

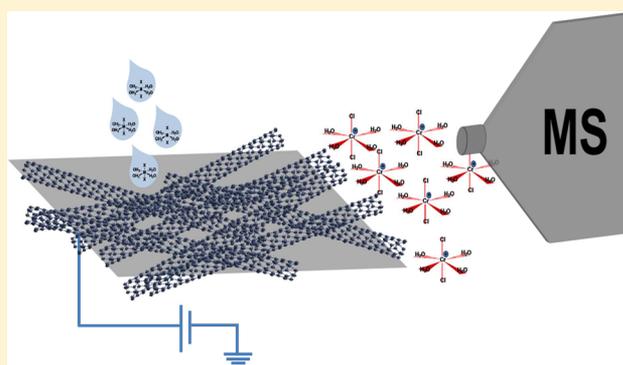
Probing Coordination Complexes by Carbon Nanotube-Assisted Low-Voltage Paper Spray Ionization Mass Spectrometry

Rahul Narayanan and Thalappil Pradeep*[✉]

DST Unit of Nanoscience and Thematic Unit of Excellence, Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

Supporting Information

ABSTRACT: Fragile transition metal complex ions such as $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$, 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 D_2O and ROH ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \dots$) 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.^{1,2} While many of the structural insights of these complex ions have been derived from physical property measurements,^{3–7} as in the case of magnetism,^{8–10} 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.^{11–14} Observing such complex species directly in solution has been difficult, although there have been reports of this in the recent past.^{15,16} Although coordination complexes have been studied in solution phase, only a few studies have been carried out in the gas phase.^{17–19}

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,^{20,21} 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.²⁰ Extension of this technique to other nanostructures showed anisotropy in molecular ionization when two-dimensionally aligned Te nanowires (NWs) were used for ionization.²¹ Analytical performance was shown with volatile and nonvolatile compounds and a variety of matrixes. 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 mm 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.

Received: March 27, 2017

Accepted: September 20, 2017

Published: September 20, 2017

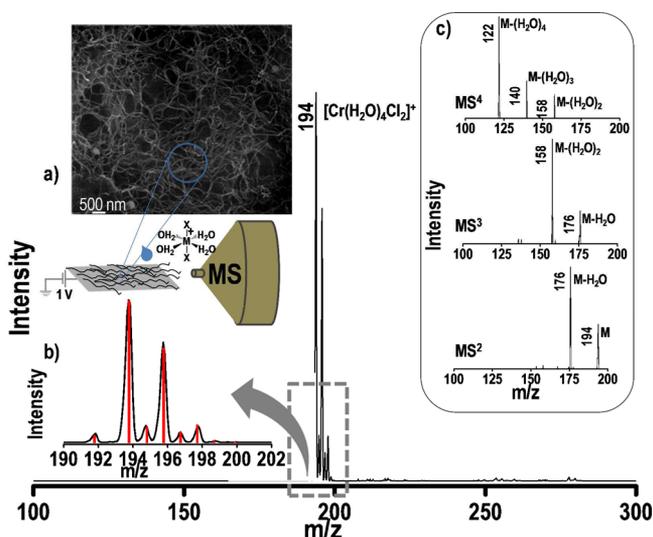


Figure 1. Mass spectrum of $CrCl_3 \cdot 6H_2O$ in water at 1 V. The hexacoordinated aquochloro chromium complex ion at m/z 194 is seen as the most prominent feature. A schematic of the process along with the field emission scanning electron microscopy (FE SEM) image of the CNT-coated paper (a), experimental 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.

$CrCl_3 \cdot 6H_2O$ and $CrBr_3 \cdot 6H_2O$ were purchased from Sigma-Aldrich, India. D_2O 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 $CrCl_3 \cdot 6H_2O$, which is the most common chromium hydrate that imparts green color to its solution due to the presence of the $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$ complex.^{22,23} 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 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 194 corresponds to $[^{52}Cr(^1H_2^{16}O)_4^{35}Cl_2]^+$, 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.²⁰ The identity of the gas-phase complex ion was confirmed by collision-induced dissociation, and the results are shown in Figure 1c. The MS^2 spectrum of the mass-selected molecular ion, $[^{52}Cr(^1H_2^{16}O)_4^{35}Cl_2]^+$, 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 $[Cr(H_2O)_4Cl_2]^+$ 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 ($[Cr(H_2O)_4Cl_2]^+$). The four water ligands surrounding chromium can be substituted by D_2O by treating the precursor metal halide with D_2O . For this, a 50 ppm solution of $CrCl_3 \cdot 6H_2O$ was made in 50:50 (by volume) water/ D_2O mixture and the spectrum was collected at low voltage. The result is shown in Figure 2.

