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# Characterization and differentiation of ruthenium(II) complexes with 1,4,7-trithiacyclononane and nitrogen heterocycles by electrospray mass spectrometry

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Electrospray ionization mass spectrometry (ESIMS) was used to characterize a series of new ruthenium(II) complexes with several nitrogen heterocycles and a common ligand: the crown thioether 1,4,7-trithiacyclononane, [9]aneS<sub>3</sub>. ESIMS allows the easy identification of the [Ru<sup>II</sup>Cl([9]aneS<sub>3</sub>)Y]X complexes, where Y is a bidentate nitrogen heterocycle and X is Cl<sup>−</sup> or PF<sub>6</sub><sup>−</sup>, through the formation of two diagnostic ions by fragmentation of the common ligand [9]aneS<sub>3</sub>. Structures for these ions and mechanisms for their gas-phase formation are proposed based on data from product ion spectra. Copyright © 2001 John Wiley & Sons, Ltd.

**KEYWORDS:** ruthenium complexes; crown thioether; bidentate nitrogen heterocycles; diagnostic ions; electrospray mass spectrometry

## INTRODUCTION

Ruthenium(II) complexes of nitrogen heterocycles with extended  $\pi$ -systems, such as 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen) and dipyrrodo[3,2-*a*:2',3'-*c*]phenazine (dppz), have been tested as probes for DNA structure and conformation since 1976.<sup>1–4</sup> Two different types of interaction between these complexes and DNA have been described: intercalation between the stacked base pairs and binding along the grooves, the type of binding being dependent both on the nitrogen heterocycle and on the other ligands.<sup>5–7</sup>

The study of the chemical and structural characteristics of ruthenium(II) complexes with different potential intercalating ligands and one common, non-intercalating ligand could clarify the mechanism of the interaction of these complexes with DNA. The crown thioether 1,4,7-trithiacyclononane, [9]aneS<sub>3</sub>, (ligand **16**, Fig. 1) forms stable octahedral complexes with several middle and late transition elements, coordinating in a facial manner,<sup>8</sup> and cannot intercalate between the DNA bases. [9]aneS<sub>3</sub> was chosen as the common, non-intercalating ligand for the synthesis of a new series of ruthenium(II) five-membered chelates of nitrogen heterocycles, [Ru<sup>II</sup>Cl([9]aneS<sub>3</sub>)Y]X, where Y is one of the nitrogen heterocycles in Fig. 1 and Table 1 (compounds **1–9**) and X is Cl<sup>−</sup> or PF<sub>6</sub><sup>−</sup>.

Electrospray ionization mass spectrometry (ESIMS) has been used to study transition metal complexes and their reactions in solution since 1990, when Chait and co-workers<sup>9</sup> applied ESIMS to the complexes [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> and [Ru(phen)<sub>3</sub>]Cl<sub>2</sub>. ESIMS was also applied to both tris(bpy)Ru<sup>II</sup> complexes and bis(bpy)Ru<sup>II</sup> complexes with other ligands by Arakawa *et al.*<sup>10</sup> Arakawa and co-workers also used ESI to study photosubstituted bis(bpy)Ru<sup>II</sup> and related complexes.<sup>11,12</sup>

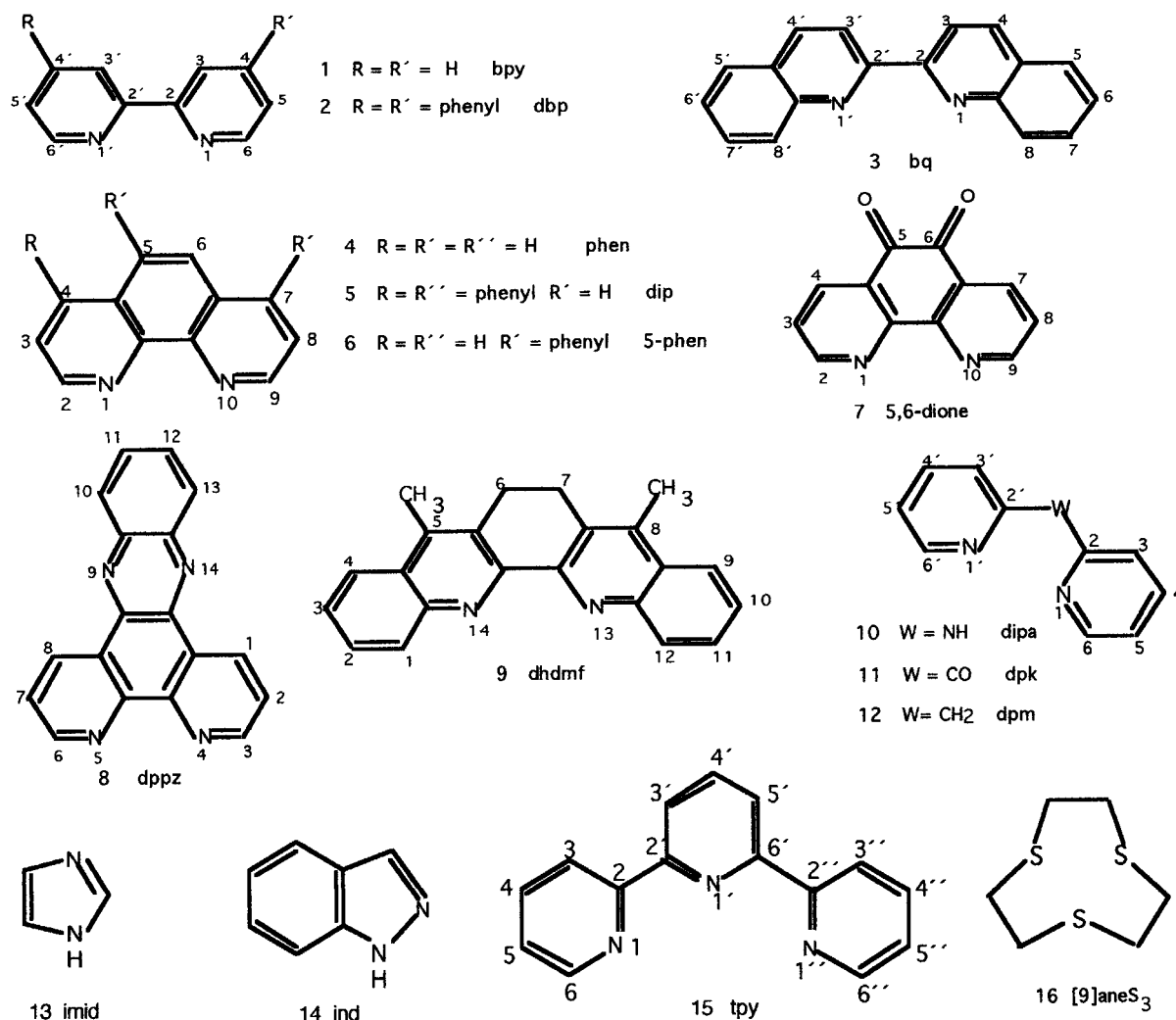
Tris(bpy)Fe<sup>II</sup> and tris(bpy)Ni<sup>II</sup> complexes were used by Gatlin and Turecek<sup>13</sup> as model systems to study the acidity of microdroplets formed by electrospray, and Shen and Brodbelt<sup>14</sup> used electrospray to generate doubly charged mixed-ligand complexes of several transition metals with polyether–pyridyl ligands.

