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Investigation of the coordination modes of tris(pyrazolylmethane)/1,4,7-trithiacyclononane ruthenium(II) complex ions by electrospray ionization mass spectrometry

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ABSTRACT

Electrospray ionization mass spectrometry (ESIMS) was used to investigate the coordination modes of the complexes $[Ru^{II}([9]aneS_3)(HCpz_3)Cl]Cl$, $[Ru^{II}([9]aneS_3)(HCpz_3)](Cl)PF_6$ and $[Ru^{II}([9]aneS_3)(HCpz_3)](PF_6)_2$ ($[9]aneS_3$ = 1,4,7-trithiacyclononane; $HCpz_3$ = tris(1-pyrazolyl)methane) in methanol, acetonitrile and methanol/water solutions. The complex $[Ru^{II}([9]aneS_3)(HCpz_3)Cl]Cl$ shows a rapidly exchangeable Cl ligand, with formation of a doubly charged ion $[Ru^{II}([9]aneS_3)(HCpz_3)]^{2+}$, *m/z* 248, but the $[Ru^{II}([9]aneS_3)(HCpz_3)Cl]^+$, *m/z* 531, is also observed and both species still coexist after 16 h. The formation of the $[Ru^{II}([9]aneS_3)(HCpz_3)]^{2+}$ and $[Ru^{II}([9]aneS_3)(HCpz_3)Cl]^+$ ions by electrospraying solutions of $[Ru^{II}([9]aneS_3)(dmso)Cl_2]$ (dmso = dimethylsulfoxide) and $HCpz_3$ in water/methanol was also studied.

Fragmentation of the $[Ru^{II}([9]aneS_3)(HCpz_3)]^{2+}$ ions by losses from the $[9]aneS_3$ ligand seems to point to a k^3 strained coordination mode, whereas fragmentation of the $[Ru^{II}([9]aneS_3)(HCpz_3)Cl]^+$ points to a less strained complex and to two isomers: the complex $[Ru^{II}([9]aneS_3)(HCpz_3)Cl]^+$ and the ion pair $[Ru^{II}([9]aneS_3)(HCpz_3)+Cl]^+$. Further support for the ion pair hypothesis is the strong increase of the relative abundance of the $[Ru^{II}([9]aneS_3)(HCpz_3)+PF_6]^+$ ion, *m/z* 641, formed from solutions of the $[Ru^{II}(k^3\text{-}[9]aneS_3)(k^3\text{-}HCpz_3)](Cl)PF_6$ and $[Ru^{II}(k^3\text{-}[9]aneS_3)(k^3\text{-}HCpz_3)](PF_6)_2$ complexes, after 16 h.

The high stability of the ion pairs indicates that they may be *inner sphere ion pairs* and that either $[9]aneS_3$ or $HCpz_3$ changes from a k^3 to a k^2 coordination mode. The results support an equilibrium between a full $k^3\text{-}[9]aneS_3/k^3\text{-}HCpz_3$ complex and a k_2+k_3+Cl/PF_6 ion pair.

1. Introduction

Transition metal compounds including both polyaromatic nitrogen-containing ligands and macrocyclic thioethers in the coordination sphere [1–9] have been synthesized and characterized since 1993, when Barton and co-workers presented a rhodium(III) complex with 1,4,7,10-tetrathiacyclo-dodecane ($[12]aneS_4$) and phenanthrenoquinone-9,19-diimine (phi) [1].

In the course of our studies of ruthenium(II) complexes with macrocyclic thioethers and aromatic diimines [10–13], one of us published the synthesis and characterization of the complexes $[Ru^{II}([9]aneS_3)(HCpz_3)Cl]Cl$, $[Ru^{II}([9]aneS_3)(HCpz_3)]Cl(PF_6)$ and $[Ru^{II}([9]aneS_3)(HCpz_3)](PF_6)_2$], where $[9]aneS_3$ and $HCpz_3$ are the potentially tridentate ligands 1,4,7-trithiacyclononane and tris(1-pyrazolyl)methane (Scheme 1), and where both ligands compete for full coordination [14].

