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Observation of Doubly Charged Ions in Fast Atom Bombardment Mass Spectrometry: Ruthenium(II) Complexes in a Nitrobenzyl Alcohol Matrix

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The fast atom bombardment (FAB) mass spectrometric analysis of several series of ruthenium–bidentate ligand complexes such as $[RuLL'L'']X_2$, $[RuL_2L']X_2$, and $[RuL_3]X_2$ are discussed, where L, L', and L'' include 2,2'-bipyridine, 1,10-phenanthroline, their derivatives, and related compounds. Surprisingly abundant, intact, doubly charged cations $[RuL_3]^{2+}$, $[RuLL'L'']^{2+}$, and $[RuL_2L']^{2+}$ are observed for most complexes studied. Structurally significant fragment ions are generally observed for all complexes in addition to singly charged molecular cationic species such as $[RuLL'L'']^+$ and $[RuLL'L'']X^+$. The $[RuLL'L'']^{2+}/[RuLL'L'']^+$ ratio, where $L = L' = L''$, $L = L' \neq L''$, or $L \neq L \neq L''$ depending on the series involved, varies from 3.5 to 0.35 over the 22 complexes studied. Reasons for the observation of these unique abundant doubly charged ions in a FAB spectrum, especially in a nitrobenzyl alcohol matrix, are discussed. Ions indicative of ligand exchange reactions between ruthenium centres are not observed for mixed ligand complexes.

Introduction

There has been growing interest in the subject of excited-state electron- and energy-transfer reactions of the tris(2,2'-bipyridine)ruthenium(II) complex, $Ru(bpy)_3^{2+}$, over the last decade.[1-4] The interest in $Ru(bpy)_3^{2+}$ and related complexes stems in part from the fact that these compounds have promise for the conversion of solar power into electrical and chemical energy.[1,5]

Coordination compounds have been characterized by mass spectrometric techniques such as field desorption (FD),[6,7] fast atom bombardment (FAB),[8-10] secondary ion mass spectrometry (SIMS),[11,12] electrohydrodynamic mass spectrometry (EHMS),[13] and laser mass spectrometry (LMS).[14] Usually only singly charged ions are reported, even though the analyte contained multiply charged cationic species. Doubly charged ions such as $[Ru(bpy)_3]^{2+}$ and $[Fe(bpy)_3]^{2+}$ are however reported with EHMS.[13] Only one example of doubly charged ions from coordination compounds has been reported with FAB, in this case $[Ru(bpy)_3]^{2+}$ from its perchlorate salt[9] in a sulfolane matrix.

Generally mass spectrometry is used for the purpose of molecular weight determination and structural elucidation. Recently, it has been demonstrated that the results obtained from LMS[14] and FAB[15] for a series of coordination complexes can be correlated with their solution chemistry properties. In the present work, FAB has been used to investigate a series of 22 ruthenim complexes of the following types: (a) $[RuL_3]X_2$, (b) $[RuL_2L']X_2$, and (c) $[RuLL'L'']X_2$. Ligands include a combination of the following: 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), bis(2-pyridyl)amine (dpa), 4,4'-dimethyl-2,2'-bipyridine (dmb), di-2-pyridyl ketone (dpk),, 4,5-diazafluoren-9-one (dzf), 3,4,7,8-tetramethyl-1,10-phenanthroline (tmp), 2,2'-biquinoline (bqy), and 4,4'-diisopropyl-2,2'-bipyridine (dip). X^- may be Cl^-, PF_6^-, $CF_3SO_3^-$, and $CF_3CO_2^-$.

Generally ions corresponding to $[RuL_3X]^+$, $[RuL_3]^+$, $[RuL_2]^+$, $[RuL]^+$, and $(L + H)^+$ were observed for $[RuL_3]X_2$; similar types of ions were observed in the other cases. The striking observation in this study is the presence of doubly charged intact cations of high abundance in a 3-nitrobenzyl alcohol matrix.