When using ESIMS to characterize the synthesized [Ru<sup>II</sup>Cl([9]aneS<sub>3</sub>)Y]X complexes, we found that it was specially suited for this purpose, owing to the formation of two diagnostic ions. In order to confirm these findings, we further used ESIMS to study other Ru<sup>II</sup>([9]aneS<sub>3</sub>) complexes with different types of nitrogen heterocycles (Fig. 1 and Table 1): monodentate ligands (imidazole and indazole, compounds **13** and **14**), a potential tridentate ligand (terpyridine, compound **15**) and bidentate six-membered chelating ligands (compounds **10–12**).

## EXPERIMENTAL

The [Ru<sup>II</sup>Cl([9]aneS<sub>3</sub>)Y]X complexes (Y = bpy, dbp, bq, phen, dip, 5-phen, 5,6-dione, dppz, dhdmf, dipa,

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Contract/grant sponsor: University of Aveiro.

**Figure 1.** Structures of the nitrogen heterocyclic ligands.**Table 1.** Nomenclature of the nitrogen heterocyclic ligands

No.	Name	Abbreviation
1	2, 2'-Bipyridine	bpy
2	4, 4'-Diphenyl-2, 2'-bipyridine	dbp
3	2, 2'-Biquinoline	bq
4	1,10-Phenanthroline	phen
5	4,7-Diphenyl-1,10-phenanthroline	dip
6	5-Phenyl-1,10-phenanthroline	5-phen
7	1,10-Phenanthroline-5,6-dione	5,6-dione
8	Dipyrido[3,2- <i>a</i> :2',3'- <i>c</i> ]phenazine	dppz
9	6,7-Dihydro-5,8-dimethyldibenzo- [ <i>b</i> , <i>j</i> ][1,10]-phenanthroline	dhdmf
10	2, 2'-Dipyridylamine	dipa
11	2, 2'-Dipyridyl ketone	dpk
12	2, 2'-Dipyridylmethane	dpm
13	Imidazole	imid
14	Indazole	ind
15	2, 2' : 6' , 2''-Terpyridine	tpy

dpk, dpm and tpy, Fig. 1, and  $X = Cl^-$ ,  $PF_6^-$ ) and  $[Ru^{II}Cl([9]aneS_3)dmsolZ]Cl$ , where Z is imid or ind and dmso is dimethyl sulfoxide, were synthesized by the

reaction of the thioether,  $[9]aneS_3$ , with the complex  $cis-[Ru^{II}Cl_2(dmso)_4]$ , in which the intermediate compound  $[Ru^{II}Cl_2([9]aneS_3)(dmso)]$  was formed, followed by the addition of the nitrogen ligands, under mild conditions: reflux, 80–95 °C, ethanol.<sup>15–17</sup>

The starting material  $cis-[Ru^{II}Cl_2(dmso)_4]$  was synthesized according to published procedures.<sup>18</sup>

The ligands  $[9]aneS_3$ , bpy, dbp, bq, phen, dip, 5-phen, dhdmf, dipa, dpk, ind, imid and tpy were purchased from Sigma-Aldrich and used without further purification. The ligands dpm, 5,6-dione and dppz were prepared according to published procedures.<sup>19–22</sup>

All the complexes were characterized by elemental analysis and UV–visible; IR and  $^1H$  NMR, spectroscopy. The complexes with bpy and phen<sup>15</sup> and dipa, bq, dip, dppz, dpk and dpm<sup>17</sup> were also characterized by single-crystal x-ray diffraction spectroscopy.

Mass spectra were acquired with a VG AutoSpecQ spectrometer (VG Analytical, Manchester, UK) working in an EBE geometry mode. The instrument was equipped with a VG electrospray source and a Phoenix 20CU syringe pump (Fisons Instruments). Methanol–water (50:50) was employed as the eluent. The applied accelerating voltage was 4 kV.

The electrospray parameters were optimized in order to obtain good signal-to-noise ratios for the ions of interest; the voltage was 2.5 kV and the average sampling cone voltage was 50 V. The mass spectrometer was operated at a nominal mass resolution of 1000 (10% valley). The spectra were obtained at a scan rate of 8 s decade<sup>-1</sup>.

The compounds were dissolved in methanol or in a few cases in acetonitrile. The concentration of the solutions varied from 0.1 to 0.2 mM.

