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Ruthenium diimine complexes in unusual charge states formed in collisional electron transfer

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Abstract

Ruthenium diimine complexes, $Ru(L)_3^{2+}$ (L = bipy = 2,2′-bipyridine or phen = 1,10-phenanthroline), were formed in the gas phase by electrospray ionization and accelerated through a 50-kV electrostatic potential. In collisions between $Ru(L)_3^{2+}$ and O_2, fragment ions were produced in addition to $Ru(L)_3^{+}$ and $Ru(L)_3^{3+}$ formed in collisional electron transfer. Cross-sections for the electron stripping and electron capture reactions are 10 ± 0.2 Å^2 and 1.7 ± 0.1 Å^2, respectively, for L = bipy and 3.8 ± 0.2 Å^2 and 0.8 ± 0.1 Å^2, respectively, for L = phen. In collisions between $Ru(L)_3^{2+}$ and Na electron capture was the major reaction channel and resulted in $Ru(L)_3^{+}$ as well as $Ru(L)_3^{-}$ (as a result of multiple-collision conditions). Cross-sections are of the order of 100 Å^2 for the formation of one-electron reduced $Ru(L)_3^{+}$ ions. The kinetic energy released by the dissociation of $Ru(L)_3^{2+}$ and $Ru(L)_3^{3+}$ into $Ru(L)_2^{+/2+}$ and L^+ after collisional activation was measured to be 1.5 eV for $Ru(bipy)_3^{2+}$, 3.7 eV for $Ru(phen)_3^{2+}$, 8 eV for $Ru(bipy)_3^{3+}$, and 6 eV for $Ru(phen)_3^{3+}$.

Keywords: Charge separation processes; Kinetic energy release; Electron transfer; Metal ion complexes

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1. Introduction

In high-energy (50 keV or higher) collisions between cations and oxygen, electron stripping is a highly probable process [1–3]. Likewise, electron capture is dominant when the collision gas is sodium vapor [4], whereas noble gases lead mainly to collision-induced dissociation (CID) instead of collisional electron transfer [1–3]. A proper choice of the target gas hence allows for preparation of characteristic product ions in unusually low or high charge states.

The kinetic energy release (KER) of a charge separation process provides insight into the barrier height for the opposite process in which two charged ions combine. There exists a vast amount of data on charge separation processes of cations, and some examples include multiply charged cations of CS_2 [5], CO_2 [6,7], Cl_2O [8], CH_3I [9], hydrated metal ions [10], fullerene ions [11–13], and argon clusters [14]. To our knowledge only two KER measurements have been made for dianions, $IrBr_6^{2-}$ [15] and $Cr(SCN)_4^{2-}$ [16]. Dianions are more difficult to handle as electron autodetachment competes with the formation of two atomic or molecular fragment ions.

In this work we have used ruthenium diimine, $Ru(L)_3^{2+}$, complexes in high-energy collision experiments. L is a diimine ligand, either bipy or phen. We demonstrate that triply charged cations are produced with high yields when O_2 is the collision gas, whereas singly charged cations dominate when Na is the collision gas. The kinetic energy released when doubly and triply charged complexes dissociate into charged fragments was measured. A triply charged complex is in an unusually high charge state and its fragmentation chemistry is governed by the charge repulsion within the ion. We have earlier reported on the Coulomb explosion of a dianion complex formed upon electron capture to a monoanion [16]. In the present experiment, we go in the opposite direction and generate a cation in an unusually high positive charge state and probe its dissociation dynamics when it dissociates into cations after electron loss.

