Probing Coordination Complexes by Carbon Nanotube-Assisted Low-Voltage Paper Spray Ionization Mass Spectrometry

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Supporting Information

ABSTRACT: Fragile transition metal complex ions such as [Cr(H₂O)₄Cl₂]⁺, difficult to be observed by gas-phase spectroscopy, are detected easily with carbon nanotube (CNT)-assisted low-voltage ambient ionization mass spectrometry. Observation of various substituted ions with D₂O and ROH (R = CH₃, C₂H₅, . . .) established the versatility of the technique in detecting diverse species. Ligand substitution occurring in solution was captured by the low-voltage technique. The extreme softness of the technique coupled with nanoscale ion sources enabled the creation of such species. Analysis was extended to other halides as well. The intensity of these fragile ions gradually disappeared at voltages beyond 500 V and are completely absent in standard high-voltage ionization. Detection of inorganic complexes further enhances the scope of low-voltage ionization.

Ever since the celebrated efforts of Alfred Werner, coordination complexes of transition metal ions have been the subjects of continued interest. While many of the structural insights of these complex ions have been derived from physical property measurements, as in the case of magnetism, existence of individual ions in solution has been a question. Optical spectra of these complexes and their interpretation in terms of ligand field theory are some of the highlights of introductory coordination chemistry. Observing such complex species directly in solution has been difficult, although there have been reports of this in the recent past. Although coordination complexes have been studied in solution phase, only a few studies have been carried out in the gas phase.

Mass spectrometry (MS), being the most prominent tool to observe molecular species in isolation, is an automatic choice for such investigations, although dissociation of the fragile gas-phase ion prohibits the observation of intact complexes. Recent advances in ambient ionization, and especially low-voltage ionization, have prompted us to look again at the possibility of observing intact transition metal complexes directly from solution. Incorporation of carbon nanotubes (CNTs) on paper substrates has helped us to achieve molecular ionization at low voltage (1 V) from various substrates. Extension of this technique to other nanostructures showed anisotropy in molecular ionization when two-dimensionally aligned Te nanowires (NWs) were used for ionization. Analytical performance was shown with volatile and nonvolatile compounds and a variety of matrices. Being a soft ionization process, the low-voltage ionization technique has helped us in identifying molecular systems with minimum internal energy. In this paper, we describe a systematic investigation of transition metal complex ions and present a case study of their rapid substitution with other ligands.

Low-voltage ionization has many advantages in comparison to other ambient ionization methods. One simplification is that the ionization source can be driven by ordinary batteries, which reduces the complication of having larger power supplies. Another advantage is the ability to provide a cleaner mass spectrum with high signal-to-noise ratio (S/N). The spectrum contains only molecular ion peaks (in most cases) with very less fragmentation. These factors led us to utilize this technique for the analysis of weakly bound coordination complexes in detail.

EXPERIMENTAL SECTION

Carbon nanotube-coated paper was made by drop-casting a CNT suspension over Whatman 42 filter paper. The paper was cut in rectangular shape (4 mm × 6 mm, base × height) and dried at room temperature. This was held in front of the mass spectrometer inlet with the help of a copper clip at a distance of 1 m from it (schematic representation in Figure 1). All measurements were done on an ion trap LTQ XL of Thermo Scientific, San Jose, CA. A source voltage of 1 V was used for all the measurements. All analytes were used at concentrations of 50 ppm, and a 2–3 μL volume of analyte was used for each measurement. Following are the experimental conditions: capillary temperature, 150 °C; capillary voltage, 0 V; tube lens voltage, 0 V.

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CrCl$_3$·6H$_2$O and CrBr$_3$·6H$_2$O were purchased from Sigma-Aldrich, India. D$_2$O was bought from Acros Organics, India. All organic solvents used in this experiment (methanol, ethanol, propanol, butanol, and pentanol) were purchased from Sigma-Aldrich, India. The collision-induced dissociation technique was used for MS$^2$ analysis. A field emission scanning electron microscope (FE SEM) was used for imaging measurements.