A thorough bibliographic search confirms the clear preference of $[9]aneS_3$ for a k^3 coordination mode in octahedral complexes. The only known example of a stable k^2-$[9]aneS_3$ is $[Ir^{III}(k^3\text{-}[9]aneS_3)(k^2\text{-}[9]aneS_3)H]$, where the presence of the strongly coordinating H^- ligand inhibits the facial coordination of the macrocycle [15]. The remaining known examples of a $[9]aneS_3$ hypodentation, not caused by lack of available coordination positions or inadequate geometry, occur in unstable compounds. However, even those are restricted to high oxidation hard Lewis acid centers, with a strong preference for hard donors over soft S atoms, or to intermediates isolated due to their insolubility in the synthetic media [16–18].

The tripodal ligand $HCpz_3$ has been widely used both in coordination and organometallic chemistry [19]. In the case of

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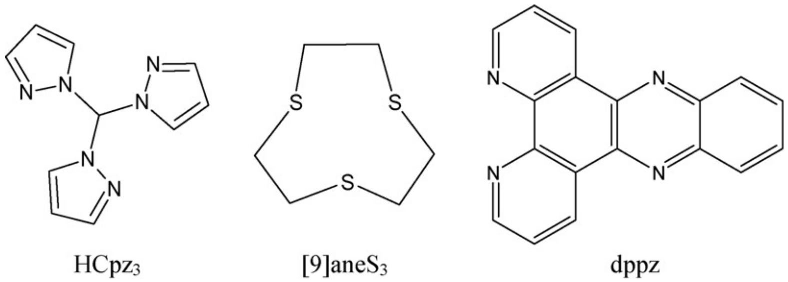

Scheme 1.

ruthenium(II), like in many other metal centers, $HCpz_3$ has predominantly a k^3 coordination [19,20] but, in a few cases, k^2 structures were also reported [21–24]. The latter type of coordination was found for octahedral complexes with bulky ligands and when four positions were occupied [21,24]. In the absence of such restrictions k^2- and k^3-$HCpz_3$ might coexist but an $k^2 \rightarrow k^3$ interconversion is typically observed in solution [23,25,26].

Regardless the fact that several $[Met(k^3\text{-}HCpz_3)_2]^{n+}$ complexes (Met = metal) have been prepared with metallic cations of similar or larger size than Ru^{2+} [27–30], $[Ru^{II}(k^3\text{-}HCpz_3)_2]^{+2}$ was never reported, and only $[Ru^{II}(k^3\text{-}HCpz_3)(k^2\text{-}HCpz_3)Cl]^+$ is known [22]. Displacement of the Cl ligand leads to solvent coordination, not to tri-coordination of the second $HCpz_3$. It is however possible that this is an apparent restriction, since an analogous $[Ru^{II}(k^3\text{-}HBpz_3)_2]$ complex was obtained in a very slow reaction [31]. Taken together, these results suggest that k^2- and k^3-$HCpz_3$ coordination modes may coexist in solution, the interconversion process depending on the stereochemical hindrance between the co-ligands and on the lability of the leaving groups.

In the present case single-crystal X-ray diffraction studies established two different coordination modes, k^3-$HCpz_3$ and k^2-$HCpz_3$, for two different complexes, $[Ru^{II}([9]aneS_3)(HCpz_3)]Cl(PF_6)$ and $[Ru^{II}([9]aneS_3)(HCpz_3)Cl]Cl$, respectively, but. data from ^1H NMR spectra suggested a coordination mode change. Also, preliminary theoretical studies, performed at the DFT level, indicated that, for $[Ru^{II}([9]aneS_3)(HCpz_3)]Cl(PF_6)$, a structure with k^3-$HCpz_3$ did not correspond to the minimum of energy [14].

To further elucidate the k^2/k^3 coordination modes of $[9]aneS_3$ and $HCpz_3$ we used electrospray ionization mass spectrometry (ESIMS), which was applied, as early as 1990, to investigate the gas-phase formation of complexes of metal(II) ions with organic ligands [32]. Several publications followed [33–47] and, in particular, polyether/diimine mixed-ligand metal(II) complexes, were studied by Shen and Brodbelt [48].

