



Binuclear ruthenium(II) complexes with polypyridil bridging ligands: Gas-phase chemistry and ligand structure

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ABSTRACT

Ru(II) binuclear complexes with the general formula $[(Ru[9]aneS_3Cl)_2(\mu L)](PF_6)_2$, where $\mu L = 3,6$ -bis(2-pyridyl)-1,2,4,5-tetrazine (bptz), 2,3-bis(2-pyridyl)pyrazine (dpp), and 2,2'-bipyrimidine (bpym), have been studied by electrospray mass spectrometry (ESI/MS) and electrospray mass spectrometry/mass spectrometry (ESI/MS/MS), in the positive ion mode, to investigate their fragmentation patterns in relation to their structural and spectroscopic properties and also to find out the differences with the gas-phase fragmentations patterns of their mononuclear counterparts.

We observed that the presence of two connected metal centres leads to the formation of specific ionic species, in particular, for the compound with bptz, gas-phase formation of fluoride anion adducts. These species can be related to the electronic structure of the bptz compound, in particular to its LUMOs (lowest unoccupied molecular orbitals) that lie low than the LUMOs of the other two compounds.

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1. Introduction

Since the first reports, in the second half of the 20th century, on the Creutz–Taube ion [1,2], a ligand-bridged mixed valence ruthenium complex, great attention has been paid to the synthesis of polynuclear transition metal with bridging ligands. These compounds are not only interesting from a fundamental chemistry point of view [3–5] but also promising for a variety of potential applications [6–10] as the bridging ligand has, among other properties, the ability to mediate electronic communication between the metal centres [11–13].

Electronic transfer processes are extremely important in biological systems and information about them has been obtained by using relatively simple synthetic models. This is the case of binuclear ruthenium(II) complexes with polypyridyl bridging ligands and crown thioethers [14,15] specially because many biological electron transfer systems involve transition metals coordinated to sulphur atoms [16].

Previous studies [14,15] showed that metal–metal interactions in isovalent Ru(II) binuclear complexes with the general formula $[(Ru[9]aneS_3Cl)_2(\mu L)](PF_6)_2$, where $\mu L =$ bridging ligand, $\mu L = 3,6$ -bis(2-pyridyl)-1,2,4,5-tetrazine (bptz), **1**, $\mu L = 2,3$ -bis(2-pyridyl)pyrazine (dpp), **2**, $\mu L = 2,2'$ -bipyrimidine (bpym), **3**, and $[9]aneS_3 = 1,3,5$ -trithiacyclononane, **4** (Scheme 1 and Table 1) are

sufficiently intense to generate Ru^{III}/Ru^{II} mixed valence states, the binuclear complexes possessing relatively weak electrostatic interactions but large resonance energies.

On the other hand the electrolytic nature of some of the processes, occurring when electrospray mass spectrometry (ESI-MS) is used, has been established for some time [17,18]. Redox processes in electrospray mass spectrometry have been comprehensively investigated by Van Berkel and collaborators [19–22] and it is generally accepted that oxidation reactions in the metal capillary sprayers of mass spectrometers, operating in the positive mode, are responsible for charge balance, whereas in the negative mode this balance is achieved through reduction reactions [17,18].

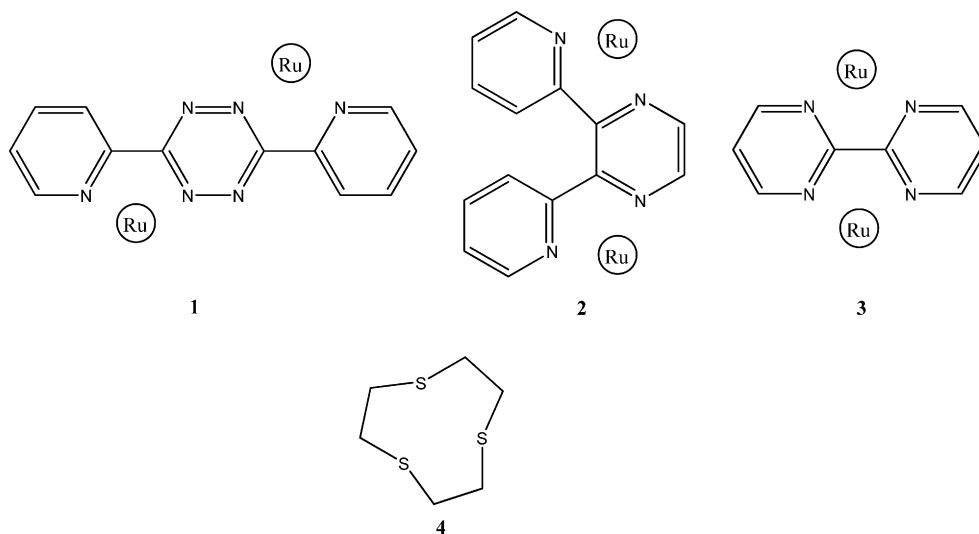
In the case of the isovalent Ru(II) binuclear complexes, mentioned above, the inner sphere $[(Ru[9]aneS_3Cl)_2(\mu L)]^{2+}$ ions already exist in solution, thus further oxidation in the electrospray needle, in the positive ion mode, could lead to the formation of triply charged mixed valence species $[(Ru[9]aneS_3Cl)_2(\mu L)]^{3+}$.

