Novel coordination chemistry of monopositive metal ions in the gas phase as studied by the laser ablation-molecular beam (LAMB) method. Reactions with ammonia–acetone binary clusters

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Abstract

Reactions of monopositive metal ions (Al^+, Co^+ and Mn^+) with ammonia–acetone binary clusters in the gas phase have been studied with the laser ablation-molecular beam (LAMB) method. Relative abundance of the resulting metal complex ions $M^+(NH_3)_m(CH_3COCH_3)_n$ ($M^+ = Al^+$, Co^+, Mn^+) has been probed for several stagnation ratios of $NH_3/CH_3COCH_3/Ar$. The relative abundance for the same stagnation ratio was highly metal-specific, indicating occurrence of complete reorganization during the reactions. Structures of the metal complex ions are discussed based on the metal-specific pattern of the relative abundance. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Laser ablation; Metal complex ions

1. Introduction

Reactions of metal ions with neutral molecules or clusters produce a variety of metal complex ions. Although multivalent metal complex ions in aqueous solutions have been investigated throughout the long history of chemistry, it is only in recent years that non-alkali monopositive metal complex ions in the gas phase have received much attention. Metal complex ions ($M^+(L)_n$, L=H_2O, NH_3, CH_3OH, etc.) have been studied both experimentally [1–5] and theoretically [5–12]. For example, non-alkali metals [3,4] show quite a contrasting behavior to that of alkali metals [1,2]. However, mixed-ligand metal complex ions, such as $M^+(L_1)_m(L_2)_n$, are scarcely studied so far. They are particularly interesting in that we can tell by properly designed experiments which and/or how many ligands occupy the first coordination sphere.

We have developed a very simple and versatile experimental technique named laser ablation-molecular beam (LAMB) method [13] to study reactions of monopositive metal ions with molecules or clusters in the gas phase. In this method pulsed laser light is focused on a metal substrate in vacuum. Monopositive metal ions are prepared by laser ablation and they react with molecules or clusters in the molecular beam injected near by. Product ions are probed by a quadrupole mass spectrometer.

Many types of novel product ions were observed by this method in the reactions of amines [14], benzene [15], benzene clusters [16], $Cr(CO)_6$ [17], $Mn_2(CO)_{10}$ [18], ammonia clusters [19], and methanol clusters [20]. In the last two cases relative abundance of complex ions showed a discontinuous decrease at a certain cluster ion size, which is called the "intensity gap", the positions of which give information on the number of ligands in the first coordination sphere. The pattern of relative abundance was found to be specific to each metal ion. Use of binary clusters, ammonia–methanol [21] and ammonia–water [22], in the molecular beam gave additional important information as to which ligand is preferred in the coordination, i.e., which ligand occupies the first coordination sphere. A simple kinetic simulation procedure based on Klots' evaporative ensemble model [23] reproduced some of the essential features in the ammonia–water case [24].

Competitive coordination involving ketones like acetone is an interesting topic. Selegue et al. [25] studied $Cs^+(CH_3COCH_3)_n(CH_3OH)_m$ system by vibrational spectroscopy. They used a CO_2 laser and only probed C–O stretch in methanol. They attributed the change in band position between $n=3$, $m=1$ and $n=4$, $m=1$ to hydrogen bond formation among the ligands in the first coordination sphere.

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In the present paper, the LAMB technique was used to prepare mixed-ligand metal complex ions $M^+(NH_3)_m$-$(CH_3COCH_3)_n$ by the reactions of monopositive metal ions with ammonia–acetone binary clusters $(NH_3)_p(CH_3COCH_3)_q$, and relative abundances of the mixed-ligand metal complex ions were studied. Three mononuclide metals, Al, Mn and Co, were chosen.