**RESULTS AND DISCUSSION**

A modified paper spray ionization source, consisting of a rectangularly cut CNT-coated Whatman 42 filter paper (see the Experimental Section) connected with a low-voltage power supply, was used for the current experiments. The paper spray source was held in front of the MS inlet at a distance of 1 mm from it, and analytes were introduced with a micropipette on the paper. Volumes of 2–3 μL of the analyte solution in a suitable solvent were used for each measurement, and the ions ejected were detected.

The initial set of measurements were done with CrCl$_3$·6H$_2$O, which is the most common chromium hydrate that imparts green color to its solution due to the presence of the [CrCl$_3$(H$_2$O)$_4$]Cl·2H$_2$O complex. The green crystals were weighed, and solution was made in water at a concentration of 50 ppm. This was analyzed at 1 V with the help of a CNT-coated rectangular paper spray source. The mass spectrum collected is shown in Figure 1.

The mass spectrum shows a series of peaks starting from $m/z$ 192 to $m/z$ 200 with $m/z$ 194 as the base peak. The peak at $m/z$ 194 corresponds to $[^{52}\text{Cr}(^{16}\text{O})_4]^{2+}$, which is due to the most probable isotopic combination for the complex ion system. A well-resolved mass spectrum of the complex ion is shown in Figure 1b along with the simulated spectrum. The experimental and simulated mass spectra show good agreement in both signal intensity and isotope distribution. Various signals in the resolved experimental mass spectrum represent different combinations of all the isotopes in the complex ion, with signal intensity determined by the isotopic abundance. A schematic of the ionization process is shown in Figure 1a. It shows the rectangularly cut CNT-coated Whatman 42 filter paper and the MS inlet. The presence of CNTs on the paper was confirmed by microscopic imaging, and an FE SEM image is shown in Figure 1a. The image shows CNTs spread over the paper, part of which also project out of the paper. These CNTs expel gas-phase ions from the paper at voltages above 1 V. The mechanism of ionization has been explained in our previous publication. The identity of the gas-phase complex ion was confirmed by collision-induced dissociation, and the results are shown in Figure 1c. The MS$^4$ spectrum of the mass-selected molecular ion, $[^{52}\text{Cr}(^{16}\text{O})_4]^{2+}$, shows the loss of a water molecule from the complex, resulting in a peak at $m/z$ 176. Further loss of water molecules from the fragmented ion and the resulting ions are shown in the MS$^3$ and MS$^4$ spectra (Figure 1c). The peak at $m/z$ 194 can also be due to other combinations of isotopes that are less significant.

The ion $[\text{Cr}(^{16}\text{O})_4]^{2+}$ has been well-studied in solution phase by various techniques. Its crystal structure has been investigated by X-ray diffraction. The complex ion is a hexacoordinated entity with four water and two chloride ligands surrounding the chromium, which has a d$^3$ Cr(III) center. The transition of electrons between the d orbitals give the complex a green color. Ligands surrounding the central metal ion (Cr$^{3+}$) in the complex system can be replaced by other ligands resulting in various ligand-substituted complexes. These ligand-substituted complexes will show corresponding shift in the mass and can be analyzed at low voltage along with the main complex ion system $([\text{Cr}(^{16}\text{O})_4]^{2+})$. The four water ligands surrounding chromium can be substituted by D$_2$O by treating the precursor metal halide with D$_2$O. For this, a 50 ppm solution of CrCl$_3$·6H$_2$O was made in 50:50 (by volume) water/D$_2$O mixture and the spectrum was collected at low voltage. The result is shown in Figure 2.

The mass spectrum shows two sets of peaks with a mass difference of 8 units. The first series represents the aquohalo complex ion $([^{52}\text{Cr}(^{16}\text{O})_4]^{2+})$ with a base peak at 194. The second series is a D$_2$O-substituted complex ion where all the water ligands of the parent complex ion are replaced by D$_2$O. This series consists of many peaks due to different

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**Figure 1.** Mass spectrum of CrCl$_3$·6H$_2$O in water at 1 V. The hexacoordinated aquachloro chromium complex ion at $m/z$ 194 is seen as the most prominent feature. A schematic of the process along with the field emission scanning electron microscopy (FE SEM) image of the CNT-coated paper (a), experimental and simulated (sticks) mass spectra of the complex ion peak (b), and fragmentation patterns of the base peak at 194 by MS/MS methods (c) are shown in the inset.