Also, in previous studies, we have observed that mononuclear ruthenium(II) complexes with polypyridyl ligands and the crown thioether $[9]aneS_3$, when electrosprayed from solutions, presented a characteristic gas-phase fragmentation, with formation of penta-coordinated diagnostic ions [23].

We then used electrospray mass spectrometry (ESI/MS) and electrospray mass spectrometry/mass spectrometry (ESI/MS/MS), in the positive ion mode, to investigate the correlations of the gas-phase behaviour of the $[(Ru[9]aneS_3Cl)_2(\mu L)](PF_6)_2$ complexes with their electrochemical and spectroscopic properties, including a possible formation of Ru^{III}/Ru^{II} mixed valence species. We also

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Scheme 1.

Table 1
Compounds and monoisotopic masses

Compound	Formula	Monoisotopic mass (Da)
1	bptz	236
2	dpp	234
3	bpym	158
4	[9]aneS ₃	180
5	[(Ru[9]aneS ₃ Cl) ₂ (bptz)](PF ₆) ₂	1160
6	[(Ru[9]aneS ₃ Cl) ₂ (dpp)](PF ₆) ₂	1158
7	[(Ru[9]aneS ₃ Cl) ₂ (bpym)](PF ₆) ₂	1082

wanted to find out the differences between their gas-phase fragmentation patterns and the gas-phase fragmentations patterns of their mononuclear counterparts.

We observed that, although formation of the [(Ru[9]aneS₃Cl)₂(μL)]³⁺ species did not occur and although some of the gas-phase processes are similar to those of the mononuclear species, the presence of two connected metal centres leads to the formation of specific ionic species, in particular for the compound with the tetrazine **1**.

2. Experimental

The complexes have been synthesized according to published procedures [14,15] and characterized by elemental analysis, ¹H-RMN, UV/vis and FTIR. X-ray single crystal spectroscopic data for compound **7** was available from a previous study [15].

Electrospray mass spectra were acquired with a Micromass Q-ToF 2 (Micromass, Manchester, UK), with a Z-spray source, an electrospray probe, and a syringe pump, operating in the positive ion mode. Source block and desolvation temperatures were 80 and 120–150 °C, respectively. The capillary voltage was 3000 V. The instrument was operated at a nominal resolution of 9000 (50% valley). The spectra were acquired for a range of cone voltages (30–60 V) in order to obtain good signal-to-noise ratio, either for the precursor, or for the fragment ions of interest. Nitrogen was used as nebuliser gas and argon as the collision gas. The samples were dissolved in chloroform and a 50:50 methanol–water mixture was used as the eluent. The samples were introduced at a flow rate of 10 μl min⁻¹.

Product ion spectra were obtained by selecting the ion of interest with the quadrupole analyser and using the hexapole collision cell, for a range of collision energies (20–80 eV).

3. Results and discussion

3.1. ESI mass spectra of the M(PF₆)₂ coordination compounds

The data obtained from the electrospray mass spectra revealed the presence of ions characteristic of the binuclear species, such as the inner sphere complexes [(Ru[9]aneS₃Cl)₂(μL)]²⁺ and the adducts with one counter ion [(Ru[9]aneS₃Cl)₂(μL)](PF₆)⁺. A mononuclear species [Ru([9]aneS₃)Cl(μL)]⁺, corresponding to the loss of a Ru([9]aneS₃)Cl moiety was also observed. In Table 2 the formulae and the mass to charge ratios, *m/z*, of the ions observed in the ESI mass spectra are shown.