2. Experimental

The experimental setup is essentially the same as reported previously [19,20]. In short, a metal substrate (0.3 cm×1 cm) was located near the entrance region (in front of ion extraction optics) of a quadrupole mass spectrometer (Extrel, 4-162-8, inner diameter 9.5 mm) set in a vacuum chamber evacuated to a base pressure of 2×10^{-6} Torr by a turbomolecular pump. Metal samples were purchased from Wako (Al) and NILACO (Co, Mn). The second harmonic (532 nm) of a Nd:YAG laser (Quanta-Ray, DCR-2(10)) was focused on the surface of the metal substrate using a quartz lens (f=60 cm). However, the metal substrate was placed slightly off-focus, because too intense laser irradiation gave rise to much noise in the mass spectra. Laser power was 1.5 mJ/pulse. Prepared monopositive metal ions (M^+) entered into the entrance region perpendicularly to the axis of the quadrupole. Neither multivalent metal ion (M^{n+}, $n \geq 2$), nor metal cluster ion (M_n^+, $n \geq 2$) were observed in the experimental conditions. Mixed sample gas consisting of ammonia, acetone and argon stored in a reservoir tank was led into a pulsed nozzle through a stainless steel pipe. Three stagnation conditions NH_3/CH_3COCH_3/Ar(in Torr)=300/10/450 (a), 500/10/250 (b), and 700/10/50 (c) were used. A pulsed beam of ammonia–acetone binary clusters was injected through a pulsed nozzle. The cluster beam was skimmed by a skimmer (1 mm in diameter) and then introduced into the entrance region perpendicularly to both of the quadrupole mass spectrometer axis and the flow of M^+. Mixed-ligand metal complex ions $M^+(NH_3)_m(CH_3COCH_3)_n$ were produced by reactions of metal ions with binary clusters in the reaction region. Product ions were mass-selected by the quadrupole and were detected by a channeltron (Galileo 4816). Signals were integrated by a Boxcar integrator (NF BX-530a), digitized and fed to a personal computer (NEC PC-9801VX). Correction for the mass-dependent sensitivity of the quadrupole mass spectrometer was made as reported in [21].

3. Results and discussion

3.1. Distribution of binary clusters $(NH_3)_m(CH_3COCH_3)_n$ in the molecular beam probed by electron impact ionization

In order to monitor the distribution of binary clusters in the molecular beam, mass spectra of the beam for three

stagnation ratios used were obtained by electron impact ionization in the absence of laser ablation. The relative abundance of protonated binary clusters $H^+(NH_3)_m(CH_3COCH_3)_n$ observed for stagnation ratio (b) (Fig. 2) and those for (a) and (c) (not shown) were featured with a prominent decrease at n=3, $m \geq 0$. This indicates that the protonated acetone trimer may correspond to some stable structure. (However, Castleman et al. [26] reported rather a smooth decrease of the ion intensity with the increasing cluster size.) Although these mass spectra suffer from fragmentation on electron impact, we can safely say that the distribution of neutral binary clusters in the molecular beam was increasingly biased to acetone side with increasing acetone/ammonia mixing ratio.

3.2. Mixed-ligand metal complex ions produced by reactions of several metal ions with binary clusters

Mixed-ligand metal complex ions are formed by the reaction of metal ions with binary clusters:

$$(NH_3)_p(CH_3COCH_3)_q + M^+ \rightarrow M^+(NH_3)_m(CH_3COCH_3)_n$$
$$+ (p-m)NH_3 + (q-n)CH_3COCH_3$$
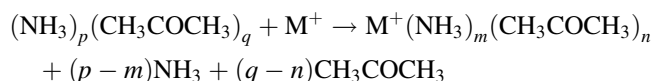
As an example of observed mass spectra, that of $Co^+(NH_3)_m(CH_3COCH_3)_n$ is shown in Fig. 1. Peaks can be assigned to (m, n), except for a small one at m/z=87 ascribable to Co^+CO given by elimination of C_2H_6.