Mass-analyzed ion kinetic energy collision-activated dissociation (MIKE-CAD) spectra were taken using helium as the collision gas at a pressure such as to reduce the precursor peak to nearly 50% of its original height. The above-mentioned experimental work was carried out at the University of Aveiro, Portugal.

In the course of publishing this work, the use of the VG electrospray source interfaced to the VG AutoSpecQ instrument was discontinued and a Micromass Q-Tof-2 instrument was installed at the University of Aveiro. With the latter instrument we acquired, for the complex [Ru<sup>II</sup>Cl([9]aneS<sub>3</sub>)(phen)]Cl, spectra at several cone voltages ranging from 10 to 60 V. The eluent was also methanol–water (50:50). The capillary needle voltage was 3 kV.

MS<sup>n</sup> spectra were acquired for the [Ru<sup>II</sup>Cl([9]aneS<sub>3</sub>)-(dppz)]Cl complex with a Finnigan (San Jose, CA, USA) LCQ ion trap mass spectrometer equipped with an ESI source. The samples were introduced with a syringe pump. The solvent system was a mixture of acetonitrile, water and methanol (200 ml of acetonitrile to 20 ml of a 50:50 water–methanol mixture). Collisional activation was done using helium by subjecting the precursor ions to kinetic excitation via a tickle voltage applied to the end caps. The MS<sup>n</sup> spectra were acquired at the Washington University Mass Spectrometry Resource (St Louis, MD, USA).

## RESULTS

### ES mass spectra

The ESI mass spectra of the complexes with the formula [Ru<sup>II</sup>Cl([9]aneS<sub>3</sub>)Y]X (Y = compounds **1–8**, Figure 1; X = Cl<sup>-</sup> or PF<sub>6</sub><sup>-</sup>) show the M<sup>+</sup> ions (we will use M<sup>+</sup> to represent the monocharged inner sphere ion, which in the present case is [Ru<sup>II</sup>Cl([9]aneS<sub>3</sub>)Y]<sup>+</sup>), with relative abundances varying from 16 to 55% of the respective base peaks, and the ions with *m/z* values corresponding to [M – 64]<sup>+</sup> and [M – 92]<sup>+</sup>. The [M – 92]<sup>+</sup> ions are either the base peaks or have high relative abundances (77–100%, Table 2). The protonated nitrogen ligand, YH<sup>+</sup>, is also observed, in general with low relative abundance, but no other significant ions are observed.

In order to confirm that the [M – 64]<sup>+</sup> and [M – 92]<sup>+</sup> ions are diagnostic for Ru<sup>II</sup>Cl([9]aneS<sub>3</sub>) complexes with bidentate nitrogen heterocycles, we also acquired the ESI mass spectra of the complexes [Ru<sup>II</sup>Cl([9]aneS<sub>3</sub>)Y]X, where Y is one of the ligands **10–12** (Fig. 1 and Table 1). The same pattern, with the same type of ions, was observed (Table 2), although for the complexes with dipa and dpk the base peaks correspond to the protonated nitrogen ligands, YH<sup>+</sup>.

The ESI mass spectrum of the [Ru<sup>II</sup>Cl([9]aneS<sub>3</sub>)dbp]Cl complex (dbp is ligand **2**, Fig. 1) is shown in Fig. 2 as an

**Table 2.** Relative abundances and mass<sup>a</sup> to charge ratios of the main ions in the ESI mass spectra of [Ru<sup>II</sup>Cl([9]aneS<sub>3</sub>)Y]X complexes (X = Cl<sup>-</sup>, PF<sub>6</sub><sup>-</sup>)

Y	<i>m/z</i> (RA (%))		
	M <sup>+</sup>	[M – 64] <sup>+</sup>	[M – 92] <sup>+</sup>
bpy	473(35)	409(16)	381(100)
dbp	625(55)	561(72)	533(100)
bq	573(31)	509(25)	481(95)
phen	497(26)	433(16)	405(100)
dip	644(16)	580(12)	552(100)
5-phen	573(24)	509(17)	481(100)
5,6-dione	527(30)	463(22)	435(100)
dppz	599(43)	535(33)	507(77)
dipa	488(34)	424(12)	396(23)
dpk	501(21)	437(47)	409(22)
dpm	487(85)	423(100)	395(22)
dhdmf	627(18)	563(12)	535(23)

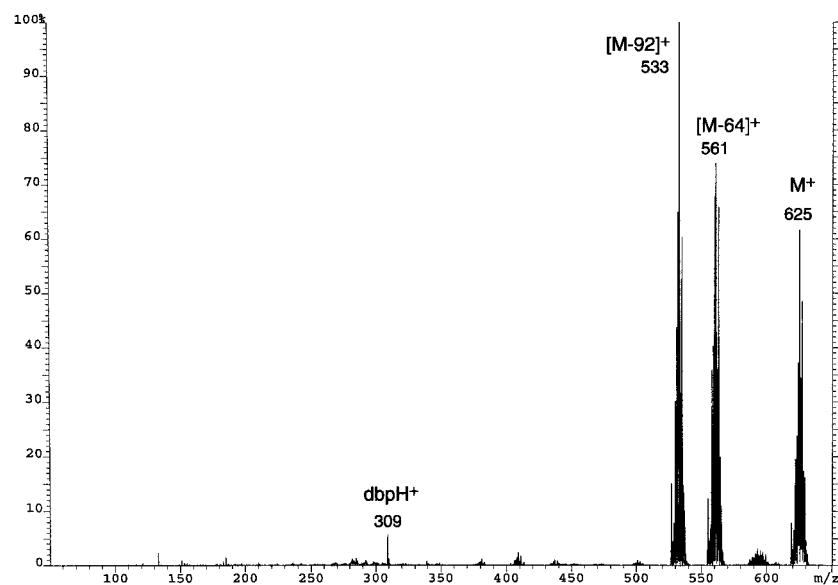
<sup>a</sup> The masses are the monoisotopic masses (<sup>102</sup>Ru isotope)

example of the ESI mass spectra of the [Ru<sup>II</sup>Cl([9]aneS<sub>3</sub>)Y]X complexes. In Fig. 3, parts of the ESI mass spectra, showing the isotopic patterns corresponding to the M<sup>+</sup>, [M – 64]<sup>+</sup> and [M – 92]<sup>+</sup> ions for the complexes with the ligand dbp and the ligand dipa (ligand **10**, Fig. 1), are illustrated. The similarity of the high-mass region of the spectra of the five-membered chelate [Ru<sup>II</sup>Cl([9]aneS<sub>3</sub>)dbp]Cl [Fig. 3a] and of the six-membered chelate [Ru<sup>II</sup>Cl([9]aneS<sub>3</sub>)dipa]Cl [Fig. 3b] is evident.