The relative abundances of the observed species vary with the cone voltages. With the increase of cone voltage, the relative abundances of the doubly charged ions, M²⁺, decrease and new doubly charged species, formed by ethene losses from the crown, are observed. The relative abundances of the singly charged species, in special of the [(Ru[9]aneS₃Cl)₂(μL)](PF₆)⁺ adducts, increase with increasing cone voltage, although other singly charged ions, formed by HCl and CH₂CH₂ losses, are also observed.

Adducts with the PF₆⁻ counterion with the whole complexes and with fragments, have been reported in the case of bimetallic complexes of rhodium(III), iridium(III) and ruthenium(II) with the bridging ligand 1,4,5,8,9,12-hexaazatriphenylene, at several cone voltages, when using ESI-MS in the positive ion mode [24].

3.2. Product ion spectra

Product ion spectra were obtained for the [(Ru[9]aneS₃Cl)₂(μL)]²⁺, [(Ru[9]aneS₃Cl)₂(μL)](PF₆)⁺ and [Ru([9]aneS₃)Cl(μL)]⁺ ions.

Table 2
Formulae and mass to charge ratio, *m/z*, of the ions from ESI mass spectra

Compound	Ions (formula and <i>m/z</i>) ^a		
	[(Ru[9]aneS ₃ Cl) ₂ (μL)](PF ₆) ⁺	[(Ru[9]aneS ₃ Cl) ₂ (μL)] ²⁺	[Ru([9]aneS ₃)Cl(μL)] ⁺
5	1015	435	553
6	1013	434	551
7	937	383	475

^a *m* = monoisotopic mass.

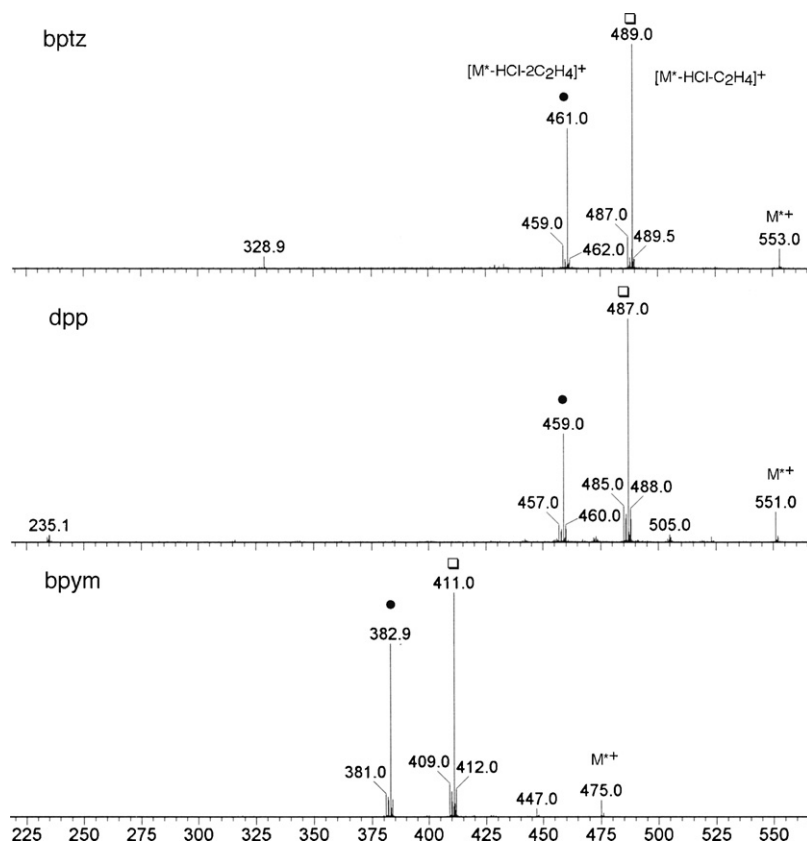


Fig. 1. Product ion spectra of the $[\text{Ru}(\text{9)aneS}_3]\text{Cl}(\mu\text{L})^+$ ions at cone voltage 50 V and collision energy 70 eV ($M^{*+} = [\text{Ru}(\text{9)aneS}_3]\text{Cl}(\mu\text{L})^+$).