Distributions of mixed-ligand metal complex ions obtained for one and the same beam condition (b) (NH_3/CH_3COCH_3/Ar=500 Torr/10 Torr/250 Torr) were highly metal-specific, as shown for Al^+, Co^+, and Mn^+ in Fig. 2. Some of these distributions are featured with intensity gaps, where relative abundance of mixed-ligand complex ions falls discontinuously.[1] The intensity gap appears at
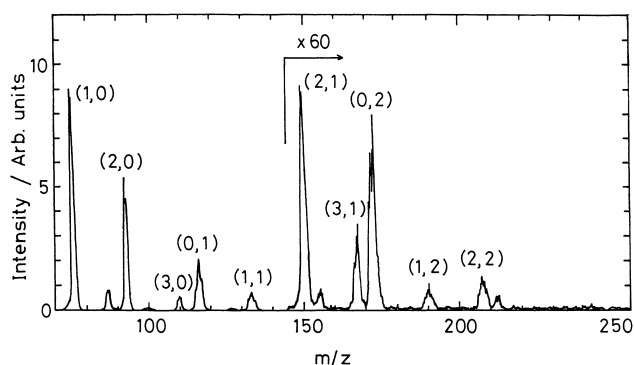

Fig. 1. Mass spectrum for $Co^+(NH_3)_m(CH_3COCH_3)_n$, for stagnation ratios of NH_3/CH_3COCH_3/Ar=500 Torr/10 Torr/250 Torr.

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[1]No definite numerical criteria for an intensity gap seems to be present. In the present paper, for convenience we define an intensity gap when intensities of any three successive cluster size I_{m-1}, I_m, I_{m+1} fulfill the relation $R_m=(I_{m+1}/I_m)/(I_m/I_{m-1}) \leq 0.20$, in more than one of the three directions (m, n)→(m+1, n), (m+1, n+1) and (m, n+1).
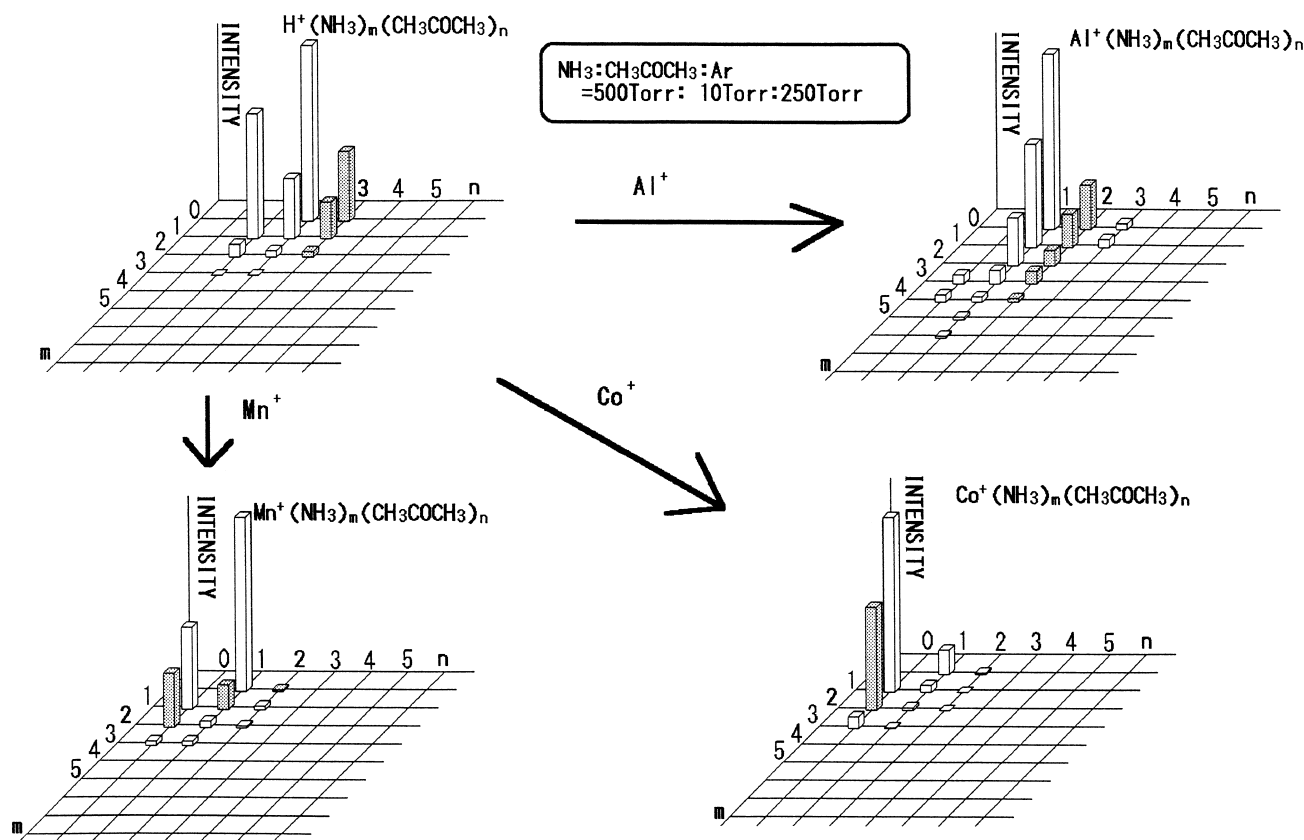
Fig. 2. Relative abundance of metal complex ions obtained for the same beam condition ($NH_3/CH_3COCH_3/Ar=500$ Torr/10 Torr/250 Torr) in comparison with that of protonated binary clusters: (a) $H^+(NH_3)_m(CH_3COCH_3)_n$, (b) $Al^+(NH_3)_m(CH_3COCH_3)_n$, (c) $Co^+(NH_3)_m(CH_3COCH_3)_n$, (d) $Mn^+(NH_3)_m(CH_3COCH_3)_n$.