2. Experiments

The experimental setup has been described elsewhere in great detail [17,18] and only a brief description is given

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here. $\mathrm{Ru(bipy)_3}^{2+}$ and $\mathrm{Ru(phen)_3}^{2+}$ ions were generated by electrospraying dilute solutions of their chloride salts in acetonitrile [19]. All cations were accelerated through a high voltage (50 kV), and the dications of interest were mass selected by a magnet. The ions were collided in a 3-cm long collision cell with either He (0.15 mTorr) or O_2 (0.15 mTorr). In other experiments, ions were collided with Na in a 4-cm long collision cell. The sodium collision cell was heated to 220 °C in order to get a suitable gas pressure (0.47 mTorr). Mass-analyzed ion kinetic energy (MIKE) spectra were obtained using a 180° hemispherical electrostatic analyzer (ESA) and a channeltron detector.

3. Results and discussions

Product ion spectra for the ruthenium complexes colliding with He, O_2, and Na collision gases are shown in Fig. 1 for $\mathrm{Ru(bipy)_3}^{2+}$ (m/z 285), and in Fig. 2 for $\mathrm{Ru(phen)_3}^{2+}$ (m/z 321). The dominant fragmentation channel in collisions with He is the loss of a neutral ligand to give $\mathrm{Ru(bipy)_2}^{2+}$ (m/z 207) or $\mathrm{Ru(phen)_2}^{2+}$ (m/z 231) (Figs. 1A and 2A). A reaction unique for $\mathrm{Ru(bipy)_3}^{2+}$ is the symmetric cleavage of a bipy ligand to give $[\mathrm{pyridyl-Ru(bipy)_2}]^{2+}$ (m/z 246) and $[\mathrm{pyridyl-Ru(bipy)}]^{+}$ (m/z 336). Pyridyl is a C_5H_4N radical. In the spectra of both complexes there is an ion series corresponding to 4, 5, 6, 8, and 10 heavy atoms. The resolution of our instrument does not allow for an exact assignment of these ions. Both $\mathrm{Ru(bipy)_3}^{2+}$ and $\mathrm{Ru(phen)_3}^{2+}$ ions lose a charged ligand with the formation of $\mathrm{Ru(bipy)_2}^{+}$ (m/z 414) and bipy^{+} (m/z 156) or $\mathrm{Ru(phen)_2}^{+}$ (m/z 462) and phen^{+} (m/z 180). Again the resolution of the instrument makes it difficult to distinguish these ions from $[\mathrm{Ru(bipy)_2-H}]^{+}$, bipyH^{+}, $[\mathrm{Ru(phen)_2-H}]^{+}$, and phenH^{+}; the former nomenclature is chosen in the rest of the paper for simplicity. $[\mathrm{Ru(bipy)_2-H}]^{+}$ and bipyH^{+} are known to be formed in low-energy collisions of $\mathrm{Ru(bipy)_3}^{2+}$ [19]. The total destruction cross-section in collisions with helium is about 100–150 Å^2.

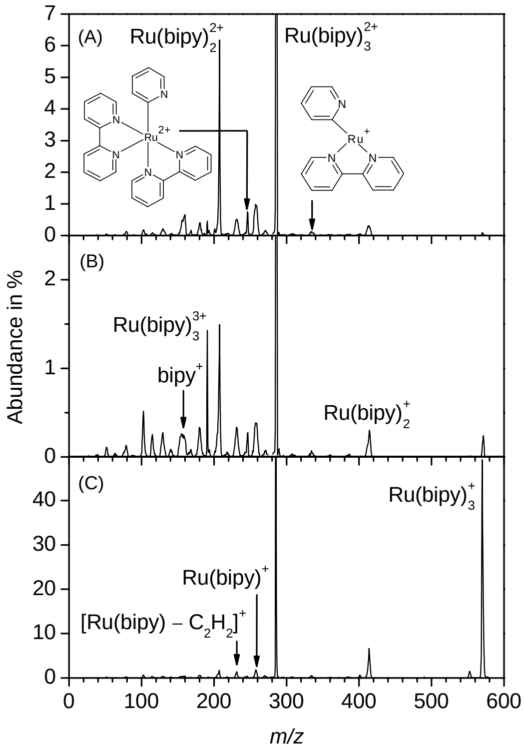

Fig. 1. MIKE product ion spectra obtained from collisions between $\mathrm{Ru(bipy)_3}^{2+}$ and He (A), O_2 (B), and Na (C). The spectra are normalized such that the peak of the parent ion is 100%.