Solutions of the synthesized complexes were electrosprayed in different experimental conditions and the formation of the $Ru^{II}([9]aneS_3)(HCpz_3)Cl]^+$ and $[Ru^{II}([9]aneS_3)(HCpz_3)]^{2+}$ ions, by electrospraying solutions of $[Ru^{II}([9]aneS_3)(dmso)Cl_2]$ (dmso = dimethylsulfoxide) and $HCpz_3$, was also undertaken.

ESIMS allowed us not only to investigate the coordination modes of the two ligands for the complexes studied but also to acquire information on the mechanisms of the formation of the $[Ru^{II}([9]aneS_3)(HCpz_3)Cl]^+$ and $[Ru^{II}([9]aneS_3)(HCpz_3)]^{2+}$ ions.

2. Experimental

The synthesis and characterization of the $HCpz_3$ ligand and the complexes $[Ru^{II}([9]aneS_3)(dmso)Cl_2]$, $[Ru^{II}([9]aneS_3)(dppz)Cl]Cl$, $[Ru^{II}([9]aneS_3)(k^2\text{-}HCpz_3)]Cl(PF_6)$ and $[Ru^{II}([9]aneS_3)(k^3\text{-}HCpz_3)](PF_6)_2$ were published elsewhere [7,12,14,49,50]. The general procedure for the formation of $[Ru^{II}([9]aneS_3)(k^2\text{-}HCpz_3)Cl]Cl$, $[Ru^{II}([9]aneS_3)(k^3\text{-}HCpz_3)]Cl(PF_6)$ and $[Ru^{II}([9]aneS_3)(k^3\text{-}HCpz_3)](PF_6)_2$ was based on the reaction of $[Ru^{II}([9]aneS_3)(dmso)Cl_2]$ and $HCpz_3$ in different experimental conditions (crystallization, recrystallization, fast precipitation or metathesis) leading to their isolation [14]. The denticities (k^n) were assigned based on the solid state characterization (X-ray, MAS, ^{13}C NMR, FTIR and elemental analysis).

The mass spectra were acquired with a Micromass Q-Tof II equipped with a Z-spray source, an electrospray probe and a syringe pump. Source block and desolvation temperatures were 80 °C and 150 °C, respectively. The capillary voltage was 3000 V. The spectra were acquired at several cone voltages ranging from 10 to 120 V. The instrument was operated at a nominal resolution of 8000. Methanol, acetonitrile or a mixture of methanol/water (50:50) were employed as eluents. Equimolar aqueous solutions of the ligand $HCpz_3$ and the precursor complexes ($\approx$1 mM) were prepared (freshly made or allowed to stay overnight, approximately 16 h), and introduced through the syringe pump.

Collision induced product ion spectra were obtained by selecting the ion of interest with the quadrupole analyzer, using the hexapole collision cell and a range of collision energies (20–150 eV).

3. Results and discussion

3.1. X-ray and NMR data

In the present case a single-crystal X-ray diffraction study has established a k^2-$HCpz_3$ coordination mode for $[Ru^{II}([9]aneS_3)(HCpz_3)Cl]Cl$ (Fig. 1A). The characterization by single-crystal X-ray diffraction of the complex $[Ru^{II}([9]aneS_3)(HCpz_3)]Cl(PF_6)$, (Fig. 1B), on the other hand, established a k^3-$[9]aneS_3$/k^3-$HCpz_3$ coordination.

The isolation of the $[Ru^{II}([9]aneS_3)(k^3\text{-}HCpz_3)]^{2+}$ cations from the $[Ru^{II}([9]aneS_3)(k^2\text{-}HCpz_3)Cl]^+$ cations could be related to a less stable Ru(II)-Cl bond; however, the analysis of the crystal structure of the second complex does not support this hypothesis. The Ru–Cl bond has a normal length,[15] and there is no pendant group in the vicinity of the Cl atom. The isolation of $[Ru^{II}([9]aneS_3)(k^2\text{-}HCpz_3)Cl]^+$ may be explained by the moderate labilising *trans* effect of the polythioethers,[51] the minimum energy conformation of free $HCpz_3$, which favors a k^2-coordination mode,[52] and the expected lower solubility of this complex, which makes it easier to crystallize than the k^3 compounds.

