Co^+ via C_3H_6 loss (step V). Similarly, for the labeled (i-

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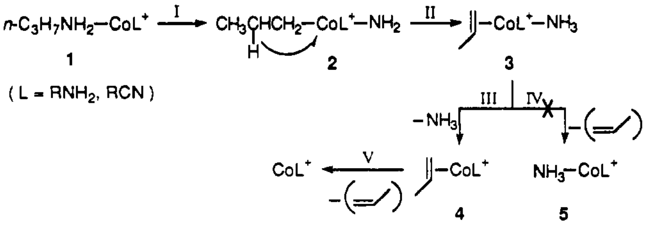
Scheme II. Proposed Mechanism for the NH_3 Loss from *n*-$C_3H_7NH_2$–CoL^+ Ions



$C_3D_7NH_2$)(*i*-$C_3H_7NH_2$)Co^+ ion, the analogous ionic product accompanied by NH_2D loss exclusively produces *i*-$C_3H_7NH_2$–Co^+ via the loss of C_3D_6, and the ion product of NH_3 loss gives *i*-$C_3D_7NH_2$–Co^+ via C_3H_6 loss. Because there is no β-H available for the $(CH_3NH_2)_2Co^+$ complex ion, NH_3 loss is not observed.

Since Co^+–NH_2R bonds are stronger than Co^+–alkene bonds,[15] complexed ions such as **3** should prefer to lose alkene rather than NH_3. This is opposite to the experimental results, which show that alkene loss is completely absent. However, this unusual case may not be sufficient to negate the proposed mechanism in Scheme II, since a number of examples have been reported illustrating that the more strongly bound ligand might be preferably eliminated.[1] For instance, when Co^+ reacts with ethanol, the products are C_2H_4–Co^+ ($D(C_2H_4$–$Co^+)$ = 37 kcal/mol[15]) and H_2O–Co^+ ($D(H_2O$–$Co^+)$ = 37–40 kcal/mol[16]), with the former preferred, while only H_2O–$CoNO^+$ is observed with $CoNO^+$ instead of Co^+.[17] It has been found that NO is more strongly bound than H_2O to Co^+ but is more weakly bound than H_2O to $CoCO^+$.[18] This is interpreted in terms of antisymbioses.[19] In light of these previous works, our results indicate that alkenes are more weakly bound than NH_3 or RNH_2 to Co^+ (in ion **4**) but are more strongly bound than NH_3 to RNH_2Co^+ (in ion **3**), probably due to ligand–ligand repulsion between ammonia and RNH_2 and increased π-bonding between the alkenes and the metal ions in **3**.[18]

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(15) Although the RNH_2–Co^+ bond energies are not available, it is found, in general, that $D(RNH_2$–$M^+) > D($alkene–$M^+)$. For example, NH_3–Co^+ (58.8 kcal/mol) > C_2H_4–Co^+ (37 kcal/mol): Armount, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6628.

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