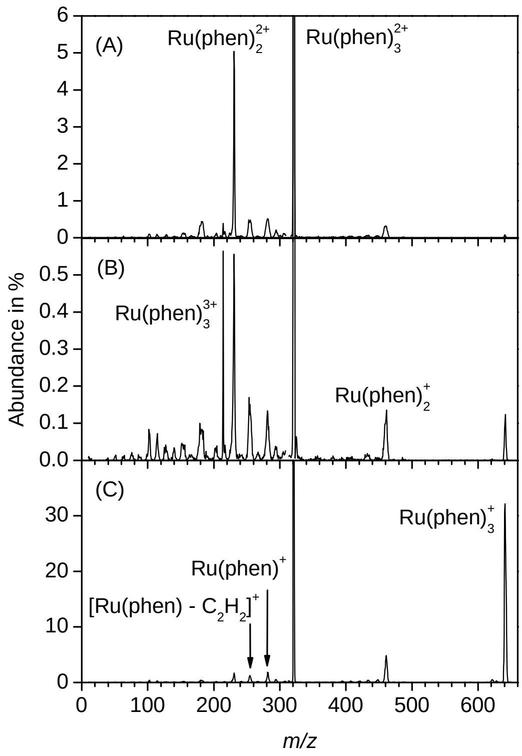

Fig. 2. MIKE product ion spectra obtained from collisions between $\mathrm{Ru(phen)_3}^{2+}$ and He (A), O_2 (B), and Na (C). The spectra are normalized such that the peak of the parent ion is 100%.

In collisions with O_2 new peaks appear in the spectra which correspond to the ions $\mathrm{Ru(bipy)_3}^{3+}$ (m/z 190) and $\mathrm{Ru(bipy)_3}^{+}$ (m/z 570) formed from $\mathrm{Ru(bipy)_3}^{2+}$ and $\mathrm{Ru(phen)_3}^{3+}$ (m/z 214) and $\mathrm{Ru(phen)_3}^{+}$ (m/z 642) formed from $\mathrm{Ru(phen)_3}^{2+}$ (Figs. 1B and 2B). These ions result from collisional electron transfer between parent ions and O_2 target molecule. The peaks of 3+ ions are narrow as expected for product ions that are not fragment ions. Electron-transfer cross-sections, σ, are given in Table 1. The data reveal that

Table 1
Electron-transfer cross-sections σ (in Å^2) from collisions between 2+ ions and O_2

Reaction	$O_2 \rightarrow O_2^{+}$	$O_2 \rightarrow O_2^{-*}$
$\mathrm{Ru(bipy)_3}^{2+}$	1.7 ± 0.1	10 ± 0.2
$\mathrm{Ru(phen)_3}^{2+}$	0.8 ± 0.1	3.8 ± 0.2

molecular oxygen is much more efficient at electron stripping ($\sigma \sim$ 4–10 Å^2) than electron donation ($\sigma \sim$ 1–2 Å^2).

In contrast, in collisions with sodium vapor, large abundances of one-electron reduced ions $Ru(bipy)_3{}^+$ and $Ru(phen)_3{}^+$ are formed (Figs. 1C and 2C). The electron-transfer cross-sections for their formation are in the order of 100 Å^2, significantly larger than those in O_2 (1–2 Å^2). Indeed, electron capture in collisions with Na has a similar cross-section to collision-induced dissociation in helium. The energy defect for the electron-transfer reaction is lower in collisions with Na than with O_2 as Na has a significantly lower ionization energy than O_2 ($IE(Na) = 5.14\,eV$ versus $IE(O_2) = 12.07\,eV$). There is a remarkably high abundance of the ions $[Ru(bipy) - C_2H_2]^+$ (*m/z* 232, Fig. 1) and $[Ru(phen) - C_2H_2]^+$ (*m/z* 256, Fig. 2) compared to other fragment ions. These ions likely arise from $Ru(L)_3{}^+$ which demonstrates how electron capture opens up new fragmentation channels. This behaviour is well known from electron capture dissociation (ECD) of proteins since ECD is a different process than CID [20].