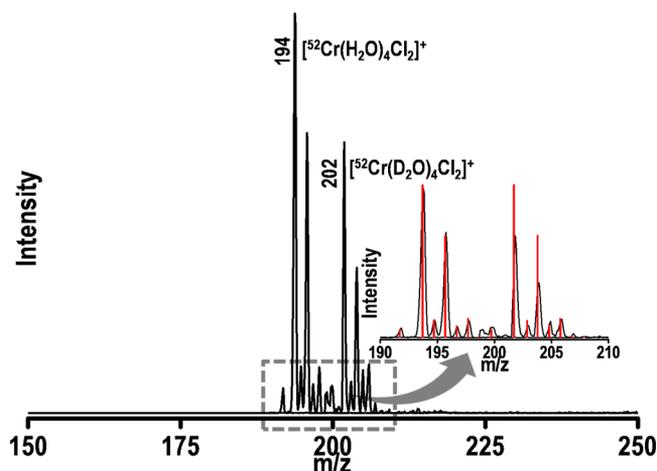


Figure 2. Mass spectrum of $CrCl_3 \cdot 6H_2O$ in water/ D_2O (1:1 by volume) at 1 V showing the presence of $[Cr(H_2O)_4Cl_2]^+$ and $[Cr(D_2O)_4Cl_2]^+$. The experimental and simulated (sticks) mass spectra are shown in the inset.

The mass spectrum shows two sets of peaks with a mass difference of 8 units. The first series represents the aquohalo complex ion ($[^{52}Cr(^1H_2^{16}O)_4^{35}Cl_2]^+$) with a base peak at 194. The second series is a D_2O -substituted complex ion where all the water ligands of the parent complex ion are replaced by D_2O . This series consists of many peaks due to different

possible combinations of various isotopes of the constituent elements, as explained above. The base peak is at m/z 204, which represents $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ 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 $[\text{Cr}(\text{H}_2\text{O})_2(\text{D}_2\text{O})_2\text{Cl}_2]^+$). 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 $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ 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.

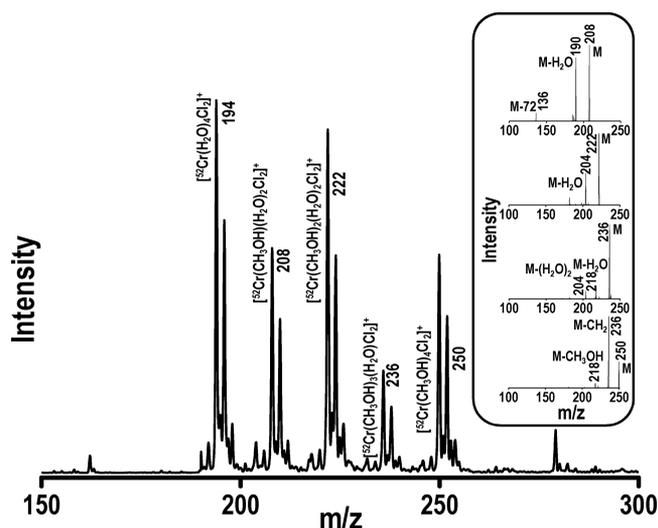


Figure 3. Mass spectrum of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ in methanol at 1 V showing the presence of $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ and ligand (methanol) substituted complexes. MS² spectra of various complex ions are shown in the inset.

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 ($[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$). 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 $[\text{Cr}(\text{H}_2\text{O})_3(\text{CH}_3\text{OH})\text{Cl}_2]^+$, 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 $[\text{Cr}(\text{H}_2\text{O})_2(\text{CH}_3\text{OH})_2\text{Cl}_2]^+$, $[\text{Cr}(\text{H}_2\text{O})(\text{CH}_3\text{OH})_3\text{Cl}_2]^+$, and $[\text{Cr}(\text{CH}_3\text{OH})_4\text{Cl}_2]^+$, 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 steric instability in the system. This instability is reflected in the peak intensity in the mass spectrum. All substituted complex ions are less intense compared to the parent complex ion. Among the ligand-substituted complex ions, that at m/z 236 shows the least intensity. This ion 236 represents $[\text{Cr}(\text{H}_2\text{O})(\text{CH}_3\text{OH})_3\text{Cl}_2]^+$, which is an asymmetrically substituted

system. Symmetrical configuration around the central metal ion gave more stability to the system and is reflected in the peak intensity in the mass spectrum. As a result, the peak at m/z 250 due to $[\text{Cr}(\text{CH}_3\text{OH})_4\text{Cl}_2]^+$, although the most 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 MS² 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 $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ 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 6×10^0 at 0 V. But it did not give any signal at basic conditions. Similarly, it gave an absolute intensity of 2×10^0 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, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ 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