Experimental Section

FAB mass spectra were obtained on a Kratos (AEI) MS 30 mass spectrometer, retrofitted[16] with a Kratos FAB source in beam 1 and interfaced to a Kratos DS55 data system. Xenon was used as the bombarding gas with atom gun (Ion Tech) energies of 6–8 kV and a gun current of approximately 1 mA. The operating pressure of the ion source was typically $\sim 10^{-5}$ Torr and the ions were accelerated at 4 kV. The source was operated at room temperature at resolution 1000. The data system was calibrated with tris(perfluoroheptyl)-*s*-triazine; data were acquired as time files and converted into mass files after acquisition. Samples dissolved in a liquid matrix were placed on the 2 mm diameter beveled stainless steel probe tips for spectra acquisition. The results for each sample reported here are from an average of 6–10 scans, after matrix background subtraction.

Matrix liquids such as sulfolane, thioglycerol, 2,2'-thiodiethanol, glycerol, *p*-nitrophenyl octyl ether, and 3-nitrobenzyl alcohol (NBA) were tried. Since the overall results obtained with NBA were comparatively better than those with other matrices with respect to the ion intensities from the analyte, NBA was used as the matrix in this study. NBA was the only matrix to show abundant doubly charged ions, though a few were observed with a sulfolane matrix. The samples were synthesized by using methods that have been reported in part elsewhere,[17,18] with complete details to follow in a subsequent publication. The purity of most of the complexes with three different ligands was generally established by HPLC[17] while a crystal structure of a representative complex has also been carried out.[18]

Results and Discussion

The positive-ion FAB spectrum of $[Ru(phen)(dmb)_2](PF_6)_2$ is shown in Figure 1. Doubly charged intact cations corresponding to $[Ru(phen)(dmb)_2]^{2+}$ ($m/z = 325$, i.e. the designated m/z value being the most intense peak in the isotopic cluster) are observed

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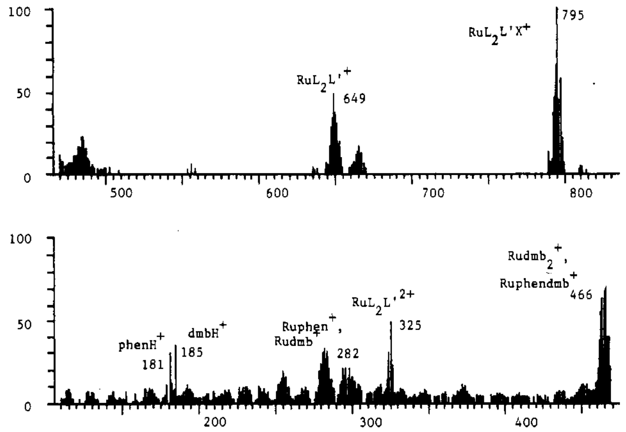

Figure 1. Positive-ion FAB mass spectrum of $[Ru(dmb)_2(phen)](PF_6)_2$. The ion cluster at $m/z = 650$, $RuL_2L'^+$, has a contribution from the ion cluster centered at m/z 649 corresponding to $(RuL_2L - H)^+$, which makes the peak at m/z 649 the most intense in the cluster.

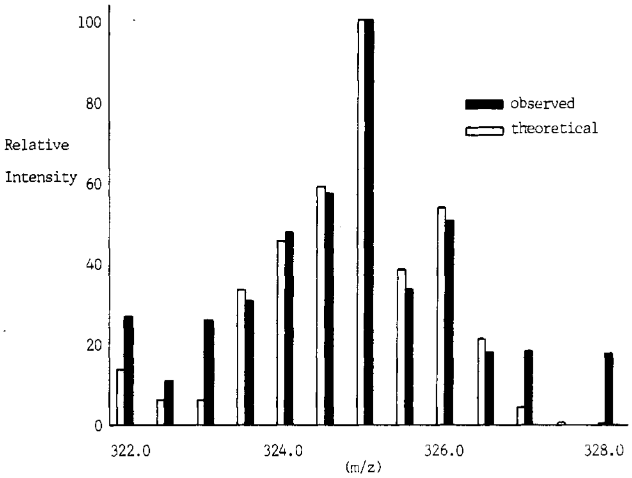

Figure 2. Comparison of observed and theoretical isotopic patterns for the $[Ru(phen)(dmb)_2]^{2+}$ ion.