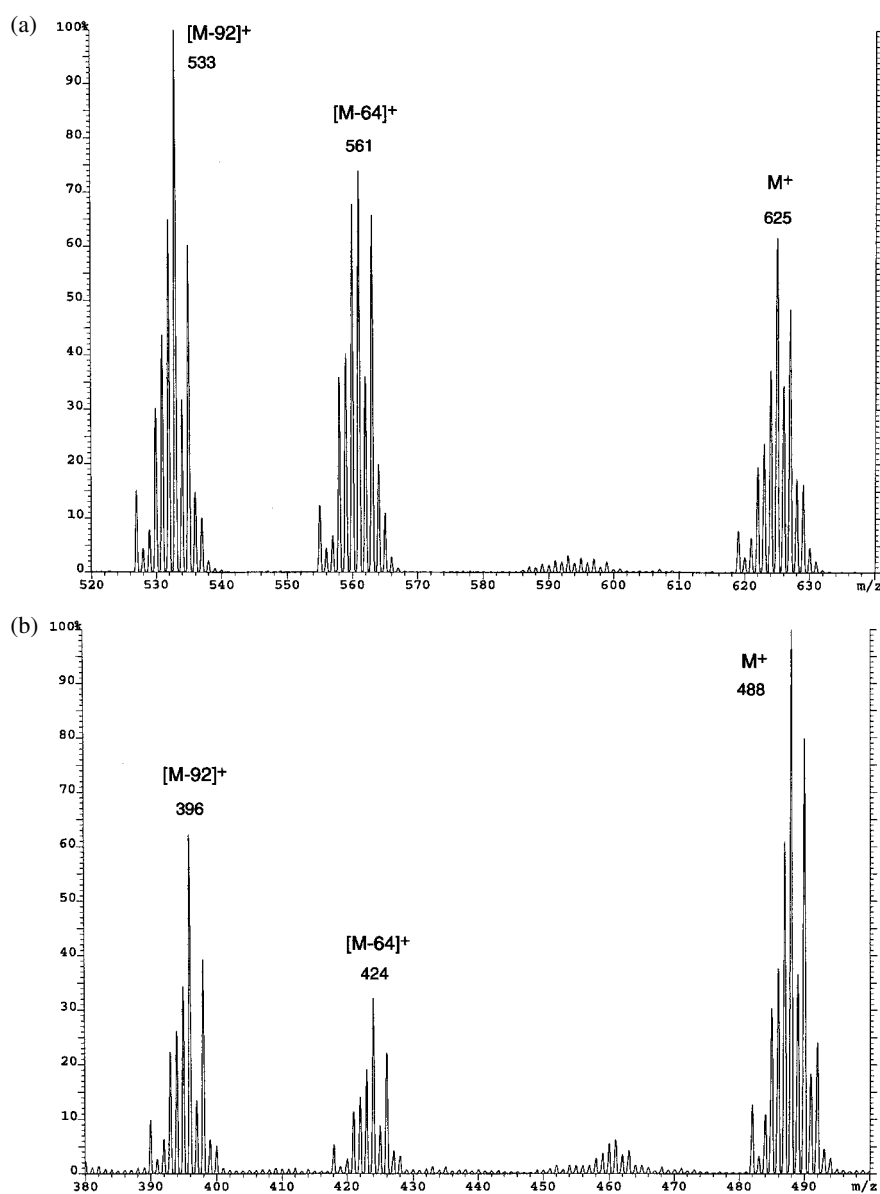
The attempt to isolate the complex with the bidentate ligand dhdmf (ligand **9**, Fig. 1) from the excess of non-reacting ligand was unsuccessful. However, the ESI mass spectrum of the solid obtained shows the M<sup>+</sup> ion and the diagnostic ions [M – 64]<sup>+</sup> and [M – 92]<sup>+</sup>, which is evidence that the complex was formed.

To test further the utility of the diagnostic ions for the differentiation of the complexes with bidentate nitrogen heterocycles, two complexes of monodentate nitrogen heterocycles, imid (imidazole, ligand **13**, Fig. 1) and ind (indazole, ligand **14**, Fig. 1) were also studied by ESIMS. The general formula of these complexes is [Ru<sup>II</sup>Cl([9]aneS<sub>3</sub>)dmsoZ]Cl, where Z is imid or ind and dmso is dimethyl sulfoxide. In both cases the M<sup>+</sup> ions are seen (M<sup>+</sup> = [Ru<sup>II</sup>Cl([9]aneS<sub>3</sub>)dmsoZ]<sup>+</sup>), but no ions corresponding to the [M – 64]<sup>+</sup> or [M – 92]<sup>+</sup> formulations can be observed. However, significant peaks corresponding to the ions [M – 106]<sup>+</sup> (ions formed by loss of dmso plus loss of 28 u) are observed for both complexes.

