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Gas-Phase Metal Trications in Protic Solvent Complexes

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Ligated multiply charged metal (M) ions in the gas phase have become topical lately. These species were not accessible until the 1990s, because, unlike M^+, metal polycations generally do not ligate when passing through the ligand (L) vapor.[1] Instead, they are normally reduced by L on contact (The second ionization potentials (IPs) of all metals except Ca, Sr, and Ba are above 12 eV, while the IPs of most solvent molecules are 8−12 eV. The third IPs of metals lie above 19 eV). However, solvated M^{2+} and M^{3+} can be generated by electrospray ionization (ESI) that transfers the solvated ions into the gas phase, inside a solvent shell.[2−10] This circumvents the small size range where the charge transfer occurs. An alternative is to ligate M or M^+ and ionize the ML_n (M^+L_n) complex, as implemented in the pick-up[11,12] and charge-stripping[13] techniques. These methods have produced clusters of M^{2+} with both protic and aprotic solvents, including water,[2−4,6−8,10−13] alcohols,[4,5,11,12] ethers,[11] ketones,[4,8,11,12] dimethyl sulfoxide,[2,4] benzene,[12] acetonitrile,[4,5,9,11,12] and pyridine.[5,12]

However, known complexes of M^{3+} had been limited to four aprotic ligands: DMF,[14] DMSO,[4,14] acetonitrile,[4,15] and acetone.[4,15] Despite sustained efforts for water and simple alcohols, no complexes of metal trications with any protic ligand (HOR) could be produced.[4,14,15] Instead, charge-reduced species such as $M^{2+}X(HOR)_n$ (X is the counterion of dissolved metal salt) or $M^{2+}OR(HOR)_n$ were typically observed in ESI. The reason for that is not obvious, considering that the third IPs of two metals (La 19.2 eV and Ce 20.2 eV) are below the second IP of Cu (20.3 eV), but Cu^{2+} readily forms gas-phase complexes with water and alcohols.[3,4,7,12,13] Here we report the observation of metal trication complexes with a protic ligand (L), diacetone alcohol (below termed DAA), $(CH_3)_2C(OH)CH_2COCH_3$. Dissociation of these species is studied to elucidate the size ranges of their existence.

This work was performed using the Finnigan TSQ 7000 MS/MS system. Ligated M^{3+} ions were generated from $M(NO_3)_3$ dissolved in aqueous DAA. The ESI needle was at 4 kV, sheath gas flow was low, and auxiliary gas was off. The heated capillary was at 110−150 °C. $M^{3+}L_n$ ions found in the Q1 scan usually had $n = 7-11$. They were fragmented in Q2 at the lab energies (E) of 0−240 eV by collisions with Ar at 0.3 mTorr (close to single-collision conditions) or 1.3 mTorr (multicollisional CID). To verify the assignments, most experiments were reproduced using d_{12}-DAA/D_2O and, where possible, different metal isotopes.

Lanthanum has the lowest third IP of all trivalent metals. The Q1 scan (Figure 1A) reveals (along with usual charge-reduced species) a substantial yield of $La^{3+}(DAA)_n$ for $n = 8-12$, with a maximum at $n = 9$. Could those features be $La^{3+}(acetone)_{2n}$ arising from an adventitious acetone impurity in DAA? (Acetone complexes of La^{3+} and Ho^{3+} were reported.[4,15]) The absence of $La^{3+}(acetone)_{2n+1}$ peaks convinces that the features observed truly are DAA complexes. This would be confirmed in the MS/MS experiments. $M^{3+}(DAA)_n$ complexes were also identified for Y and all other rare-earth elements studied: Ce, Pr, Sm, Eu, Gd, Tb, Ho, Yb, Lu (Nd, Dy, Er, and Tm were not tried). The third IPs of these metals range from 20 eV (Ce) to 25 eV (Eu and Yb). Increasing third IP values favor charge reduction, and the yields of trications go down while the distribution maxima shift to slightly higher sizes at $n = 10-11$ (Figure 1B).