To record spectra of anions formed in collisions with sodium, the polarity of the ESA was changed to obtain the charge-reversal spectrum, $^-CR^+$ (Fig. 3). Despite the necessity of transfer of three electrons (likely after two or three collisions), several anions were produced including the complexes: $Ru(bipy)_3{}^-$ and $Ru(phen)_3{}^-$. It is possible that a hydrogen atom has been lost from the bipyridine complex to give a metallocarbacycle, $Ru(bipy)_2(bipy - H)^-$, in which C_3 or C_3' of a (bipy − H) ligand is coordinated to the metal instead of the nitrogen. This reaction requires rotation along the C_1C_1'-bridge that connects the two pyridine rings. Also, complexes with fewer ligands were formed: $Ru(bipy)_2{}^-$, $Ru(phen)_2{}^-$, and $Ru(phen)^-$ again with the possibility of H-atom loss in the case of bipyridine complexes. At low *m/z* there is a large peak that is assigned to the acetylenide $HC_2{}^-$ or the cyanide CN^- anion. More peaks are seen which correspond to ions that contain 2, 3, 4, ... heavy atoms but they cannot be assigned with certainty.

Not only dicationic but also tricationic complexes can be selected for further investigation. In order to produce trications O_2 was added to the region before the magnetic sector to carry out the electron stripping just after the acceleration [3]. In this way triply charged ruthenium diimine complexes were formed, selected with the magnet and collided with He, and spectra are shown in Fig. 4. The spectra are strikingly different from those of the 2+ ions. The major fragment ions are $Ru(L)_2{}^{2+}$ and L^+. Hence an increase in the charge state selectively enhances the charge separation process. The competition between loss of a neutral ligand and a charged ligand depends on the charge state of the system and its size. As electrostatic repulsion becomes more severe within the ion, the loss of charged fragments becomes more important. This phenomenon is observed for cases like $C_{60}^{n+} \rightarrow C_{58}^{n+} + C_2$ versus $C_{60}^{n+} \rightarrow C_{58}^{(n-1)+} + C_2{}^+$ [12] and $M(H_2O)_n^{2+} \rightarrow M(H_2O)_{(n-1)}^{2+} + H_2O$ versus, where M is a metal [21].