$m=2$, $n=0$ for Mn^+ and Co^+. For Al^+, a prominent decrease in intensity is observed at $n=2$, $m\geq0$.

Such a finding clearly indicates that a complete reorganization of clusters occurs during the formation of these metal complex ions. In the process of such a reorganization, the metal ion breaks into the binary clusters and occupies the center of the product metal complex ion, and component ligands of binary clusters are coordinated around the central metal ion. When we assume that a metal ion with little kinetic energy ($KE\approx0$) reacts with a binary cluster, the energy corresponding to the metal-ligand bond formation is released, to heat the cluster. During this process, evaporation of some component ligands and/or collisions with another species such as M^+, binary clusters, Ar, or complex ions must occur. During these reorganization processes, ligands with the higher coordination ability are bound directly to the central metal ion, forming the first coordination sphere. After the completion of the first coordination sphere, other ligands are coordinated outside the first coordination sphere, forming the second coordination sphere, and so on. The positions of intensity gaps correspond to discontinuous decrease in binding energy and hence tell which and how many ligands can occupy the first coordination sphere. (We have shown for $M^+(NH_3)_n$ case [19] that observed intensity gaps correspond, without fail, to discon-

tinuous decrease of reported binding energy values.) Fig. 2 tells another thing. Distribution of ammonia ligands extends out of the intensity gap. In other words, the number of the hydrogen-bond forming ligand (ammonia) in the complex is larger than the number of ligands in the first coordination sphere, suggesting that some of these are in the second coordination sphere and so on, forming hydrogen bonds to the ligands in the first coordination sphere. Although reactions of Fe^+, Co^+ and Ni^+ with acetone to eliminate C_2H_6 or CO have been reported [27,28], indication of such an elimination reaction was absent or only of minor importance in our case.