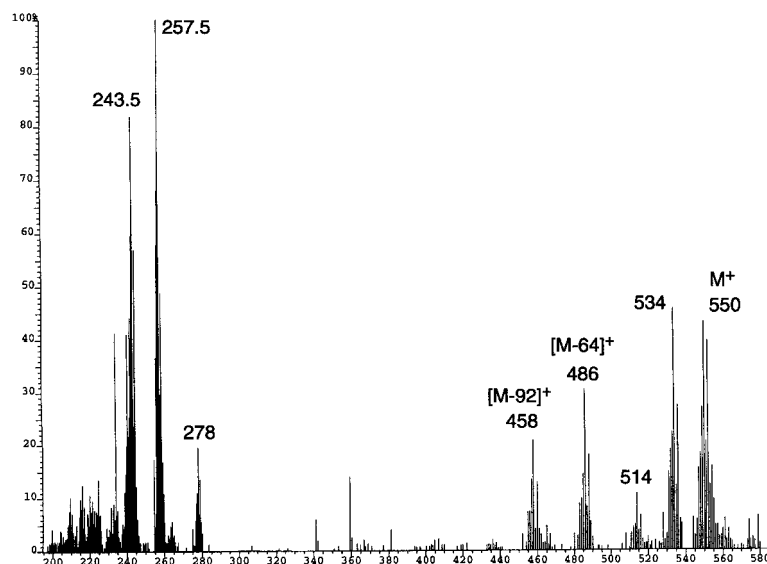
A final test of the utility of the diagnostic ions was the acquisition of ESI mass spectrum of the complex with tpy (terpyridine, ligand **15**, Fig. 1). Terpyridine is a potential tridentate ligand, but its ESI mass spectrum shows the characteristic ions of a bidentate complex, [M – 64]<sup>+</sup> and [M – 92]<sup>+</sup> (Fig. 4). We must bear in mind that the monocharged inner sphere ion [Ru<sup>II</sup>Cl([9]aneS<sub>3</sub>)tpy]<sup>+</sup> or M<sup>+</sup> (where tpy acts as a bidentate ligand) and the adduct species ([Ru<sup>II</sup>([9]aneS<sub>3</sub>)tpy]Cl)<sup>+</sup> or MCl<sup>+</sup> (where tpy acts as a tridentate ligand and M<sup>2+</sup> is the doubly charged inner sphere ion) cannot be easily differentiated, when formed by



**Figure 2.** ESI mass spectrum of the  $[\text{Ru}^{\text{II}}\text{Cl}([9]\text{aneS}_3)(\text{dbp})]\text{Cl}$  complex.



**Figure 3.** High-mass region of the ESI mass spectra of (a) the  $[\text{Ru}^{\text{II}}\text{Cl}([9]\text{aneS}_3)(\text{dbp})]\text{Cl}$  complex and (b) the  $[\text{Ru}^{\text{II}}\text{Cl}([9]\text{aneS}_3)(\text{dipa})]\text{Cl}$  complex.



**Figure 4.** ESI mass spectrum of the  $[\text{Ru}^{\text{II}}\text{Cl}([9]\text{aneS}_3)(\text{tpy})]\text{PF}_6$  complex.

electrospray. The presence of  $[\text{M} - 64]^+$  and  $[\text{M} - 92]^+$  ions confirms that  $\text{M}^+$  really corresponds to the monocharged inner sphere ion  $[\text{Ru}^{\text{II}}\text{Cl}([9]\text{aneS}_3)\text{tpy}]^+$  and that tpy is acting as a bidentate ligand. This behaviour was expected both from our x-ray, NMR and elemental analysis results<sup>17</sup> and from literature data.<sup>23</sup> Terpyridine acts as a tridentate ligand only in the absence of significant steric hindrance from the other ligands and if *mer* coordination is available.<sup>23</sup>

Although in the present case tpy behaves as a bidentate ligand, its mass spectrum is different from those of the other bidentate ligands. The doubly charged ions of  $m/z$  243.5 and 257.5 and the monocharged species of  $m/z$  514 and 534, observed in the ESI mass spectrum of the tpy complex (Fig. 4), are not observed in the mass spectra of the other bidentate complexes and are probably due to interactions of the pendant, non-coordinating pyridyl group with the chloride ion.

### MIKE-CAD and $\text{MS}^n$ spectra

Because the bidentate ligand Y varies, the  $[\text{M} - 64]^+$  and  $[\text{M} - 92]^+$  ions must arise from fragmentation of the crown thioether. To obtain more data on the formation and structure of these ions, the MIKE-CAD spectra of the  $\text{M}^+$ ,  $[\text{M} - 64]^+$  and  $[\text{M} - 92]^+$  ions were acquired and examined.

In the MIKE-CAD spectra of the  $\text{M}^+$  ions, the main fragment ions are formed by losses of 64 and 92 u for all the synthesized complexes, as can be seen in Fig. 5a, for the complex where Y is phen (ligand 14, Fig. 1). In the MIKE-CAD spectra of the  $[\text{M} - 64]^+$  ions the main product ions result from a loss of 28 u, giving the ions with the  $[\text{M} - 92]^+$  formulation, as can be seen in Fig. 5b, for the same complex. In the MIKE-CAD spectra of the  $[\text{M} - 92]^+$  ions, the main fragment ions are formed by loss of 59 u; the ions formed by loss of 33 u and the ions corresponding to the protonated nitrogen ligand are also observed, as can be seen in Fig. 5c, for the same complex.