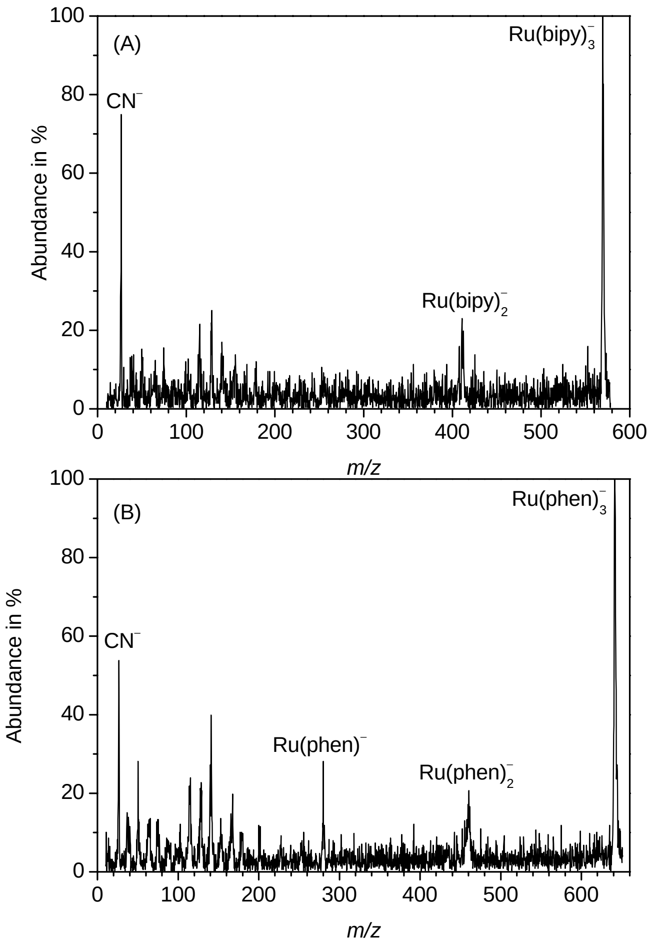

Fig. 3. Charge-reversal, $^+CR^-$, spectra obtained from collisions between $Ru(bipy)_3{}^{2+}$ and Na (A) and between $Ru(phen)_3{}^{2+}$ and Na (B) (multiple-collision conditions). The peak of the $Ru(L)_3{}^-$ ion is taken to be 100%.

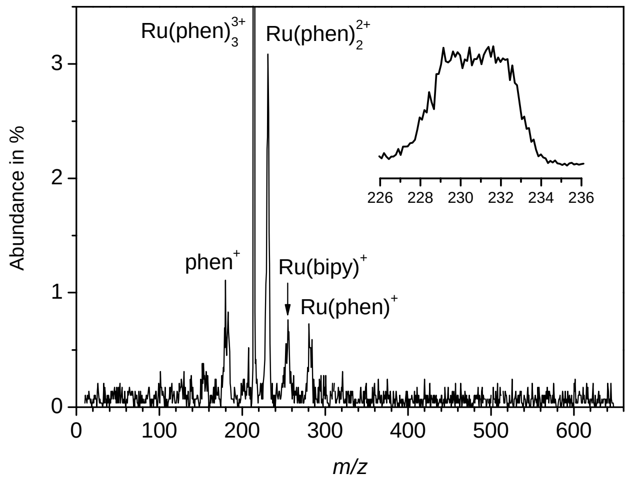

Fig. 4. MIKE-CID spectrum obtained from collisions between $Ru(phen)_3{}^{3+}$ and He. The spectra are normalized such that the peak of the parent ion is 100%. The inset shows a more detailed scan of the $Ru(phen)_2{}^{2+}$ ion.

Table 2
KER (in eV) measured for the dissociation of 2+ and 3+ ions into two fragment ions

Parent	Fragment ions		KER
$Ru(bipy)_3{}^{2+}$	$Ru(bipy)_2{}^{+}$	$bipy^{+}$	1.5 ± 0.3
$Ru(phen)_3{}^{2+}$	$Ru(phen)_2{}^{+}$	$phen^{+}$	3.7 ± 0.5
$Ru(bipy)_3{}^{3+}$	$Ru(bipy)_2{}^{2+}$	$bipy^{+}$	8 ± 1
$Ru(phen)_3{}^{3+}$	$Ru(phen)_2{}^{2+}$	$phen^{+}$	6 ± 1

The KERs measured for dissociation of 2+ and 3+ cations into two charged fragments are shown in Table 2. The KER was calculated as 100 keV $\Delta m^2/(16m_1m_2)$, where Δm is the width of the fragment ion peak in mass units and m_1 and m_2 are the masses of the two fragment ions [22]. Not surprisingly, the KER is much higher for a triply charged ion (6–8 eV) than that for a doubly charged ion (2–4 eV).

4. Conclusions

We have demonstrated that $Ru(bipy)_3{}^q$ and $Ru(phen)_3{}^q$ can exist in charge states $q = 1-, 1+, 2+$ and $3+$. The complexes can be formed in any of these charge states from the 2+ parent by a proper choice of collision gas in a 100 keV collision. The dominant reaction channel after collisional activation changes from neutral ligand loss for $Ru(bipy)_3{}^{2+}$ and $Ru(phen)_3{}^{2+}$ to dissociation into two charged fragments for 3+ ions, a process that is associated with a high kinetic energy release of 6–8 eV. The approach described here allows for the study of charge separation or Coulomb explosion of multiply charged cations in unusually high charge states formed after electron stripping. The electron stripping was done with the O_2 target gas. In contrast, collisions with Na reduced the charge state of the ions and a large yield of 1+ ions were formed which display new fragmentation channels.