**Figure 2.** Mass spectrum of CrCl$_3$·6H$_2$O in water/D$_2$O (1:1 by volume) at 1 V showing the presence of $[\text{Cr}(^{16}\text{O})_4]^{2+}$ and $[\text{Cr}(^{16}\text{O})_4]^{2+}$. The experimental and simulated (sticks) mass spectra are shown in the inset.
possible combinations of various isotopes of the constituent elements, as explained above. The base peak is at m/z 204, which represents \([^{52}\text{Cr}(^{12}\text{CH}_3\text{O})_4^{35}\text{Cl}_2]^{+}\) which is the most probable isotopic combination possible. The inset represents the experimental and simulated mass spectra for the two complex ions. The identity of the species was confirmed from these and also from MS/MS. We have not observed other mixed ligand complex systems (like \([\text{Cr}(^{12}\text{H}_2\text{O})_4^{16}\text{O}_2^{35}\text{Cl}_2]^{+}\)). The cause of this needs additional investigation.

The ligand exchange experiment was extended to many other ligands, which resulted in a variety of gas-phase complex ions. Another batch of experiments was done with a homologous series of alcohols from methanol to pentanol. Alcohols are neutral ligands and have the potential to exchange with other neutral ligands in the coordination complex. For this, a solution of CrCl\(_3\)·6H\(_2\)O was made in water/methanol (1:1 by volume) and it was analyzed by low-voltage paper spray ionization mass spectrometry. Figure 3 shows the results.

![Figure 3](image)

Figure 3. Mass spectrum of CrCl\(_3\)·6H\(_2\)O in methanol at 1 V showing the presence of \([\text{Cr}(^{12}\text{H}_2\text{O})_4^{35}\text{Cl}_2]^{+}\) and ligand (methanol) substituted complexes. MS\(^2\) spectra of various complex ions are shown in the inset.

The main spectrum (Figure 3) shows five sets of peaks with base peak positions at m/z 194, 208, 222, 236, and 250. The first series of peaks around m/z 194 (base peak) correspond to the parent complex ion (\([^{52}\text{Cr}(^{12}\text{H}_2\text{O})_4^{35}\text{Cl}_2]^{+}\)). This hexacoordinated complex ion gave another four sets of methanol-substituted ions in the high-mass range. These new ligand-substituted ions occur at different m/z values and differ by 14 mass units. The peak at 208 represents \([^{52}\text{Cr}(^{12}\text{CH}_3\text{O})_4^{35}\text{Cl}_2]^{+}\), which is a monoligand-substituted complex ion where one among the four water molecules is substituted by a methanol molecule. Similarly, the other peaks at m/z 222, 236, and 250 represent \([^{52}\text{Cr}(^{12}\text{CH}_3\text{O})_4^{33}\text{Cl}_2]^{+}\), \([^{52}\text{Cr}(^{12}\text{CH}_3\text{O})_2^{16}\text{O}^{35}\text{Cl}_2]^{+}\), \([^{52}\text{Cr}(^{12}\text{CH}_3\text{O})_2^{16}\text{O}^{33}\text{Cl}_2]^{+}\), and \([^{52}\text{Cr}(^{12}\text{CH}_3\text{O})_2^{16}\text{O}^{16}\text{O}^{33}\text{Cl}_2]^{+}\), respectively. As the methanol to aquo ligand substitution proceeds, there will be a crowded environment around the central metal ion, which will lead to a sterically crowded entity, shows a slightly more enhanced intensity than the trisubstituted ion. Each of these methanol-substituted complex ions was fragmented by collision-induced dissociation, and the resultant fragment ion peaks along with the parent peaks are shown in the MS\(^2\) spectra. This is shown in the inset of Figure 3. Similarly, the experimental mass spectra of all the four methanol-substituted complex ions were compared with the theoretical spectra, and the results are shown in Figure S1. Both experimental and simulated mass spectra showed exact match in both intensity and mass. Ion formation with CNT-coated paper is not a 0 V process. A minimum of 1 V is required for the ionization to happen. In order to prove this, a control experiment was performed with CrCl\(_3\)·6H\(_2\)O in methanol with and without voltage. The results are shown in Figure S2. Here the CNT-coated paper gave a blank mass spectrum at 0 V while analyzing the complex species.