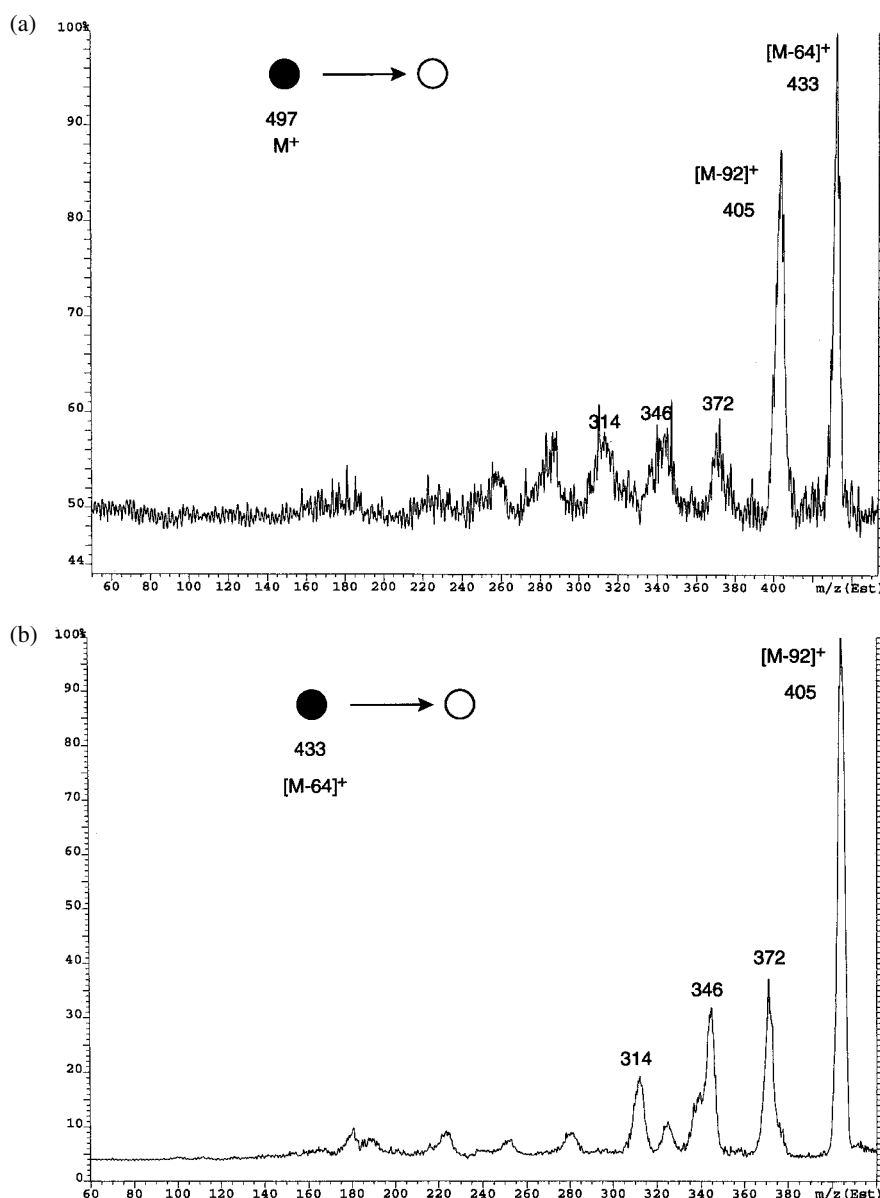
For a final confirmation of the structure and formation of the  $[\text{M} - 64]^+$  and  $[\text{M} - 92]^+$  ions,  $\text{MS}^n$  experiments using an ion trap were also performed for the complex with the ligand dppz (ligand 8, Fig. 1). The  $\text{MS}^2$  spectrum of the

$\text{M}^+$  ions,  $\text{M}^+ \rightarrow$  products, shows fragment ions formed by losses of 28, 64 and 92 u. The  $\text{MS}^3$  spectrum for the sequence  $\text{M}^+ \rightarrow [\text{M} - 64]^+ \rightarrow$  products shows only the ions formed by loss of 28 u, corresponding to the formulation  $[\text{M} - 92]^+$  (Fig. 6). The  $\text{MS}^4$  spectrum for the sequence  $\text{M}^+ \rightarrow [\text{M} - 64]^+ \rightarrow [\text{M} - 92]^+ \rightarrow$  products shows three main fragment ions, two formed by losses of 33 and 64 u and the third being the protonated nitrogen heterocycle,  $\text{dppzH}^+$ . This  $\text{MS}^4$  spectrum is slightly different from the MIKE-CAD spectra of the  $[\text{M} - 92]^+$  ions, where a loss of 59 u is observed, instead of a loss of 64 u.

### DISCUSSION

As it is apparent from the acquired data, the  $[\text{M} - 64]^+$  and  $[\text{M} - 92]^+$  ions arise from the fragmentation of the crown thioether, and not from fragmentation of the nitrogen heterocycles, especially if we recall that the protonated nitrogen heterocycle is formed by gas-phase fragmentation of the  $[\text{M} - 92]^+$  ions (MIKE-CAD and  $\text{MS}^4$  spectra for the complex with dppz). From the analysis of the data we propose that the  $[\text{M} - 64]^+$  ions are formed by a concomitant loss of an ethene molecule and a hydrogen atom, from the crown, and of the coordinated chloride atom. A second loss of an ethene molecule gives rise to the  $[\text{M} - 92]^+$  ions. Hence the  $[\text{M} - 64]^+$  and  $[\text{M} - 92]^+$  ions can be formulated as  $[\text{M} - \text{Cl} - \text{H} - \text{CH}_2\text{CH}_2]^+$  and  $[\text{M} - \text{Cl} - \text{H} - 2\text{CH}_2\text{CH}_2]^+$ , respectively.

The loss of the coordinated chloride atom points to a higher lability of this ligand in the case of the complexes with bidentate ligands, when compared with the complexes with monodentate ligands. This lability is especially apparent in the case of the complex with tpy, in which mass spectrum, besides the  $[\text{M} - 64]^+$  and  $[\text{M} - 92]^+$  ions, one can observe the doubly charged ions at  $m/z$  257.5 and 243.5 and the monocharged ions at  $m/z$  534 and 514. The doubly charged ions at  $m/z$  257.5 and 243.5 can be formulated as  $[\text{M} - \text{Cl}]^{2+}$  and  $[\text{M} - \text{Cl} - \text{CH}_2\text{CH}_2]^{2+}$  respectively, and the monocharged species at  $m/z$  534 and 514 can be formulated



**Figure 5.** MIKE-CAD spectra of selected ions of the  $[\text{Ru}^{\text{II}}\text{Cl}(\text{9]aneS}_3)(\text{phen})]\text{Cl}$  complex: (a)  $\text{M}^+$  ion; (b)  $[\text{M} - 64]^+$  ion; (c)  $[\text{M} - 92]^+$  ion.

as  $[\text{M} - \text{Cl} + \text{F}]^+$  and  $[\text{M} - \text{Cl} - \text{H}]^+$ . The presence of all these ions points to a increased lability of the Cl ligand, caused by steric hindrance due to the non-coordinated pyridyl group. This is specially apparent in the case of the  $[\text{M} - \text{Cl} + \text{F}]^+$  ion. The coordination of a relatively large species such as the chloride ion causes a considerable steric interaction with the pendant pyridyl group, but the coordination of smaller ions, such as the fluoride ion (arising from the  $\text{PF}_6^-$  counter ion) is possible.

