

Analysis of Multiply Charged Ions of Ruthenium(II) Tetranuclear Complexes by Electro spray Ionization Mass Spectrometry

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Introduction

The synthesis of polymetallic complex assemblies has played an important role in the recent development of multicomponent system for solar energy conversion,^{1–8} and in the study of photoinduced intramolecular energy or electron transfer reactions.^{9–11} Experimental achievement is really dependent on the availability of the metal complexes in which a desired process takes place. For example, a trinuclear Ru(II) complex $[\{Ru(bpy)_2(CN)_2\}_2Ru(bpy(COO)_2)_2]^{2-}$, can act as an antenna-sensitizer or increase the electron-injection efficiency into the TiO₂ semiconductor electrode.⁴ The same antenna effect can be observed in tetranuclear Ru(II) complexes.⁸ Recently, we have reported the proton-induced switching of metal–metal interaction or intramolecular electron-transfer in binuclear complexes.¹¹ To extend these studies into tetranuclear complexes, we have synthesized two extranuclear Ru(II) complexes denoted by $[RuL_2B]_3RuX_8$, where L is bpy (=2,2'-bipyridine) and bridging ligands, B, are 1,1'-dimethyl-2,2'-bis(2''-pyridyl)-6,6'-bibenzimidazole(dmbpbim) and 2,2'-bis(2''-benzimidazolyl)-4,4'-bipyridine(bbbpyH₂), and X is ClO₄⁻ (Figures 1 and 2). In the synthesis of polynuclear compounds, one of the problems is to show a clear identification of the structure of a complex synthesized. Structural information has been commonly ob-

tained from electrochemical and spectroscopic studies of metal complexes. NMR spectroscopy has not been usually used for the structural assignment of coordination compounds because of complexity of the NMR spectra.

Mass spectrometry of fast atom bombardment (FAB)¹² has been widely used for characterizing metal compounds such as Ru(II) complexes^{13–17}. FAB technique generally produces singly charged ions for metal complexes. But, it has been reported that doubly charged ions of Ru(II)–bidentate ligand complexes were observed in the FAB spectra.^{14,16} In these cases, it was necessary to select an appropriate matrix or combination of matrices to produce doubly charged ions effectively. In FAB spectra of organometallic and coordination compounds, side processes occurred frequently on ionization; the formation of a proton-extracted species $[Ru(bpy)_2 - H]^+$ and of oxidized species was detected.¹⁷ These processes depended upon the matrix solvent used. Moreover, the fragmentation involving the removal of ligands complicated the FAB mass spectra.

Electrospray ionization mass spectrometry (ESI-MS) is useful for the mass analysis of nonvolatile and thermally labile species. In addition, it is characterized by soft ionization and efficient production of multiply charged ions. The ESI technique has been applied for metal complexes such as $Ru(bpy)_3Cl_2$,¹⁸ metalloporphyrins,¹⁹ and $Cu(mbp)_2BF_4$ (mbp = 6-methyl-2,2'-bipyridine).²⁰ Recently, we have measured the ESI mass spectra of mono- and binuclear complexes of Ru(II), Rh(III), and Co(III) ions bridged with the tetradentate ligands 2,6-bis(2'-pyridyl)benzodimidazole etc.²¹ The highly charged ions of 5+ were observed for Ru(II)–Rh(III) binuclear complexes.

In the present paper, we show that ESI-MS is a powerful tool for the identification of the Ru(II) tetranuclear complexes just synthesized and for detecting impurities. For this purpose, it is necessary to make sure what extent of multiply charged ions is clearly observed for such polynuclear complexes, and to understand the formation mechanism of multiply charged ions. Moreover, it is of importance to confirm whether fragment ions generated by the removal of ligands are detected or not.

Experimental Section

A sector type mass spectrometer (JEOL-D300) connected with a homemade ESI interface was used to obtain ESI mass spectra. The

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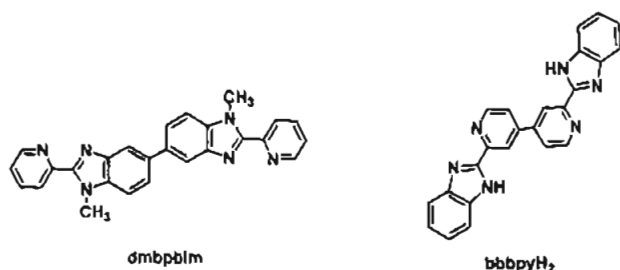


Figure 1. Structures of bridging ligands, 1,1'-dimethyl-2,2'-bis(2''-pyridyl)-6,6''-bibenzimidazole (dmbpbim) and 2,2''-bis(2''-benzimidazolyl)-4,4''-bipyridine (bbbpyH₂).