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References

[1] M. Sørensen, J.S. Forster, P. Hvelplund, T.J.D. Jørgensen, S.B. Nielsen, S. Tomita, Chem. Eur. J. 7 (2001) 3214.
[2] P. Hvelplund, T.J.D. Jørgensen, S.B. Nielsen, M. Sørensen, J.U. Andersen, J. Am. Soc. Mass Spectrom. 12 (2001) 889.
[3] S.B. Nielsen, J.U. Andersen, P. Hvelplund, T.J.D. Jørgensen, M. Sørensen, S. Tomita, Int. J. Mass Spectrom. 213 (2002) 225.
[4] P. Hvelplund, B. Liu, S.B. Nielsen, S. Tomita, Int. J. Mass Spectrom. 225 (2003) 83.
[5] C.P. Safvan, V.R. Bhardwaj, G.R. Kumar, D. Mathur, F.A. Rajgara, J. Phys. B 29 (1996) 3135.
[6] C. Cornaggia, M. Schmidt, D. Normand, J. Phys. B 27 (1994) L123.
[7] J. Chen, H. Ren, R. Ma, X. Li, H. Yang, Q. Gong, Int. J. Mass Spectrom. 228 (2003) 81.
[8] C.S. O'Connor, S.D. Price, Int. J. Mass Spectrom. 184 (1999) 11.
[9] P. Siozos, S. Kaziannis, C. Kosmidis, Int. J. Mass Spectrom. 225 (2003) 249.
[10] M.K. Beyer, R.B. Metz, J. Phys. Chem. A 105 (2001) 10054.
[11] S. Tomita, H. Lebius, A. Brenac, F. Chandezon, B.A. Huber, Phys. Rev. A 65 (2002) 053201.
[12] S. Tomita, H. Lebius, A. Brenac, F. Chandezon, B.A. Huber, Phys. Rev. A 67 (2003) 063204.
[13] J. Jensen, H. Zettergren, A. Fordi, H.T. Schmidt, H. Cederquist, Nucl. Instrum. Methods Phys. Res. B 205 (2003) 643.
[14] V. Kumarappan, M. Krishnamurthy, D. Mathur, Phys. Rev. Lett. 87 (2001) 085005.
[15] J. Friedrich, S. Gilb, O.T. Ehrler, A. Behrendt, M.F. Kappes, J. Chem. Phys. 117 (2002) 2635.
[16] A.B. Nielsen, P. Hvelplund, B. Liu, S.B. Nielsen, S. Tomita, J. Am. Chem. Soc. 125 (2003) 9592.
[17] O.V. Boltalina, P. Hvelplund, T.J.D. Jørgensen, M.C. Larsen, M.O. Larsson, D.A. Sharoitchenko, Phys. Rev. A 62 (2000) 023202.
[18] M.O. Larsson, P. Hvelplund, M.C. Larsen, H. Shen, H. Cederquist, H.T. Schmidt, Int. J. Mass Spectrom. Ion Processes 177 (1998) 51.
[19] V. Katta, S.K. Chowdhury, B.T. Cait, J. Am. Chem. Soc. 112 (1990) 5348.
[20] R.A. Zubarev, Mass Spectrom. Rev. 22 (2003) 57.
[21] A.T. Blades, P. Jayaweera, M.G. Ikonomou, P. Kebarle, Int. J. Mass Spectrom. 102 (1990) 251.
[22] R.G. Cooks, J.H. Beynon, R.M. Caprioli, G.R. Lester, Metastable Ions, Elsevier, Amsterdam, 1973.