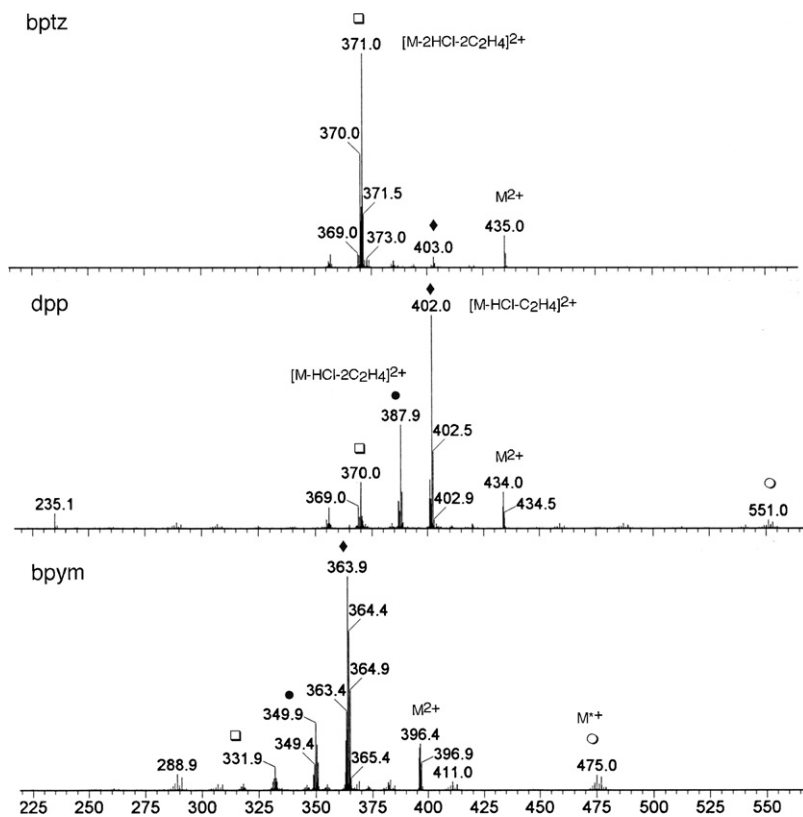


Fig. 2. Product ion spectra of the $[(\text{Ru}(\text{9)aneS}_3\text{Cl})_2(\mu\text{L})]^{2+}$ ions at cone voltage 30 V and collision energy 50 eV ($M^{2+} = [(\text{Ru}(\text{9)aneS}_3\text{Cl})_2(\mu\text{L})]^{2+}$).

The product ion spectra of the mononuclear species $[\text{Ru}(\text{[9]aneS}_3)\text{Cl}(\mu\text{L})]^+$ (shown in Fig. 1, cone voltage 50 V, collision energy 70 eV) are similar for the three compounds and show the diagnostic ions formed by losses of 64 and 92 Da, respectively, the $[\text{Ru}(\text{[9]aneS}_3)\text{Cl}(\mu\text{L})-\text{HCl}-\text{C}_2\text{H}_4]^+$ and the $[\text{Ru}(\text{[9]aneS}_3)\text{Cl}(\mu\text{L})-\text{HCl}-2\text{C}_2\text{H}_4]^+$ ions.

Losses of C_2H_4 (alone or with $\text{C}_2\text{H}_4\text{O}$) were observed in the dissociation of monocharged transition metal/polyether complex ions, in a quadrupole ion trap instrument, by Brodbelt and collaborators [25,26]. The authors proposed a mechanism for ethene elimination involving two successive 1, 3 hydrogen shifts, with the formation of ketone and alcohol functionalities [26].

Joint losses of the labile chloride and one hydrogen atom from the crown, plus one and two ethene molecules, from the macrocycle, have been reported for the mononuclear $[\text{Ru}(\text{[9]aneS}_3)\text{Cl}(\text{NN})]^+$ ions, where NN are bidentate ligands such 2,2'-bipyridine and dipyrrodo[3,2-a:2',3'-c]phenazine, the cleavage of the C–S bonds being triggered by π backbonding of Ru(II) d electrons to antibonding σ^* C–S orbitals [23].