Moreover, 0 V ionization requires specific experimental conditions and is applicable only in exceptional cases. An additional experiment was performed with DPA and thymine under different pH values, and the results illustrated the strong dependence of pH in ionizing these molecules. The results are shown in Figure S3. DPA under highly acidic (pH = 2) and neutral conditions gave absolute intensity of 6 × 10\(^{-6}\) at 0 V. But it did not give any signal at basic conditions. Similarly, it gave an absolute intensity of 2 × 10\(^{-6}\) at acidic pH at 0 V but did not produce ion signals at neutral pH at 0 V. Moreover, the signal intensities of both these species at 0 V are negligibly small compared with those at 1 V. By comparing these two results, it is clear that 0 V ionization is a phenomenon which is heavily dependent on the molecular characteristics as well as experimental conditions.

The experiment was continued for the other alcohols in the homologous series too. For this, CrCl\(_3\)·6H\(_2\)O solution was made at a concentration 50 ppm in four different alcohols—ethanol, propanol, butanol, and pentanol, respectively. These were analyzed in the same manner as explained above. Figure 4 depicts the resultant spectra collected at 1 V. The mass spectra
showed the presence of alcohol-substituted complex ions along with the parent aqua halo complex system. These substituted complex ions showed similar variation in peak intensity as in the case of methanol. The symmetrically substituted systems showed higher peak intensity compared to the asymmetric ones.

The possibility of creating ligand-exchanged complex ions in the gas phase at low voltages has led to the thought of creating new mixed ligand complex ions. For this, a slight modification was done in the previous experimental procedure. CrCl₃·6H₂O was taken in different alcohol mixtures (in equimolecular proportions), and the analysis was done at low voltages. This has resulted in new mixed ligand complex ions, along with the normal complex ions. Figure 5 shows the results obtained with this experiment.

**Figure 5.** Low-voltage analysis of various chromium complexes in different combinations (equimolecular proportions) of alcohols: CrCl₃·6H₂O (1:1 by volume) in (a) methanol/ethanol, (b) ethanol/butanol, and (c) propanol/butanol. The peaks corresponding to the mixed ligand complexes are indicated by their m/z values (black, in large font size). Other peaks are due to normal ligand-substituted complexes (indicated in red font).

In the figure, trace a represents the complex ions obtained with a 50 ppm solution of CrCl₃·6H₂O in 1:1 (by volume) methanol/ethanol. There are nine sets of peaks including the starting parent complex ion centered around m/z 194. These are around m/z 194, 208, 222, 236, 250, 264, 278, 292, and 306, respectively. The feature at 194 represents [Cr(H₂O)₄Cl₂]+, which we have noted before. The other eight series include methanol-substituted complex ions, ethanol-substituted complex ions, and mixed ligand complexes. Peaks at m/z 208 and 236 represent methanol-substituted complex ions: [Cr(CH₃OH)(H₂O)₂Cl₂]⁺ and [Cr(CH₃OH)₂(H₂O)Cl₂]⁺, respectively. Peaks at m/z 222 can be a mixture of both [Cr(CH₃OH)₂(H₂O)₂Cl₂]⁺ and [Cr(H₂O)₂(C₂H₅OH)Cl₂]⁺, since both have the same molecular mass. Same is the case with the peak at m/z 250, representing a mixture of both [Cr(CH₃OH)₂Cl₂]⁺ and [Cr(H₂O)₃(C₂H₅OH)₂Cl]⁺. Similarly, the peak at m/z 306 represents an ethanol-substituted complex ion, [Cr(C₂H₅OH)₂Cl₂]⁺. Among the other three peaks (m/z 264, 278, and 292), that at m/z 278 is a mixture of an ethanol-substituted complex ion and a mixed ligand complex ion ([Cr(H₂O)(C₂H₅OH)₂Cl₂]⁺ and [Cr(CH₃OH)₂(C₂H₅OH)Cl₂]⁺). The other two peaks at m/z 264 and 292 represent mixed ligand complex ions, [Cr(CH₃OH)₂(C₂H₅OH)Cl₂]⁺ and [Cr(CH₃OH)(C₂H₅OH)Cl₂]⁺ respectively. The second spectrum shows gas-phase complex ions from the solution of CrCl₃·6H₂O in ethanol/butanol, and the third represents complex ions from propanol/butanol (all 50:50 by volume). Here also we can see both the mixed ligand complexes as well as normal alcohol-substituted ones. All the mixed ligand complexes are listed in Table S1 with molecular formula and m/z values.