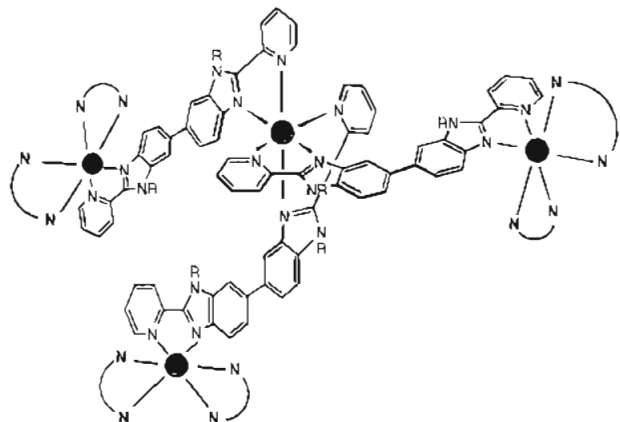


Figure 2. Structure of the Ru(II) tetranuclear complex bridged with dmbpbim (R = CH₃).

interface is similar to that of the ESI ion source designed by Fenn.²² The sample solution was sprayed at the tip of a needle applied by 3.5 kV higher than the counter electrode. This electrode consisted of a 12-cm long capillary pipe of stainless steel. A heated N₂ gas (70 °C) flowed between the needle and the capillary electrode to aid the desolvation of charged droplets sprayed. Ions entered the vacuum system through the first and the second skimmers whose orifices were 0.5 mm in diameter. The pressures of their region were about 10 and 0.1 Torr. The flow rate of a sample solution was 2–3 μL/min. The ion beam was focused with a lens system and traveled about 20 cm before entering the main slit. This region was pumped down to a typical pressure of 2 × 10⁻⁶ Torr. A rotary and a mechanical booster pump for differential pumping stages were floating electrically to depress discharge. The voltage of the second skimmer determines a translational energy of ions in the mass spectrometer. In the present case, the ion translational energy was 2 kV. The voltage of the first skimmer was 50 V higher than that of the second, and that of the capillary electrode is 100 V higher than that of the first.

Two Ru(II) tetramers were synthesized by a simple "complexes as ligands" method; the reaction of mononuclear [Ru(bpy)₂B]²⁺ (B = dmbpbim and bbbpyH₂) with RuCl₃·3H₂O with 3:1 ratio gave the desired tetranuclear complexes. The resulting tetramers were purified by a SP-Sephadex column chromatography with CH₃CN–buffer (1:1 v/v) + 0.2 M NaCl as the eluent. Elemental analysis fitted in with the expected values for the tetranuclear complexes.

For measurements of ESI mass spectra, all of the samples were dissolved in freshly distilled acetonitrile to prepare a sample concentration of less than 0.1 mM. Acetonitrile having a large dielectric constant provided the simplest ESI mass pattern and the most multiply charged ions for the present samples.

Results and Discussion

Figure 1 shows the bridging ligands used here. The structure of the Ru(II) tetramer complex bridged with dmbpbim is illustrated in Figure 2. This dmbpbim complex exhibited the

metal-to-ligand charge transfer (MLCT) bands at 460 nm (ϵ 49 300). The analogous MLCT band for bbbpyH₂ tetranuclear complex was observed at 518 nm (ϵ 65 600). The molar absorption constant of these complexes are four times larger than those of the corresponding mononuclear complexes. The dmbpbim tetranuclear complex is oxidized at +0.607 and +0.779 V vs Fc⁺⁰. The first oxidation process involved one-electron, and the second process involved three electrons. Similarly, the bbbpyH₂ complex showed the stepwise one-electron and three-electron processes at +0.68 and +0.80 V. The detailed discussion of the electrochemistry and UV spectra for these tetramers will be reported in due course.²³