The data from the MIKE-CAD and  $\text{MS}^n$  spectra show that the diagnostic ions  $[\text{M} - 64]^+$  and  $[\text{M} - 92]^+$  are formed in the gas phase. In Scheme 1 we propose mechanisms for their formation and possible structures. The chlorine and hydrogen atoms are lost probably as HCl, as this process is more favourable energetically, than the loss of two radicals.

In Scheme 1 we used a convention proposed some years ago by Westmore and Fung<sup>24</sup> for the representation of the bonds connecting the metal centre with the coordinating

atoms. In this convention, for the bonds represented by arrows, the electrons are attributed to the donor atom, whereas in the bonds represented by straight lines, the electrons are attributed one to the metal centre and the other to the coordinating atom.

The concurrent/posterior loss of ethene leading to the formation of the  $[\text{M} - 64]^+$  ion and the posterior loss of the same molecule leading to the formation of the  $[\text{M} - 92]^+$  ion (Scheme 1) point to a weakening of some of the S—C bonds in the crown, when compared with the coordinating S—Ru bonds. The loss of a methylene hydrogen atom may activate the S—C cleavage, but some of the S—C bonds are probably weakened by  $\pi$  back-donation of the  $t_{2g}$  electrons of the metal centre to the S—C  $\sigma^*$  orbitals.

If we assume an octahedral geometry for the  $\text{Ru}^{\text{II}}$  complexes studied, from crystallographic and other data, then the  $t_{2g}$  orbitals are completely filled. Thus the empty S—C  $\sigma^*$  orbitals lying in the plane of the filled  $t_{2g}$  orbitals,

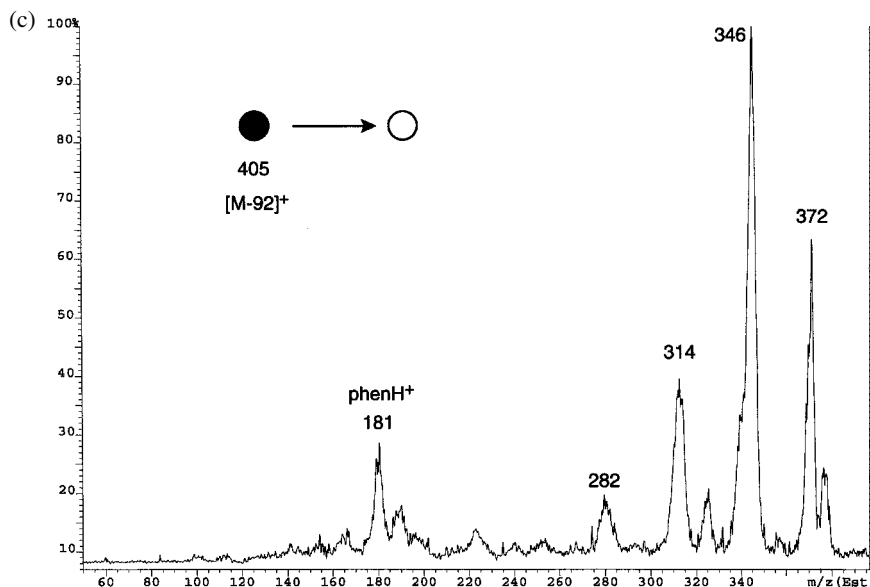
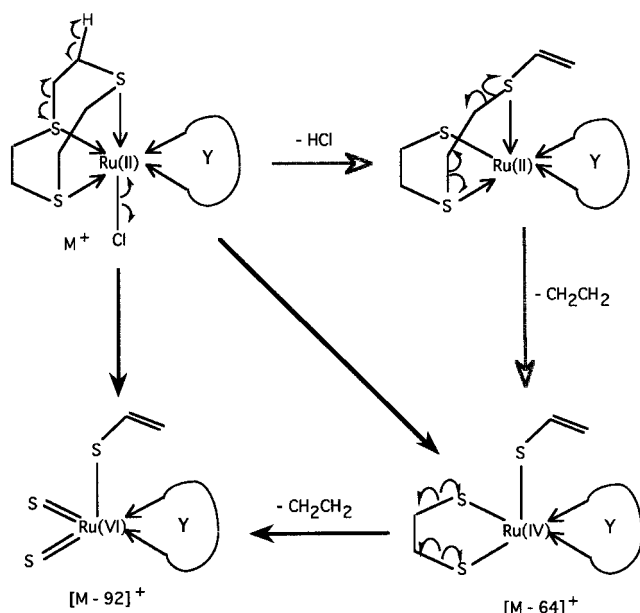


Figure 5. (Continued).



Scheme 1

can accept the  $t_{2g}$  electrons. One of the S—C bonds of the thioether chelate rings will thus be lengthened and will require less energy to break.<sup>25</sup>

The  $\pi$  back-donation is probably the major factor responsible for the ethylene losses. This is specially the case with the  $[M - Cl - CH_2CH_2]^{2+}$  ions in the case of the tpy complex and the  $[M - 106]^+$  ions ( $[M - dmsO - CH_2CH_2]^+$ ) in the case of the complexes with monodentate ligands.