3.3. Variation in the distributions of product metal complex ions with the stagnation ratio of the component gases

$Al^+(NH_3)_m(CH_3COCH_3)_n$. Fig. 3 shows distributions of mixed-ligand metal complex ions obtained by reaction of aluminum ion (Al^+) with ammonia–acetone binary clusters prepared at three stagnation ratios (a), (b), and (c). In cases (a) and (b), a prominent decrease in intensity is observed at the series of $n=2$, $m\geq0$, while intensities at $n=2$, $m\geq1$ decrease and the prominent decrease is observed at $m+n=2$ in the case of (c). This indicates that Al^+ combines selectively with two acetone molecules and these constitute the
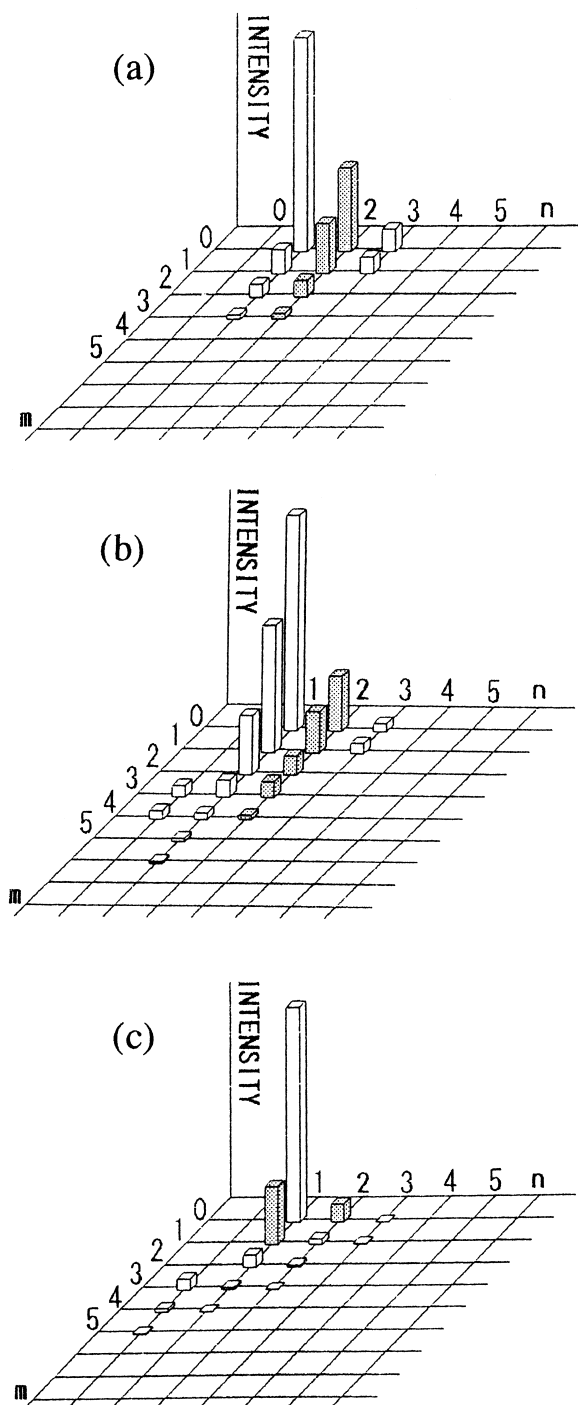
Fig. 3. Relative abundance of $Al^+(NH_3)_m(CH_3COCH_3)_n$ observed on stagnation ratios of (a) $NH_3/CH_3COCH_3/Ar$=300 Torr/10 Torr/450 Torr, (b) 500 Torr/10 Torr/250 Torr, and (c) 700 Torr/10 Torr/50 Torr.

first coordination sphere, when ammonia/acetone stagnation ratio is not too large. Such a selectivity for the species in the first coordination sphere can be reasonably explained by the difference of binding energy of acetone to Al^+ (48.3 kcal/mol [5]) and that of ammonia to Al^+ (33.9 kcal/mol [8]). After the completion of the first coordination sphere, ammonia molecules rather than acetone molecules occupy the

second coordination sphere owing to their stronger hydrogen-bonding ability with acetone molecules in the first coordination sphere. This is evident because the prominent decrease in intensity appears not only at n=2, m=0 but extends out to the series of n=2, m>0. According to SCF MO calculations of Bauschlicher et al. [5] on $Al(CH_3COCH_3)_2^+$, two acetone molecules in the first coordination sphere bind to Al^+ on the same side, spanning a degree of 86.3°.