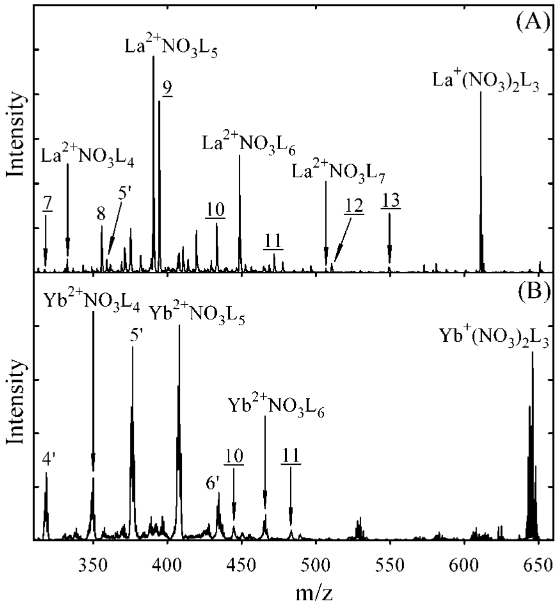

Figure 1. Q1 mass spectra of $M(NO_3)_3$ dissolved in diacetone alcohol/H_2O for M = La (A) and Yb (B). Underlined numerals n are for $M^{3+}(DAA)_n$ trications, numerals with apostrophes m' are for $M^{2+}(DAA\text{-}H)(DAA)_{m-1}$. The symbol "L" stands for DAA ligand.

The hallmark property of ligated metal polycations is the dissociative electron or proton transfer. As reviewed above, the difference in IPs makes nearly all M^{k+}−ligand heterodimers thermodynamically unstable (although metastability due to the energy barrier preventing charge transfer is common[16]). In the other extreme, metal di- and trications exist in the bulk solvents, and macroscopic droplets of such solutions evaporate by the "neutral ligand loss" only. Hence, there must be a critical size (n_{crit}) at which a shrinking droplet first charge-reduces. There also may be a minimum size ($n_{min} \leq n_{crit}$) for which the $M^{k+}L_n$ complex could still be observed. For precursors with $n_{min} < n \leq n_{crit}$, the ligand loss and dissociative charge transfer compete.

To elucidate the size range of their existence (i.e., determine n_{crit} and n_{min}), $M^{3+}(DAA)_n$ species for all metals listed above were probed using CID. Experiments at the low- and high-collision gas pressures produced essentially identical findings. Fragmentation

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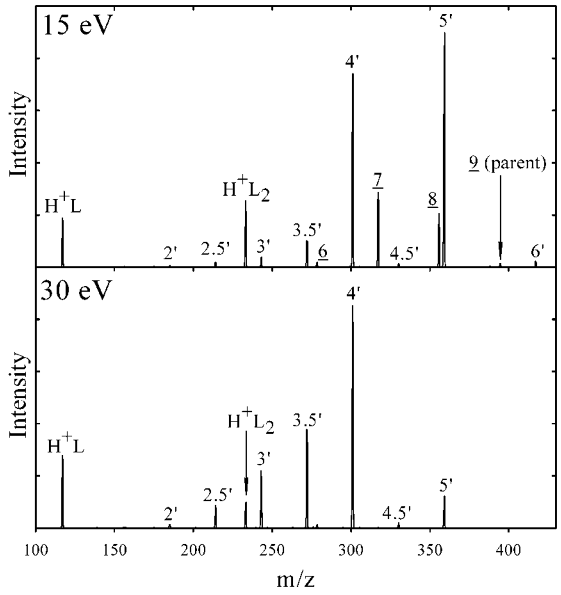

Figure 2. CID spectral windows for $^{139}La^{3+}(DAA)_9$. The collision energies (lab frame) were 15 eV (top) and 30 eV (bottom), the Ar gas pressure was 1.3 mTorr. Nomenclature follows that in Figure 1. Half-integer m' mark the features of $M^{2+}(DAA\text{-}H)(acetone)(DAA)_{m-1.5}$ stoichiometry, presumably resulting from a retro-aldol reaction accompanying reduction. There are absolutely no equivalent half-integer peaks for trications.