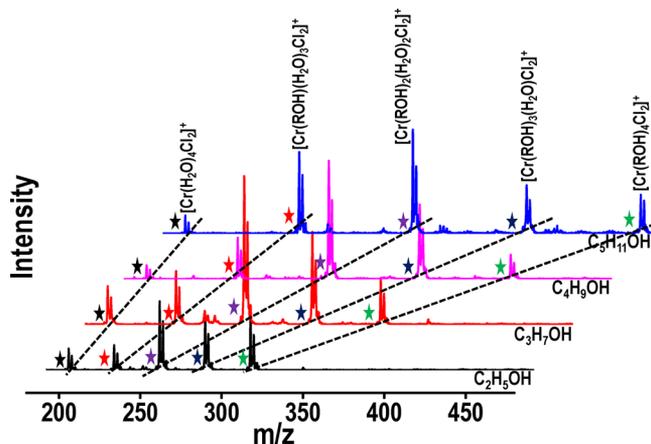


Figure 4. Mass spectra of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ in various alcohols at 1 V, showing the presence of $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ and ligand (alcohol) substituted complexes. The ligand-substituted complexes for alcohols are represented by a general formula, and the peaks show a corresponding shift in the m/z values. Guide lines indicating the peaks are also shown.

showed the presence of alcohol-substituted complex ions along with the parent aquahalo 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. $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ was taken in different alcohol mixtures (in equimolar 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.

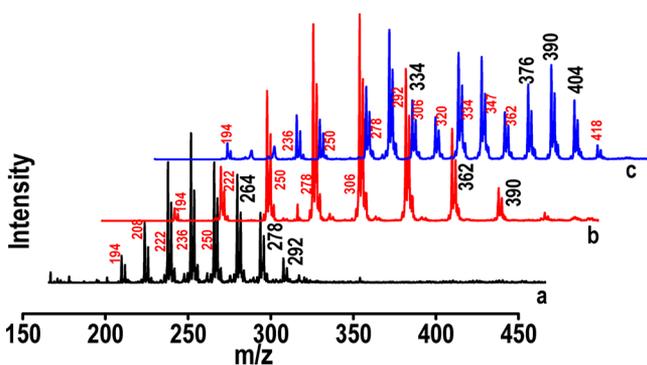


Figure 5. Low-voltage analysis of various chromium complexes in different combinations (equimolar proportions) of alcohols: $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (1:1 by volume) in (a) methanol/ethanol, (b) ethanol/butanol, and (c) propanol/butanol. The peaks corresponding to the mixed ligand complexes 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 $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ 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 $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$, 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, $[\text{Cr}(\text{CH}_3\text{OH})(\text{H}_2\text{O})_2\text{Cl}_2]^+$ and $[\text{Cr}(\text{CH}_3\text{OH})_3(\text{H}_2\text{O})\text{Cl}_2]^+$, respectively. Peaks at m/z 222 can be a mixture of both $[\text{Cr}(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})_2\text{Cl}_2]^+$ and $[\text{Cr}(\text{H}_2\text{O})_3(\text{C}_2\text{H}_5\text{OH})\text{Cl}_2]^+$, since both have the same molecular mass. Same is the case with the peak at m/z 250, representing a mixture of both $[\text{Cr}(\text{CH}_3\text{OH})_4\text{Cl}_2]^+$ and $[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{H}_5\text{OH})_2\text{Cl}_2]^+$. Similarly, the peak at m/z 306 represents an ethanol-substituted complex ion, $[\text{Cr}(\text{C}_2\text{H}_5\text{OH})_4\text{Cl}_2]^+$. 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 ($[\text{Cr}(\text{H}_2\text{O})(\text{C}_2\text{H}_5\text{OH})_3\text{Cl}_2]^+$ and $[\text{Cr}(\text{CH}_3\text{OH})_2(\text{C}_2\text{H}_5\text{OH})_2\text{Cl}_2]^+$). The other two peaks at m/z 264 and 292 represent mixed ligand complex ions, $[\text{Cr}(\text{CH}_3\text{OH})_3(\text{C}_2\text{H}_5\text{OH})\text{Cl}_2]^+$ and $[\text{Cr}(\text{CH}_3\text{OH})(\text{C}_2\text{H}_5\text{OH})_3\text{Cl}_2]^+$, respectively. The second spectrum shows gas-phase complex ions from the solution of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ 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.^{20,21} 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. $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ 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