in addition to the other ions characteristic of the molecular weight such as $[Ru(phen)(dmb)_2]X^+$ ($m/z = 795$) and $[Ru(phen)(dmb)_2]^+$ ($m/z = 649$), where $X = PF_6^-$. The doubly charged ions were identified by the isotopic clusters occurring with half-integral mass separtion in the expected mass/charge range expected for $[Ru(phen)(dmb)_2]^{2+}$ as shown in Figure 2; the observed and calculated isotope distributions are in good agreement. Thus, the formula weight of the complex can be deduced from these ions. Fragment ions such as $[Ru(phen)(dmb)]^+$ ($m/z = 466$), $[Ru(dmb)_2]^+$ ($m/z = 470$), $[Ru(phen)]^+$ ($m/z = 282$), $[Ru(dmb)]^+$ ($m/z = 286$), $(dmb + H)^+$ ($m/z = 185$), and $(phen + H)^+$ ($m/z = 181$) can be used to identify the number and the nature of the ligands present in the complex. The absence of ions such as $[Ru(phen)_2(dmb)]^+$, $[Ru(phen)_2]^+$, etc. arising from ligand scrambling indicates that FAB can be used for preliminary identification of mixed-ligand complexes and for identification of mixtures.

The positive-ion FAB spectra of all of the complexes studied showed results similar to those of $[Ru(phen)(dmb)_2]X_2$. For example, ions corresponding to $[RuL_3]X^+$ (25.1–1.8% of total ruthenium-containing ions), RuL_3^+ (28.6–1.6%), RuL_2^+ (20.5–<0.1%), and $(RuL_n - H)^+$ ($n = 1$–3, 34.0–<0.1%) are observed for all complexes in addition to the doubly charged RuL_3^{2+} (16.2–3.8%) ions, where L refers to various ligands described in the Introduction. The RuL_3^{2+}/RuL_3^+ ratio varies from 3.5 to 0.35 over the 22 complexes studied; the intensity ratios of RuL_3^{2+}/RuL_3^+ for all the complexes are shown in Table I. The doubly charged ions are absent in the spectra of complexes having the "dpa" ligand; these spectra are dominated by ions arising from ligand proton loss.

Table I. Intensity Ratio of $[RuLL'L'']^{2+}/[RuLL'L'']^+$, Where $L = L' = L''$, $L = L' \neq L''$, or $L \neq L' \neq L''$

complex[a,b]	$[RuLL'L'']^{2+}/[RuLL'L'']^{+}$[c]
$[Ru(dmb)(phen)(bqy)](PF_6)_2$	1.9
$[Ru(dmb)(bpy)(bqy)](PF_6)_2$	1.3
$[Ru(bpy)(phen)(dpk)](PF_6)_2$	0.7
$[Ru(bpy)(phen)(dmb)](PF_6)_2$	1.4
$[Ru(dmb)(bpy)(dip)](PF_6)_2$	2.0
$[Ru(bpy)(phen)(dzf)](PF_6)_2$	0.9
$[Ru(bpy)(phen)(tmp)](PF_6)_2$	2.2
$[Ru(bpy)_2(phen)](PF_6)_2$	1.8
$[Ru(phen)_2(bpy)](PF_6)_2$	1.1
$[Ru(dmb)_2(phen)](PF_6)_2$	1.9
$[Ru(dmb)_2(bpy)](PF_6)_2$	2.0
$[Ru(bpy)_3]Cl$	0.8
$[Ru(phen)_3](PF_6)_2$	0.9
$[Ru(bpy)_3](PF_6)_2$	1.5
$[Ru(dmb)_3](PF_6)_2$	3.5
$[Ru(bpy)_3](CF_3SO_3)_2$	0.9
$[Ru(phen)_3](CF_3CO_2)_2$	0.8

[a] Complexes having the ligand "dpa" are not tabulated here; the intensities of doubly charged ions were relatively small in these cases because the spectra were dominated by ions arising from the loss of ligand protons. [b] The error due to intensity variations from spectrum to spectrum is ±15%. [c] Ratios are obtained for solutions of 1–5 μg of complex in 10 μL of NBA.

As discussed above, there are three important molecular species observed in all examples studied: (I) $[RuL_3X]^+$, (II) $[RuL_3]^+$, and (III) $[RuL_3]^{2+}$. A single loss of a counteranion from $[RuL_3]X_2$ probably leads to $[RuL_3]X^+$. Ions corresponding to $[RuL_3]^+$ are produced by dissociation followed by reduction of $[RuL_3]X_2$ in a fashion[19] common to the FAB spectra of organometallic and coordination compounds.