One of the main advantages of low-voltage ionization compared to normal high-voltage paper spray is its ability to detect molecular systems with extreme fragility. We have proved this with the identification of fragile hydrated adducts of halides at low voltage. Gas-phase metal—aquo complexes are other classes of fragile systems. Their identification can be done very well at low voltage, and there is a chance for them to undergo degradation with increase in voltage. This has been tested with various complex ions. CrCl₃·6H₂O was dissolved in a water/methanol (1:1) mixture, and the resultant ions were detected at various voltages starting from 1 to 600 V. Results are shown in Figure 6. Here we can see mass spectra collected at 1−600 V (Figure 6A). The identified species are listed in Figure 6B. From the mass spectra, it is clear that there is a gradual and sudden decrease in the peak intensities with increase in voltage (Figure 6C). This is true for all the complex ions. Complex ions show their maximum intensity in the low-voltage range, and their intensities drop almost to zero at 500−600 V (the absolute intensity values of these complexes are shown in Figure S4). This variation can be correlated with their poor stability. Several control experiments have been performed on various fragile systems in order to prove the capability of the low-voltage ionization technique for their analyses. For that, CrCl₃·6H₂O was taken and the solution was made in different solvents (water, methanol, ethanol, propanol, butanol, and pentanol) at 50 ppm concentration. This was analyzed with normal paper spray (PS) and electrospray ionization (ESI). The results are shown in Figures S5−S8. The results suggest that there is extensive fragmentation of complexes at high voltage using normal PS and ESI.

Dependence of the inlet temperature on the intensity of various complexes has been studied in a separate set of experiments. For that, various samples were chosen and analyzed at

**Figure 6.** (A) Mass spectra collected for methanol-substituted Cr complexes at various voltages, (B) list of the complexes identified with their m/z values, and (C) variation of signal intensity ratio of each complex ion with respect to the voltage applied.
1 V by varying the MS inlet temperature from 30 to 500 °C with all other parameters being the same as that of the previous experiments. The results are shown in Figures S9 and S10. The results suggest that the ion intensity is dependent on the MS inlet temperature; the intensity starts appearing from a minimum value at 30 °C and reaches the maximum at 150 °C. The gas-phase ion formation requires desolvation first, and this is assisted by various factors including the MS inlet temperature. At 30 °C, desolvation is slow and it results in weak ion intensity. After that, the intensity reaches a peak value, and finally it degrades due to the effect of high temperature on the fragile systems. These results suggested the possibility of a solvent-assisted ionization mechanism. A similar set of experiments was performed with the conventional paper spray method (high voltage) by using CrCl3·6H2O in methanol, and the results are shown in Figure S11, which indicate reduced temperature dependence on ion intensity. The results suggest that the ionization mechanism is different from that of ESI.