Gas-phase ethene losses were already reported for  $[Met([9]aneS_3)_2]^{2+}$  complexes (Met = Re, Ru, Tc, Os) formed by electrospray by Mullen *et al.*<sup>25</sup> Using tandem mass spectrometry the same authors related ethene loss to the extent of  $\pi$  back-bonding for the different metal centres.<sup>25</sup>

From what has been said above, the structure of the diagnostic ions  $[M - Cl - H - CH_2CH_2]^+$  and  $[M - Cl - H - 2CH_2CH_2]^+$  requires a penta-coordination of the  $Ru^{II}$

centre, with a square pyramid geometry for the inner coordination sphere (Scheme 1). This geometry is not very common for  $Ru^{II}$  complexes, but has been reported for dithiolene ruthenium complexes.<sup>26</sup> The assignment of a formal oxidation state in the case of the latter<sup>26</sup> and in the case of the present complex ions is somewhat arbitrary. The description of the present species as  $Ru^{II}$  complexes means that the six 4d electrons are essentially localized in the metal centre.<sup>27</sup> It is mostly for electron book-keeping purposes that in Scheme 1 we have attributed formal oxidation states to the metal centres.

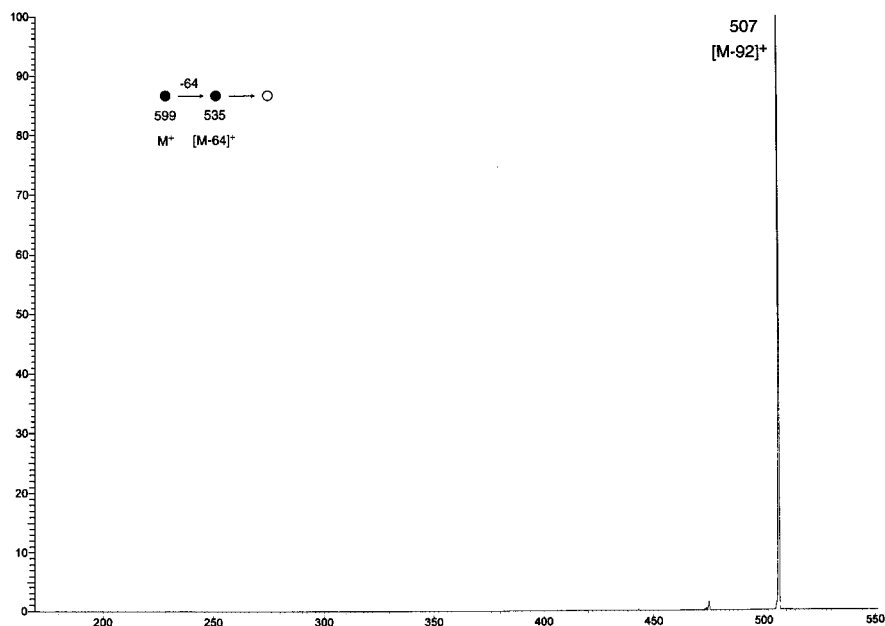
It is generally accepted that it is the solution chemistry that determines the electrospray spectra<sup>28,29</sup> but in the electrospray process the composition of the droplets may be different from that of the bulk of the solution<sup>13</sup> and the work of Shen and Brodbelt<sup>14</sup> shows that the electrospray process in itself may enhance the formation of species that might be not favoured in solution.

In the present case, with the exception of the complex with terpyridine, no doubly charged ions were observed. We could then assume that ion–molecule collisions in the interface did not play an important role in ion formation and that the charge states of gaseous ions reflected, in general, the charge states in solution.<sup>29</sup> Also, as no multimetric species were observed, we could further suggest that the ESI mass spectra reflected the ionic composition of the condensed phase.

In the case of the  $[M - 64]^+$  ion, its formation in the condensed phase would proceed by a loss of chloride ion accompanied or preceded by the loss of a proton, with the opening of the crown and ethenethiolate formation. Thus a joint loss of H and Cl, either in the condensed or in the gas phase, would give rise to a similar intermediate ionic structure.

Moreover, condensed-phase formation of the diagnostic ions (or at least of the  $[M - 64]^+$  ion) was to be expected, based on published data for similar complexes. The acidity of the methylene protons in the  $[9]aneS_3$





**Figure 6.**  $MS^3$  spectrum for the sequence  $M^+ \rightarrow [M - 64]^+ \rightarrow$  products for the  $[Ru^{II}Cl([9]aneS_3)(dppz)]Cl$  complex.

crown is enhanced by the positive charge in the metal centre. Base-induced deprotonations of methylene carbons, followed by ring opening and ethenethiolate formation, have been reported for several complex ions with the same crown,  $[Met([9]aneS_3)_2]^{3+}$  ( $Met = Co, Rh, Ir$ ), in the condensed phase.<sup>30</sup> Also, when several reducing agents were added in water to the complex ions  $[Met([9]aneS_3)_2]^{2+}$  ( $Met = Re, Tc$ ), the cleavage of two S—C bonds with release of ethene and the formation of the corresponding complex  $[Met([9]aneS_3)(SCH_2CH_2SCH_2CH_2S)]^+$  were observed.<sup>31</sup>

Spectra obtained by us for a range of cone voltages from 10 to 60 V for the complex  $[Ru^{II}Cl([9]aneS_3)(phen)]Cl$  showed that whereas the  $[M-64]^+$  ions are still present at cone voltages as low as 10 V, although with very low abundances, the  $[M-92]^+$  ions are only observed for cone voltages above 40 V.

We can establish that, whereas the formation of the  $[M-64]^+$  ion in the condensed phase may occur, although not to a significant extent, the formation of  $[M-92]^+$  ion occurs only in the gas phase.

Finally we can conclude that the ions  $[M-64]^+$  and  $[M-92]^+$  can be used as diagnostic ions for  $Ru^{II}([9]aneS_3)$  complexes with bidentate nitrogen ligands. These ions probably have a square pyramid geometry, and are formed predominantly by gas-phase processes.

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