Figure 3 and 4 display positive ESI mass spectra of [Ru(bpy)₂dmbpbim]₃Ru(ClO₄)₈ (**1**) (molecular weight, mw = 3384) and [Ru(bpy)₂bbbpyH₂]₃Ru(ClO₄)₈ (**2**) (mw = 3300), respectively. The *m/z* values given in the text, without notice, refer to calculated chemical mass. The signal to noise ratio for compound **2** was always worse than for **1**, although they were measured on the same ESI spray condition. We have no clear explanation for this result. In the ESI measurements of Ru(II) complexes we found that the spectra were sometimes greatly affected by coexisting species; for example, acid addition brought the worse and more complicate spectra for an acetonitrile solution. Generally speaking, the sample of better purity provides the spectra with better quality. Interestingly, the charge state distribution ranging from 7+ to 3+ can be clearly observed for **1**. These multiply charged ions are produced from loss of negative counterions, which is denoted by [M - *n*X]^{*n*+}, where M and X represent the molecule and ClO₄⁻, respectively. Compound **2** has six dissociating protons in the bridging ligands; the p*K*_a values in CH₃CN–buffer (1:1 v/v) are 4.0, 5.0, 6.2, 6.9, 7.8, and 9.2.²³ Thus, the major peaks observed are deprotonated ions of [M - 8X - 2H]⁶⁺, [M - 8X - 3H]⁵⁺, [M - 8X - 4H]⁴⁺, and their adduct ions with counterions.

The relative intensities of multiply charged ions for **1** are shown in Table 1, together with the previous results.²¹ It is shown that the number of counterions associated with the Ru(II) complex ion increases with increase in the nuclearity. It is one of the problems in the ESI technique whether the ESI spectra are looking at ion equilibrium in solution or not. This really depends on ionization mechanism. The ion evaporation theory proposed by Iribarne and Thomson²⁴ is generally believed to be the ESI mechanism; the dissolved ion in the liquid phase is emitted (evaporated) from very small and highly charged droplets into the gas phase. Thus, the relative intensities of multiply charged ions in ESI mass spectra probably result from both ion association equilibrium in the droplets and the emission rates of the ions. The latter emission rate is dependent on solvation energy of ions. To make this problem clear experimentally, it is essential to measure the standard solution in which the equilibrium of multiply charged species is well-known. If the ion evaporation mechanism becomes clear, the ESI technique will be a powerful tool for probing the equilibrium of ion association for polynuclear and highly charged complexes.

A most abundant peak, called a base peak, was [M - 5X]⁵⁺ of *m/z* 578 for **1**, while it was [M - 8X - 3H]⁵⁺ of *m/z* 501 for **2** due to the dissociation of three protons. The fact that the charge state of 5+ is the base peak in both mass spectra is likely related to the symmetry in structure of the tetramers. The

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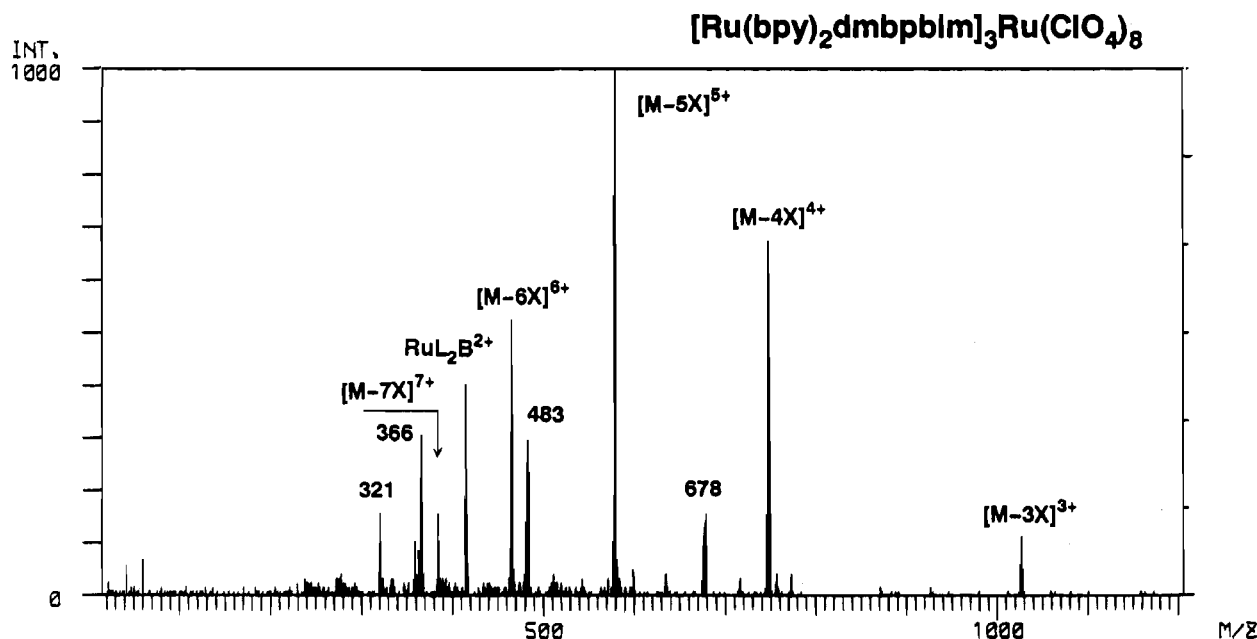