An additional experiment was done by introducing 3 μL of solution of CrCl3·6H2O in methanol directly in front of the MS inlet, and the mass spectrum was collected at different MS inlet temperatures from 30 to 500 °C. This was compared with the normal 1 V spectrum, and the results are shown in Figures S12 and S13. It shows the presence of additional peaks along with the normally observed peaks (Figure S12) with strong molecular ion abundance as there is a chance to suck more molecules compared with the normal 1 V ionization process. Results from a temperature-dependent study (Figure S13) show the role of solvent in the ionization mechanism.

The experiments conducted here mainly focus on the detection of various complexes in the gas phase and not on their existence in solution. However, to show the existence of different ligand-substituted complexes in solution, we have carried out a set of UV–vis spectroscopic measurements on CrCl3·6H2O in different solvents from water to butanol. Cr3+ (having d6 electronic configuration) exhibits two absorption maxima at 437 and 627 nm in water. These peaks are due to 4A2g → 4T1g and 4A2g → 4T2g transitions, respectively. These peaks further show a red shift (from 437 to 449 nm and from 627 to 633 nm) when there is a change in the solvent. This is reflected in the UV–vis spectrum (Figure S14A) as we change the solvent from water to methanol and other alcohols (ethanol to butanol). The shift is principally due to the change in the electronic splitting energy (Δ value) as we move from one ligand to the other. Change of water to methanol changes Δ due to the crystal field. Solvent-dependent red shifts in the optical absorption spectrum of Cr(NO3)3·9H2O were attributed to changes in the complexation shell.

Measurements were conducted by varying the solvent composition also. For that, CrCl3·6H2O was taken in different compositions of water/methanol and spectra were collected (Figure S14B). Here a systematic red shift in the high-energy peak (437 nm) can be observed as we move from 0% methanol to 25% methanol and so on (437 nm → 439 nm → 445 nm → 449 nm). This is due to the stepwise formation of different mixed ligands which includes [Cr(H2O)4(CH3OH)2Cl2]+, [Cr(H2O)2(CH3OH)OH]2Cl]+, [Cr(H2O)(CH3OH)2Cl2]+, and [Cr(CH3OH)2Cl3]+ along with [Cr(H2O)2Cl2]+. Ligand combinations around the central metal ion change the Δ and are reflected in their UV–vis spectra.

The last set of experiments was done with the Cr–bromide system. For those, we have prepared solutions of CrBr3·6H2O in various solvents and analyses were done at low voltage. The results suggest the existence of gas-phase Cr–bromide complex ions similar to the Cr–chloride system. The mass spectra collected at low voltage are shown in Figure 7. A table depicting the list of different Cr–Br complex ions is shown in the Supporting Information (Table S2).

![Figure 7. Mass spectra of CrBr3·6H2O at 1 V in (A) water, (B) methanol, (C) ethanol, (D) propanol, and (E) butanol. Different complex ions detected are indicated in the mass spectra. The inset of panel A compares the experimental and simulated (sticks) mass spectra of [Cr(H2O)·Br2]+.](image)

### CONCLUSIONS

The present study shows that it is possible to observe the gas-phase transition metal complex ions by the low-voltage ionization technique using CNTs. The extreme softness of the technique allows us to identify many complex ions with good S/N ratio. The main system under study was a hexacoordinated chromium ion, [Cr(H2O)3Cl2]+. The spectrum showed a well-resolved isotopic distribution with base peak at 194. The system was then used for ligand exchange reaction with many other ligands including D2O and alcohols. Several alcohol-substituted complex ions were detected, and further study revealed the presence of gas-phase mixed ligand complexes too. A voltage variation study was performed on these complexes, and it confirmed the weak bonding in the system. These experiments proved the potential application of the low-voltage ionization technique to probe fragile molecules.

### ASSOCIATED CONTENT

#### Supporting Information

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Mass spectra of chromium complexes, DPA, and thymine, absolute intensity values of various complexes detected at various voltages, comparison between...
low-voltage and normal paper spray analysis and ESI MS, UV–vis spectra of CrCl$_3$·6H$_2$O, and lists of different complexes detected at 1 V with their $m/z$ values (PDF)

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**Notes**
The authors declare no competing financial interest.

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