However, upon further increase of the ammonia/acetone stagnation ratio to the case (c), Al^+ ion accepts two molecules (either acetone or ammonia) in rather a non-selective manner. This is due to the increase of ammonia-rich clusters in the molecular beam. It is to be noted that the number of ligands forming the first coordination sphere remains unchanged.

$Co^+(NH_3)_m(CH_3COCH_3)_n$. In Fig. 4 are shown the distributions of mixed-ligand metal complex ions obtained by the reaction of cobalt ion (Co^+) with ammonia–acetone binary clusters prepared under the three stagnation conditions (a), (b) and (c) of mixed sample gas. In (b) and (c), an intensity gap is observed at m=2, n=0, while intensities of m=1, n=1 and m=0, n=2 increase and a prominent decrease in intensity at $m+n$=2 is observed for the stagnation ratio (a). The former finding indicates that two ammonia molecules are selectively coordinated to Co^+ directly, forming the first coordination sphere. The third ligand such as ammonia molecule with higher hydrogen-bonding ability binds to these ammonia molecules. Although similar values are reported as calculated binding energy for Co^+–ammonia (53.2 kcal/mol [7]) and Co^+–acetone (52±3 kcal/mol [11]), ammonia seems to have much precedence in conditions (b) and (c). According to ab initio MO calculations of Bauschlicher and Rosi [12] on $Co(NH_3)_n^+$, coordination of NH_3 mixes the 4s orbital of Co with its 3d orbital to polarize away from the NH_3, creating an area of high electron density up and down the Co atom. Therefore it is favorable that two ammonia molecules bind to Co^+ co-linearly on both sides.

However, on the increase of acetone/ammonia stagnation ratio (the case (a)), Co^+ ion accepts two molecules (either acetone or ammonia) in a non-selective manner. This is due to the increase of acetone-rich clusters in the molecular beam. Again, the number of ligands in the first coordination sphere remains unchanged.

Incidentally, in the reaction of metal ions with ammonia–water binary clusters it has been reported [22] that the first coordination sphere is occupied with ammonia molecules and water molecules are not coordinated to Co^+ directly. Acetone molecules are able to bind to Co^+ directly. This is reasonable in view of the close similarity in the Co^+–ammonia and –acetone binding energy values, in contrast to the large difference in the ammonia–water case (Co^+–water binding energy=40.1 kcal mol^{-1} [29]).