Figure 3. Positive ion ESI mass spectrum of $[\text{Ru}(\text{bpy})_2\text{dmbpbim}]_3\text{Ru}(\text{ClO}_4)_8$ (1). L is bpy, B is the bridging ligand, dmbpbim, and X is ClO_4^- .

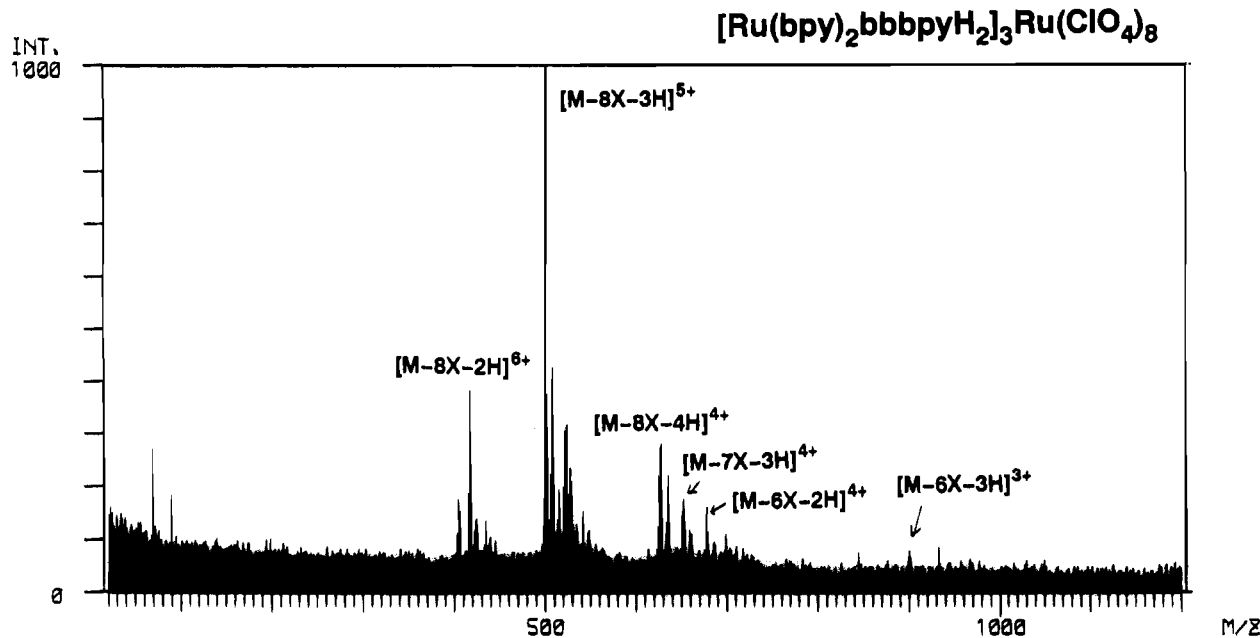


Figure 4. Positive ion ESI mass spectrum of $[\text{Ru}(\text{bpy})_2\text{bbbpyH}_2]_3\text{Ru}(\text{ClO}_4)_8$ (2).