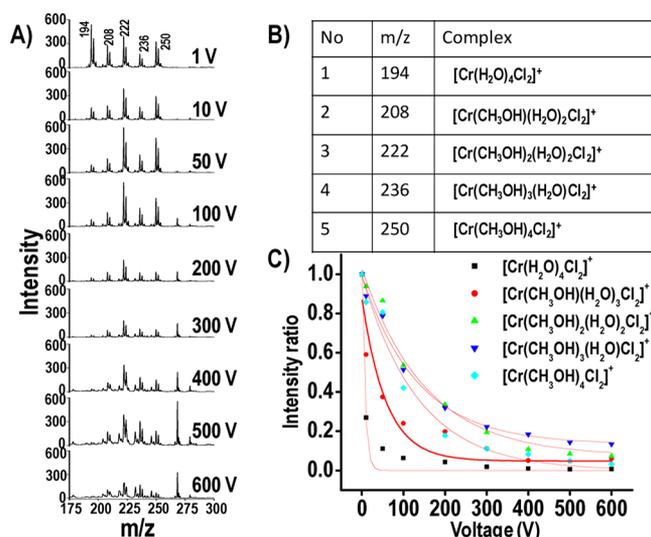


Figure 6. (A) Mass spectra collected for methanol-substituted Cr complexes at various voltages, (B) list of the complexes identified with their m/z values, and (C) variation of signal intensity ratio of each complex ion with respect to the voltage applied.

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, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ 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

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 $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ 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 $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ 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 $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ in different solvents from water to butanol. Cr^{3+} (having d^3 electronic configuration) exhibits two absorption maxima at 437 and 627 nm in water. These peaks are due to ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$ and ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$ transitions, respectively.²⁴ 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 $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were attributed to changes in the complexation shell.²⁵

Measurements were conducted by varying the solvent composition also. For that, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ 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 \rightarrow 439 nm \rightarrow 445 nm \rightarrow 449 nm). This is due to the stepwise formation of different mixed ligands which includes $[\text{Cr}(\text{H}_2\text{O})_3(\text{CH}_3\text{OH})\text{Cl}_2]^+$, $[\text{Cr}(\text{H}_2\text{O})_2(\text{CH}_3\text{OH})_2\text{Cl}_2]^+$, $[\text{Cr}(\text{H}_2\text{O})(\text{CH}_3\text{OH})_3\text{Cl}_2]^+$, and $[\text{Cr}(\text{CH}_3\text{OH})_4\text{Cl}_2]^+$ along with $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$. 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 $\text{CrBr}_3 \cdot 6\text{H}_2\text{O}$ 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

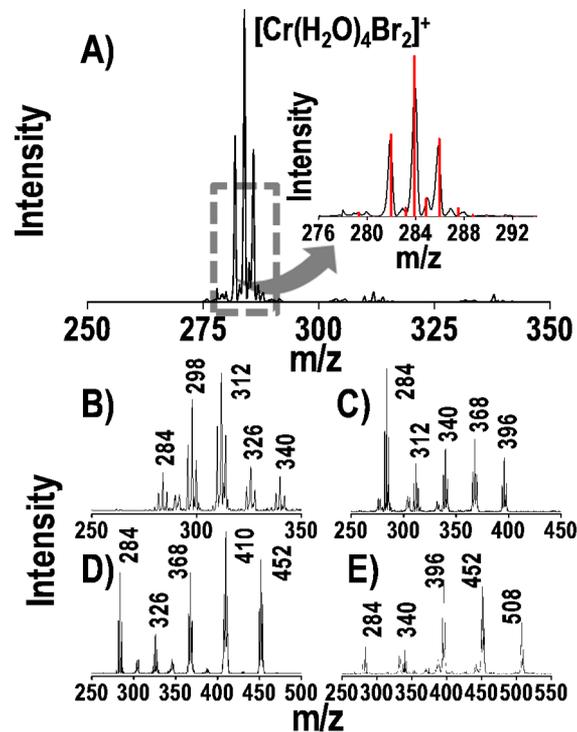


Figure 7. Mass spectra of $\text{CrBr}_3 \cdot 6\text{H}_2\text{O}$ at 1 V in (A) water, (B) methanol, (C) ethanol, (D) propanol, and (E) butanol. Different complex ions detected are indicated in the mass spectra. The inset of panel A compares the experimental and simulated (sticks) mass spectra of $[\text{Cr}(\text{H}_2\text{O})_4\text{Br}_2]^+$.

depicting the list of different Cr–Br complex ions is shown in the Supporting Information (Table S2).