Simple desorption of the dissociated product of $[RuL_3]X_2$ may lead to the doubly charged ions RuL_3^{2+}. If this is true, then one would also expect doubly charged ions of the same kind in other matrices, since the reduction potential of a particular complex varies only slightly with different solvents.[20,21] The absence of such doubly charged ions in other matrices, described in the Experimental Section, indicates that the simple desorption of $[RuL_3]^{2+}$ from the dissociated product of $[RuL_3]X_2$ is not a major process. Polarographic studies show that the reduction potentials of $[Fe(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$ are approximately the same.[22] Thus, if the production of doubly charged ions depends on the reduction potential, then one would expect $[Fe(bpy)_3]^{2+}$ ions from $[Fe(bpy)_3]X_2$ in an NBA matrix under similar mass spectrometric conditions. No doubly charged ions of any kind were observed for complexes such as $[Fe(bpy)_3](ClO_4)_2$, $[Fe(phen)_3](ClO_4)_2$, $[Co(bpy)_3](ClO_4)_2$, and $[Ni(bpy)_3](ClO_4)_2$ in the positive-ion FAB spectra from NBA matrices. Thus, the reduction potential of the complex is not a major determining factor in the production of doubly charged ions. It appears that the doubly charged $[RuL_3]^{2+}$ ions are produced by a more complicated mechanism.

The observation of abundant doubly charged ions only in an NBA matrix, out of several matrices tried, indicates that NBA is partly responsible for the production of doubly charged ions. In an attempt to confirm this, the $[Ru(bpy)_3]^{2+}/[Ru(bpy)_3]^+$ ion ratio was monitored for $[Ru(bpy)_3]Cl_2$, as a function of NBA in glycerol, with the amount of sample kept constant in each mixture. The result obtained is shown in Figure 3. No doubly charged ions of any kind were observed in a pure glycerol matrix (Figure 3), but the ratio $[RuL_3]^{2+}/[RuL_3]^+$ increases with the amount of NBA introduced into glycerol. This shows that NBA in fact plays a major role in producing observable doubly charged ions.

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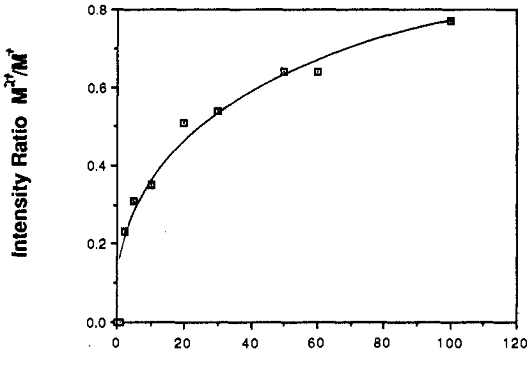

Figure 3. Effect of the addition of NBA to a $[Ru(bpy)_3]Cl_2$ solution on the intensity ratio of the doubly charged to singly charged ions, M^{2+}/M^+, where $M = Ru(bpy)_3$.

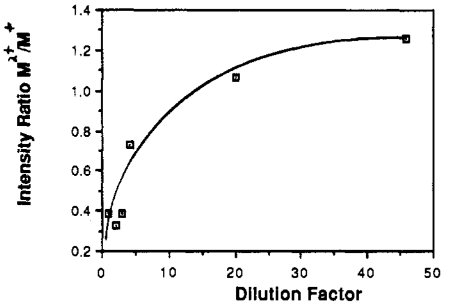

Figure 4. Effect of matrix dilution on the intensity ratio of doubly charged to singly charged ions, M^{2+}/M^+, where $M = Ru(bpy)_3$.