Table 1. Minimum Sizes Found for $M^{3+}(DAA)_n$ Complexes versus the Third Ionization Potential of M

metal	third IP, eV	n_{min}	metal	third IP, eV	n_{min}
La	19.2	5	Tb	21.9	7
Ce	20.2	6	Ho	22.8	8
Y	20.5	7	Sm	23.4	7
Gd	20.6	8	Eu	24.9	8
Lu	21.0	8	Yb	25.1	8
Pr	21.6	7			

patterns were qualitatively the same for all metals investigated; the example for La is presented in Figure 2.

Trications are evidently fragile: they essentially succumbed to charge reduction already at a modest collision energy of 30 eV. Only proton transfer, not electron transfer, took place. Mostly, protonated DAA dimers ($m/z = 233$) were ejected:

$$M^{3+}(DAA)_n = M^{2+}(DAA\text{-}H)(DAA)_{n-3} + H^{+}(DAA)_2$$

Protonated monomers at $m/z = 117$ appeared in a lower yield or at slightly higher energies, or both; however those could arise from the secondary decay of dimers. The largest charge-reduced product observed for any metal was $M^{2+}(DAA\text{-}H)(DAA)_6$. This could originate from either $M^{3+}(DAA)_8$ or $M^{3+}(DAA)_9$, depending on whether the complementary fragment was $H^{+}(DAA)$ or $H^{+}(DAA)_2$. A minute yield of both ions at the threshold needed to register the largest $M^{2+}(DAA\text{-}H)(DAA)_n$ fragment prevented the clarification; hence n_{crit} could be either 8 or 9. A constant n_{crit} despite the change of third IP from 19 to 25 eV is noteworthy. However, minimum sizes appear to increase for higher third IPs, although not smoothly (Table 1). The n_{min} value increases from 5 for La to 7 for Y, and then remains in the 7−8 range.

Discussion of the downstream dissociation of $M^{2+}(DAA\text{-}H)(DAA)_n$ species at higher CID energies is beyond the scope of this contribution. Briefly, these ions lose neutral DAA or acetone molecules or both cleaved from them and, once smaller, also fragment via other ligand cleavages and further proton transfer with the second charge reduction to monocations based on $M^{+}O$.

Similarly to $M^{3+}(DAA)_n$ here, all $M^{2+}(H_2O)_n$ charge-reduce by proton transfer only,[7] yielding H_3O^{+} and $H^{+}(H_2O)_2$. Conversely, some alcohol complexes of M^{2+} also break down by electron transfer and ligand cleavage.[5,17] These processes may be absent here because of a large precursor size compared to that in the dication case, where reduction typically proceeds for the species with one-to-four ligands only. In those complexes, all ligands are much more proximate to the metal, and this direct contact allows an electron transfer to the metal or a metal-induced cleavage. With six-to-nine large DAA molecules, some could not surround the metal immediately. Then a weaker-bound outer shell ligand could likely be charged only via a proton transfer from a metal-coordinated ligand inside.

Of course, diacetone alcohol is a peculiar protic solvent: it has a carbonyl in addition to hydroxyl. Present data do not reveal the metal attachment site(s) on DAA, or whether the binding is bidentate. From general considerations, complexation probably involves carbonyl, alone or jointly with hydroxyl. However, n_{min} is 8 for $Ho^{3+}(DAA)_n$, but only 4 for Ho^{3+} coordinated with a much smaller acetone.[15] This suggests a participation of hydroxyl destabilizing the complexes. In any event, M^{3+} can be stabilized by protic ligands including another functional group (such as carbonyl) that is compatible with (+3) charge. This is remarkable, recalling that many diketones cannot coordinate even a dication.[18] Whether trications could coexist with any regular alcohol in the gas-phase complexes remains an open question.

Summarizing, we generated triply charged metal ions solvated by diacetone alcohol, the first finding of a metal trication in gas-phase complexes with a protic ligand. These species were observed for 11 trivalent metals with the third ionization potentials of up to 25 eV. Stabilizing the triple charge takes, depending on the element, five-to-eight ligands—by far the largest minimum size reported for any metal polycation/ligand pair. For eight ligands or less, these complexes charge-reduce to dications by dissociative proton transfer ejecting the protonated ligand monomer or dimer.

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