The product ion spectra of the inner sphere complexes $[(\text{Ru}(\text{[9]aneS}_3)\text{Cl})_2(\mu\text{L})]^{2+}$ are similar for compounds 6 and 7. The base peaks in the product ion spectra of the ions $[(\text{Ru}(\text{[9]aneS}_3)\text{Cl})_2(\text{dpp})]^{2+}$ and $[(\text{Ru}(\text{[9]aneS}_3)\text{Cl})_2(\text{bpym})]^{2+}$ correspond to the ions formed by losses of 64 Da (HCl plus CH_2CH_2 from the crown). In contrast the only important fragment in the product ion spectra of the $[(\text{Ru}(\text{[9]aneS}_3)\text{Cl})_2(\text{bptz})]^{2+}$ ion, is the ion formed by a loss of 92 Da (loss of HCl plus two ethene molecules). The mononuclear species $[\text{Ru}(\text{[9]aneS}_3)\text{Cl}(\mu\text{L})]^+$, formed by charge partitioning, is also only observed for compounds 6 and 7.

The product ion spectra of the doubly charged binuclear species (cone voltage 30 V, collision energy 50 eV) are shown in Fig. 2.

Ions formed by charge partitioning were observed before, when using ESI-MS, in the product ion spectra of doubly charged binuclear and quadruply charged tetranuclear ruthenium(II) complex ions with the bridging ligand trans-1,2-bis(4-pyridyl)ethylene [27,28].

The differences in the behaviour of compound 5 are heightened in the product ion spectra of the adduct ions $[(\text{Ru}(\text{[9]aneS}_3)\text{Cl})_2(\mu\text{L})](\text{PF}_6)^+$. Although the base peaks are the same for all the compounds and may correspond to the $[\text{Ru}_2(\text{[9]aneS}_3-\text{H}-\text{C}_2\text{H}_4)(\text{[9]aneS}_3-\text{H})\text{Cl}(\mu\text{L})]^+$ ions, and although the ions corresponding to the mononuclear species $[\text{Ru}(\text{[9]aneS}_3)\text{Cl}(\mu\text{L})]^+$, are observed for all the compounds, in the case of compound 5, ions resulting from the elimination of a neutral PF_5 alone (formation of the $[(\text{Ru}(\text{[9]aneS}_3)\text{Cl})_2(\mu\text{L})]\text{F}^+$ ion, m/z 889) or alongside with other losses from the crown, give rise to abundant ions. The latter include the second most abundant ion (m/z 861), formed by the joint loss of PF_5 plus ethene from one of the crowns $[\text{Ru}_2(\text{[9]aneS}_3-\text{C}_2\text{H}_4)\text{Cl}(\text{[9]aneS}_3)\text{Cl}(\text{bptz})]\text{F}^+$. Other ions of the same group are m/z 797, m/z 769, m/z 741 and m/z 713, to which the following formulae may be attributed $[\text{Ru}_2(\text{[9]aneS}_3-\text{C}_2\text{H}_4)\text{Cl}(\text{[9]aneS}_3-\text{H}-\text{C}_2\text{H}_4)(\text{bptz})]\text{F}^+$, $[\text{Ru}_2(\text{[9]aneS}_3-2\text{C}_2\text{H}_4)\text{Cl}(\text{[9]aneS}_3-\text{H}-\text{C}_2\text{H}_4)(\text{bptz})]\text{F}^+$, $[\text{Ru}_2(\text{[9]aneS}_3-2\text{C}_2\text{H}_4)\text{Cl}(\text{[9]aneS}_3-\text{H}-2\text{C}_2\text{H}_4)(\text{bptz})]\text{F}^+$ and $[\text{Ru}_2(\text{[9]aneS}_3-3\text{C}_2\text{H}_4)\text{Cl}(\text{[9]aneS}_3-\text{H}-2\text{C}_2\text{H}_4)(\text{bptz})]\text{F}^+$, respectively.

In Fig. 3 the product ion spectra of the adduct ions $[(\text{Ru}(\text{[9]aneS}_3)\text{Cl})_2(\mu\text{L})](\text{PF}_6)^+$, for all the compounds (cone voltage 50 V, collision energy 70 eV), are shown.