$Mn^+(NH_3)_m(CH_3COCH_3)_n$. Fig. 5 shows distributions of mixed-ligand metal complex ions obtained by the reaction of manganese ion (Mn^+) with ammonia–acetone binary clusters prepared under the three stagnation conditions of mixed
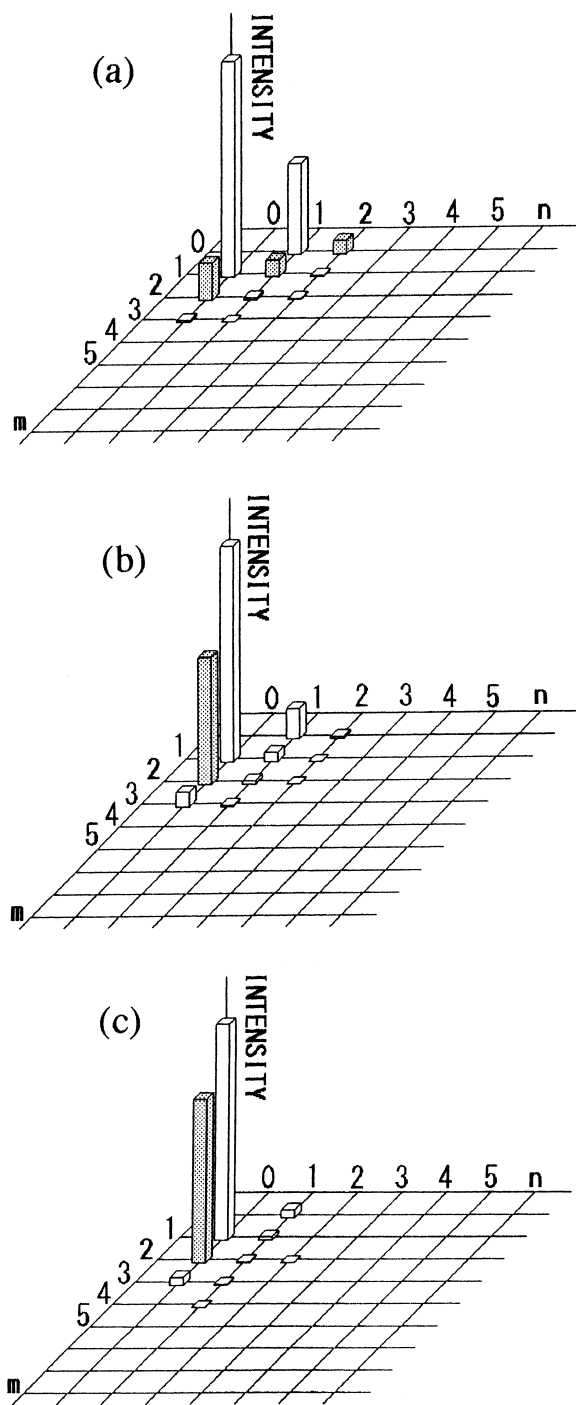
Fig. 4. Relative abundance of $Co^+(NH_3)_m(CH_3COCH_3)_n$ observed on stagnation ratios of (a) $NH_3/CH_3COCH_3/Ar$=300 Torr/10 Torr/450 Torr, (b) 500 Torr/10 Torr/250 Torr, and (c) 700 Torr/10 Torr/50 Torr.

Fig. 5. Relative abundance of $Mn^+(NH_3)_m(CH_3COCH_3)_n$ observed on stagnation ratios of (a) $NH_3/CH_3COCH_3/Ar$=300 Torr/10 Torr/450 Torr, (b) 500 Torr/10 Torr/250 Torr, and (c) 700 Torr/10 Torr/50 Torr.