Table 1. Relative Intensities of Multiply Charged Ions in the ESI Mass Spectra of Polynuclear Ru(II) Complexes^a

compound ^b	$[\text{M} - \text{X}]^+$	$[\text{M} - 2\text{X}]^{2+}$	$[\text{M} - 3\text{X}]^{3+}$	$[\text{M} - 4\text{X}]^{4+}$	$[\text{M} - 5\text{X}]^{5+}$	$[\text{M} - 6\text{X}]^{6+}$	$[\text{M} - 7\text{X}]^{7+}$	$[\text{M} - 8\text{X}]^{8+}$
$\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$		1						
$[\text{Ru}(\text{bpy})_2]_2\text{dMe}(\text{ClO}_4)_4$		0.3	0.7	1				
$\text{Ru}(\text{bpy})_2\text{dPrRh}(\text{bpy})_2(\text{ClO}_4)_5$		0.3	0.9	1	0.3			
$[\text{Ru}(\text{bpy})_2\text{dmbpbim}]_3\text{Ru}(\text{ClO}_4)_8$			0.1	0.7	1	0.5	0.2	

^a The data except for the tetranuclear complex are obtained from ref 21. ^b The symbol of dMe and dPr represents bridging ligands of 1,1-bis[2'-(2''-pyridyl)benzimidazolyl]methane and 1,3-bis[2'-(2''-pyridyl)benzimidazolyl]propane, respectively.

species of $[\text{M} - 5\text{X}]^{5+}$ will possess three ClO_4^- attaching to each metal-containing ligands, $[\text{Ru}(\text{bpy})_2\text{dmbpbim}]^{2+}$ because the metal-metal interaction between the peripheral Ru(II) ions is weak enough to allow individual addition of counterions. In the same way, the $[\text{M} - 8\text{X} - 3\text{H}]^{5+}$ ion for 2 is also symmetric because of the deprotonation from each of the three ligands, $[\text{Ru}(\text{bpy})_2\text{bbbpyH}_2]^{2+}$.

$[\text{Ru}(\text{bpy})_2\text{dmbpbim}]^{2+}$, m/z 415 in the spectrum of 1 was detected as the only product derived from ligand dissociation,

while no signal of the corresponding ion, $[\text{Ru}(\text{bpy})_2\text{bbbpyH}_2]^{2+}$ m/z 401 was observed for 2. One of the origins for this ligand ion is considered to be due to the decomposition induced by collisional activation before entering the mass spectrometer, i.e., $[(\text{RuL}_2\text{B})_3\text{Ru}^{8+}]^* \rightarrow (\text{RuL}_2\text{B})_2\text{Ru}^{6+} + \text{RuL}_2\text{B}^{2+}$. However, no signal of the correlated fragment such as $[\text{RuL}_2\text{B}]_2\text{Ru}^{6+}$, m/z 294, was observed in Figure 3. In addition, Katta et al. have studied the effect of collisional activation on ESI mass spectra for $\text{Ru}(\text{bpy})_3\text{Cl}_2$ and $\text{Ru}(\text{phen})_3\text{Cl}_2$ (phen = 1,10-phenanthroline)

complexes.¹⁸ They indicated that at the collision energy greater than 90 eV, collision-induced fragments such as $\text{Ru}(\text{bpy})_2^{2+}$ and $\text{Ru}(\text{bpy})_2^{2+}$ appeared in ESI mass spectra. The collision energy, which is defined as the potential difference between the first and the second skimmer, was 50 eV in the present measurements and thus is supposed to have little effect of collisional activation on the mass spectra.

The other origin is that $[\text{Ru}(\text{bpy})_2\text{dmbpbim}]^{2+}$ itself coexisted in the sample solution. For compound **1**, the steric hindrance between a *N*-methyl group and the third hydrogen atom of the pyridine ring results in the distortion of the 2'-(2-pyridyl)-benzimidazolyl group from a planar structure to some extent. Such effect will make the complex slightly unstable, and thus the ligand dissociation tends to occur. On the other hand, compound **2** is expected to be stable because it has no steric hindrance in the bridging ligand.

Another fragmentation was not detected in the spectrum of **1**. No protonated ion was obviously observed because of no protonated site in the complex. There are unknown peaks of *m/z* 321, 366, 483, and 678 given as nominal masses. Unfortunately, even their charge states were not determined from the

analysis of their isotope distribution. This is because the value of mass was shown as an integer in the present data processor. The isotope distribution is not correct for multiply charged ions. These peaks are perhaps due to unexpected contamination in the synthesis.

In the ESI mass spectrum of the Ru(II) tetranuclear complexes, multiply charged ions ranging from 7+ to 3+ were clearly observed. It was found that these charged ions are resulted from the combination of the dissociation of counterion and the deprotonation of the bridging ligands. Also, the charge distribution shifts to a lower charge state with increase in nuclearity. There seems to be no side reaction in the ESI process such as proton extraction from bpy, the formation of oxidized species, or a variety of ligand dissociation which are usually observed for FAB spectra.

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