Although formation of the mononuclear ions $[\text{Ru}(\text{[9]aneS}_3)\text{Cl}(\mu\text{L})]^+$, is observed in the gas-phase from both the $[\text{Ru}(\text{[9]aneS}_3)\text{Cl}(\mu\text{L})]^{2+}$, and $[\text{Ru}(\text{[9]aneS}_3)\text{Cl}(\mu\text{L})](\text{PF}_6)^+$ precursor ions, it is not a predominant process when compared with the formation of other fragment ions, which indicates that it occurs predominantly during the electrospraying process.

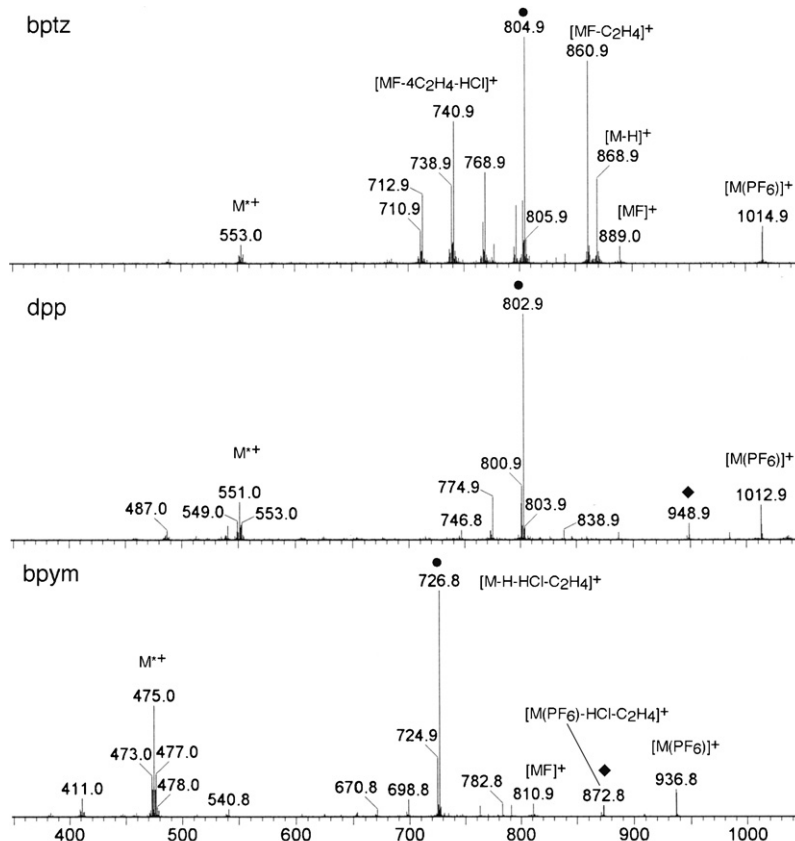
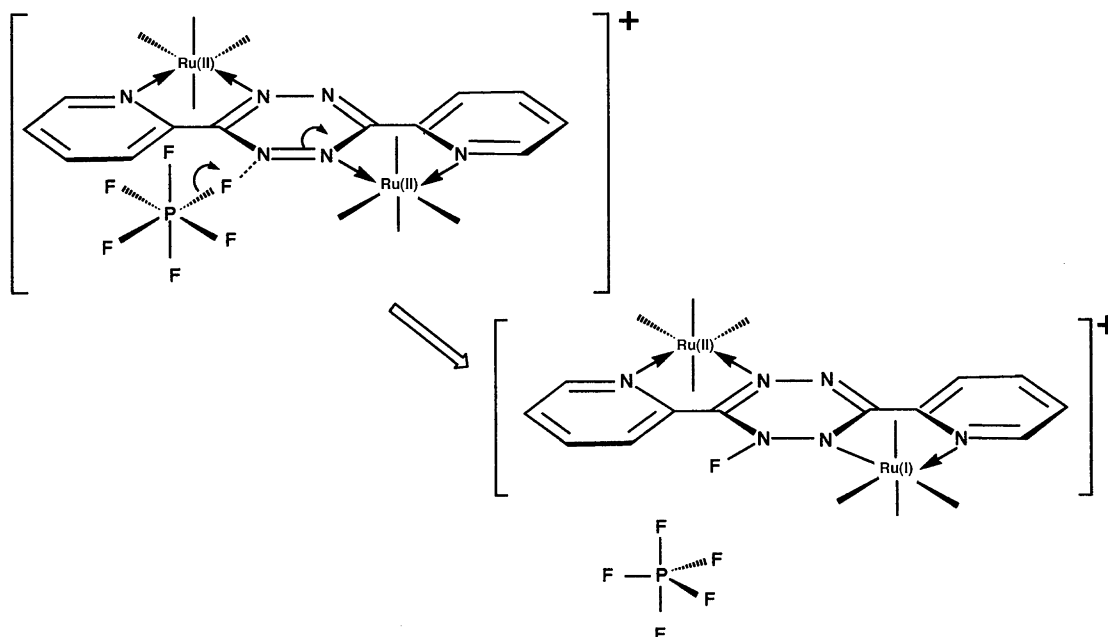