sample gas. The abundance at m=0, n=1 is high in all the three conditions. The distributions for stagnation ratio (a) manifested a rather sharp decrease at $m+n$=2, $0 \leq n \leq 2$. The abundance at m=2, n=0 increases with the change (a)→(b)→(c), and it constitutes an intensity gap in favor of ammonia in the conditions (b) and (c). An intermediate feature is observed for (b); while an intensity gap in favor of
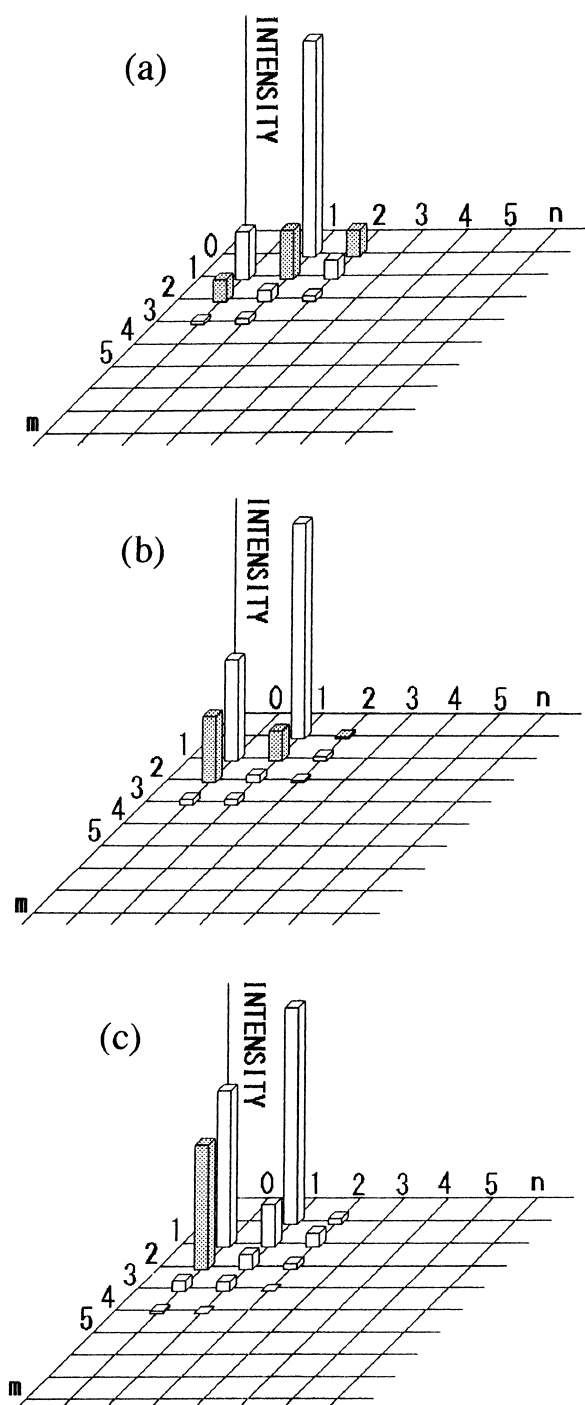
ammonia is found at m=2, n=0, the overall pattern has the non-selective appearance. In the conditions (a) and (b), both molecules are directly coordinated in the non-selective manner to Mn^+, forming the first coordination sphere. This suggests that the Mn^+–acetone and Mn^+–ammonia binding energies must be similar, though we have no such data available at present.

Table 1
Patterns of distributions of mixed-ligand complex ions $M^+(NH_3)_m(CH_3COCH_3)_n$ [a]

Beam conditions $NH_3/CH_3COCH_3/Ar$ (Torr)	Metal ion		
	Al^+	Mn^+	Co^+
300/10/450 (a)	S (n=2 in favor of acetone)	N ($m+n$=2)	N ($m+n$=2)
500/10/250 (b)	S (n=2 in favor of acetone)	N ($m+n$=2)	S (m=2 in favor of ammonia)
700/10/50 (c)	N ($m+n$=2)	S (m=2 in favor of ammonia)	S (m=2 in favor of ammonia)

[a] S: selective coordination, N: non-selective coordination.

Positions of intensity gaps or the prominent decrease in the relative abundance are shown. It is to be noted that the number indicating their positions (m, n, or $m+n$) remains unchanged for each metal ion, irrespective of beam conditions.

Observed patterns in the distributions of mixed-ligand complex ions, selective or non-selective, are summarized in Table 1.

4. Conclusions

Mixed-ligand metal complex ions $M^+(NH_3)_m$-$(CH_3COCH_3)_n$ were formed by the reactions of monopositive metal ions ($M^+=Al^+$, Co^+, Mn^+) with ammonia–acetone binary clusters using the laser ablation-molecular beam method. Produced metal complex ions were mass-selected by a quadrupole mass spectrometer. Relative abundances of mixed-ligand complex ions were obtained from observed mass spectra.

Distributions of mixed-ligand metal complex ions for the same stagnation ratio, i.e. the same distribution of binary clusters, are highly metal-specific. It clearly shows that the mixed-ligand metal complex ions are formed after a complete reconstruction.

Metal-specific intensity gaps or the prominent decrease in relative abundance at a certain cluster size give information which and how many ligand species occupy the first coordination sphere. Both of selective and non-selective cases are realized, depending on the stagnation ratio of component gases, i.e., distributions of binary clusters in the beam. However, the number of ligands forming the first coordination sphere remains the same for all stagnation ratios used.

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