Nitroaromatic compounds are well known oxidative quenchers[1,23] of the excited state of the ruthenium complex, $[RuL_3]^{2+*}$. Thus, the observed participation of NBA in the production of $[RuL_3]^{2+}$ may involve an oxidative quenching of excited-state $[RuL_3]^{2+*}$. It is reasonable to assume excitation of both ions and molecules during the FAB sputtering (ionization) process (I). It

$$ML_3^{2+} \xrightarrow{\text{atomic beam}} ML_3^{2+*} \qquad \text{(I)}$$

has been shown that the excited $[Ru(bpy)_3]^{2+*}$ is a better oxidant ($E_0([Ru(bpy)_3]^{2+*/+}) = 0.84$ V) and also a better reductant ($E_0([Ru(bpy)_3]^{2+*/3+}) = -0.86$ V) than its ground state. Thus, $[Ru(bpy)_3]^{2+*}$ can undergo either reduction, which is observed, as exemplified by the formation of ions corresponding to $[Ru(bpy)_3]^+$, $[Ru(bpy)_2]^+$, and $[Ru(bpy)]^+$, or oxidation under appropriate conditions. Since NBA is a nitroaromatic compound, it may lead to an oxidative quenching process as reported[1,23] for similar systems as shown by (II). With the availability of an

$$ML_3^{2+*} + A \rightarrow ML_3^{3+}\cdots A^- \qquad \text{(II)}$$

electron source, probably the radiation-damaged matrix, $ML_3^{+}\cdots A^-$ may separate into a pair of ions (eq III). Thus, a significant

$$ML_3^{3+}\cdots A^- \xrightarrow{e^-} ML_3^{2+} + A^- \qquad \text{(III)}$$

amount of RuL_3^{2+} may remain as a multiply charged species during the ionization process and may be sputtered into the mass spectrometer as doubly charged ions following process III. If the above argument is true, one would expect an increase in the doubly charged ion abundance with respect to that of its singly charged analogue as the sample is diluted with NBA, since the dilution will increase the probability for process II. The effect of matrix dilution on the intensity ratio of $[Ru(bpy)_3]^{2+}/[Ru(bpy)_3]^+$ is shown in Figure 4. The intensity ratio of $[Ru(bpy)_3]^{2+}/[Ru(bpy)_3]^+$ was monitored as a function of dilution; a constant volume from a standard 0.2 (2 mg/10 μL) analyte solution was diluted by a factor of 2–50 with NBA for the above experiment. The observtion of an increase in $[Ru(bpy)_3]^{2+}/[Ru(bpy)_3]^+$, with the dilution (Figure 4), indicates that the processes given by II and III are probably taking place during the ionization processes.

In an attempt to verify whether the oxidative quenching takes place with other known quenchers, we carried out the following experiment. The positive-ion FAB spectrum of $[Ru(bpy)_3]Cl_2$ was obtained in a glycerol matrix containing *m*-dinitrobenzene, with a small amount of dimethyl sulfoxide being added to increase the solubility of the *m*-dinitrobenzene. *m*-Dinitrobenzene is a well-known oxidative quencher of $[Ru(bpy)_3]^{2+*}$ with a quenching rate constant of 2.0×10^9 m^{-1} s^{-1} in acetonitrile[1]. The doubly charged ions corresponding to $[Ru(bpy)_3]^{2+}$ were observed in this experiment. Thus, the evidence appears to show that the doubly charged ions are produced in the presence of an oxidative quencher, perhaps through the mechanisms proposed in eq I–III. Attempts to investigate other reductive quenchers such as ascorbate were limited by the very low solubility of the quenchers in the matrix or by their high volatility.

The negative-ion FAB spectra of both the sample, $[Ru(bpy)_3]Cl_2$, and the matrix itself are dominated by ions corresponding to $NBA^{\bullet-}$. Thus, though the strongest peak in the negative-ion spectrum of $[Ru(bpy)_3]Cl_2$ (i.e. $NBA^{\bullet-}$) supports process III, it does not provide any conclusive evidence for the same. The production of $NBA^{\bullet-}$ depends on the availability of the electrons from various sources in the matrix rather than the pathways by which the electrons are produced. The relative intensities of $NBA^{\bullet-}/(NBA + Cl)^-$ measured from the negative-ion FAB spectra of $[Ru(bpy)_3]Cl_2$ and $[Ni(bpy)_3]Cl_2$, with identical concentrations of compound in NBA, are equal within experimental error. Thus the negative-ion spectra provide limited information but are consistent with the proposed mechanism.

Our work thus shows that the positive-ion FAB mass spectra can be correlated with the excited-state solution chemistry properties of $[Ru(bpy)_3]Cl_2$, while at the same time giving information on structure and purity of the compounds. Experimental evidence shows that doubly charged ions are produced in the presence of oxidative quenchers, and a mechanism is proposed.

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