Fig. 3. Product ion spectra of the adduct ions $[(\text{Ru}(\text{[9]aneS}_3)\text{Cl})_2(\mu\text{L})](\text{PF}_6)^+$ at cone voltage 50 V and collision energy 70 eV ($[\text{M}(\text{PF}_6)]^+ = [(\text{Ru}(\text{[9]aneS}_3)\text{Cl})_2(\mu\text{L})](\text{PF}_6)^+$).



Scheme 2.

The data show that the binuclear compound **5**, with the tetrazine bridging ligand, has a different gas-phase behaviour from the other two compounds. The doubly charged binuclear complex $[\text{Ru}(\text{[9]aneS}_3)\text{Cl}(\mu\text{L})]^{2+}$, fragments less extensively than the corresponding ions of the other two compounds, and the most abundant ion corresponds to a joint loss of the elements of two hydrogen chloride and two ethene molecules, probably from the two opposing RuCl thiacycrown moieties. The adduct ion $[\text{Ru}(\text{[9]aneS}_3)\text{Cl}(\mu\text{L})]\text{PF}_6^+$, fragments mostly through PF_5 losses (alone or with losses of other fragments) with formation of abundant fragment ions.

The typical range of the metal–metal distances found for the compounds with the three bridging ligands are similar (6.742 Å for bptz, 6.779–7.026 Å for dpp and 5.370–6.247 Å for bpym) [15], thus the M^{2+} complexes will possess similar stabilities in what concerns electrostatic repulsions, then the different behaviour of compound **5** must be due to other causes.

The complexes have similar structures and all the bridging ligands can behave as π acceptors, thus formation of adducts with the counter ion PF_6^- , through π interactions of one peripheral fluoride atom with the bridging ligands is possible. As the adduct formation with the fluoride anion occurs predominantly for the complex with bptz, this behaviour must be related with other characteristic properties of this bridging ligand. It has been reported, for other binuclear complexes with the bridging bptz and bpym ligands, that the complexes with bptz have low-lying LUMOs (lowest unoccupied molecular orbitals) than their analogues with bpym [29]. Also EPR data showed that for the complex with bptz the LUMO is located on the tetrazine bridge [15]. More recently it has been shown that π interactions of the counter ion PF_6^- with the central tetrazine ring play an important role in the solid state assembly of other binuclear bptz-bridged metal complexes [30].

In the case of the $[(\text{Ru}[\text{9]aneS}_3\text{Cl})_2(\text{bptz})]\text{F}^+$ adduct the fluoride ion is more strongly bound to the central tetrazine ring. It is possible that it may react in a nucleophilic aromatic addition with the bptz bridge (Scheme 2) this process being facilitated by an electronic transition through the bridging ligand with formation of a $\text{Ru(I)}/\text{Ru(II)}$ ($4d^7/4d^6$) mixed valence complex, similarly to charge recombination processes observed for other binuclear ruthenium complexes [31].

The focus on ligand-bridged mixed valence ruthenium compounds is mainly on $\text{Ru(II)}/\text{Ru(III)}$ ($4d^6/4d^5$) complexes (due to their inertness and chemical stability) [9]. However other species such as diruthenium $\text{Ru(III)}/\text{Ru(IV)}$ ($4d^5/4d^4$) have been described, as well as dinuclear compounds with other metals with lower oxidation number combinations such as dirhodium (I,II) ($4d^8/4d^7$) [5,15]. Thus the formation of a $\text{Ru(I)}/\text{Ru(II)}$ ($4d^7/4d^6$) mixed valence complex through fluoride addition to bptz is possible and may be the trigger for the dissociation of the PF_5 neutral moiety, with the formation of the $[(\text{Ru}[\text{9]aneS}_3\text{Cl})_2(\mu\text{L})]\text{F}^+$ ions.

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