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, $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$. 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 D_2O 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

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.7b01129.

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 $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, and lists of different complexes detected at 1 V with their m/z values (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: pradeep@iitm.ac.in.

ORCID

Thalappil Pradeep: [0000-0003-3174-534X](https://orcid.org/0000-0003-3174-534X)

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

T.P. acknowledges financial support from the Department of Science and Technology, Government of India for his research program on nanomaterials. R.N. thanks the University Grant Commission for a research fellowship.

REFERENCES

- (1) Hantzsch, A.; Werner, A. *Ber. Dtsch. Chem. Ges.* **1890**, *23*, 11.
- (2) Werner, A. *Ber. Dtsch. Chem. Ges.* **1906**, *39*, 2656–2667.
- (3) King, E. L.; Woods, M. J. M.; Gates, O. P.; Gates, H. S. *J. Am. Chem. Soc.* **1958**, *80*, 5015–5018.
- (4) Gates, H. S.; King, E. L. *J. Am. Chem. Soc.* **1958**, *80*, 5011–5015.
- (5) Werner, A. *Ber. Dtsch. Chem. Ges.* **1906**, *39*, 2673–2679.
- (6) Higgins, B.; DeGraff, B. A.; Demas, J. N. *Inorg. Chem.* **2005**, *44*, 6662–6669.
- (7) Kulkarni, A. D.; Patil, S. A.; Badami, P. S. *Int. J. Electrochem. Sci.* **2009**, *4*, 717–729.
- (8) Kallies, B.; Meier, R. *Inorg. Chem.* **2001**, *40*, 3101–3112.
- (9) Sham, T. K.; Hastings, J. B.; Perlman, M. L. *J. Am. Chem. Soc.* **1980**, *102*, 5904–5906.
- (10) Figgis, B. N. *J. Inorg. Nucl. Chem.* **1958**, *8*, 476–482.
- (11) Halpern, J.; Harkness, A. C. *J. Chem. Phys.* **1959**, *31*, 1147–1149.
- (12) de Almeida, K. J.; Murugan, N. A.; Rinkevicius, Z.; Hugosson, H. W.; Vahtras, O.; Ågren, H.; Cesar, A. *Phys. Chem. Chem. Phys.* **2009**, *11*, 508–519.
- (13) Ban, M. I.; Császár, J.; Hegyháti, M. *J. Mol. Struct.* **1973**, *19*, 455–463.
- (14) Susak, N. J.; Crerar, D. A. *Geochim. Cosmochim. Acta* **1985**, *49*, 555–564.
- (15) Yepes, D.; Seidel, R.; Winter, B.; Blumberger, J.; Jaque, P. *J. Phys. Chem. B* **2014**, *118* (2014), 6850–6863.
- (16) Seidel, R.; Thurmer, S.; Moens, J.; Geerlings, P.; Blumberger, J.; Winter, B. *J. Phys. Chem. B* **2011**, *115*, 11671–11677.
- (17) Holland, P. M.; Castleman, A. W., Jr. *J. Chem. Phys.* **1982**, *76*, 4195–4205.
- (18) Foster, M. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 4808–4814.
- (19) Corderman, R. R.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 3998–4000.
- (20) Narayanan, R.; Sarkar, D.; Cooks, R. G.; Pradeep, T. *Angew. Chem., Int. Ed.* **2014**, *53*, 5936–5940.
- (21) Narayanan, R.; Sarkar, D.; Som, A.; Wlekinski, M. S.; Cooks, R. G.; Pradeep, T. *Anal. Chem.* **2015**, *87*, 10792–10798.
- (22) Dance, I. G.; Freeman, H. C. *Inorg. Chem.* **1965**, *4*, 1555–1561.
- (23) Lennartson, A. *Nat. Chem.* **2014**, *6*, 942–942.
- (24) Lakshmanan, S. V. J.; Jacob, S. A. *Proc. Indian Natl. Sci. Acad.* **1982**, *6*, 654–658.
- (25) Inglezakis, V. J.; Loizidou, M. D. *Desalination* **2007**, *211*, 238–248.