A temperature-dependent NMR study of its methanol solution indicated a fast dynamic interchange, which was not completely solved on the NMR time scale, even at the lower limit of the study (−85 °C), pointing also to an apparent C_{3v} symmetry [14]. The different solid state structures show equivalent ^1H NMR' spectra (only one chemical environment *per* pyrazolyl proton, when two, with a 2:1 ratio, are expected for a k^2-$HCpz_3$ coordination mode). The aliphatic region is characterized by two symmetrical multiplets with a AA'BB' pattern, similar to those of the $[Ru^{II}(k^3\text{-}[9]aneS_3)_2]^{2+}$complex [53]. These results indicate an apparent C_{3v} symmetry, suggestive of a k^3 coordination both on $[9]aneS_3$ and $HCpz_3$, and also a labile Cl atom, which seems to contradict the solid

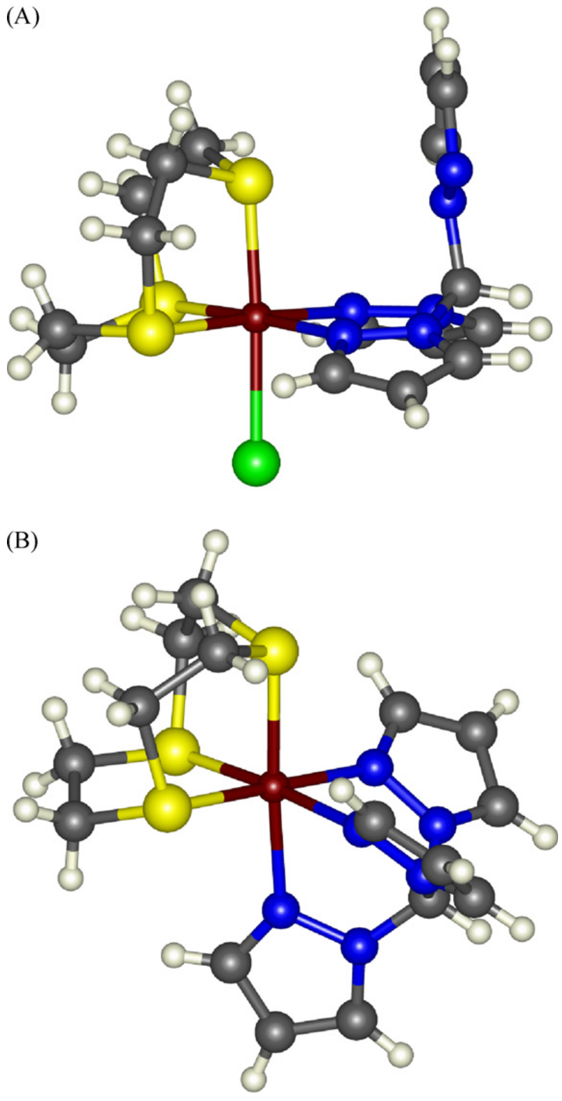

Fig. 1. X-ray crystal structures of the inner sphere cations of (A) $[Ru^{II}([9]aneS_3)(HCpz_3)Cl]Cl$ and (B) $[Ru^{II}([9]aneS_3)(HCpz_3)](PF_6)_2$.

state data and the isolation of the $[Ru^{II}([9]aneS_3)(k^2\text{-}HCpz_3)Cl]Cl$ complex during the crystallization process [14].

The ^1H NMR spectra of $[Ru^{II}([9]aneS_3)(HCpz_3)Cl]Cl$ were also acquired with decreasing temperatures (CD_3OD, 293–188 K), in order to check if the apparent symmetry was a true C_{3v} or resulted from a system in rapid change [14]. While sharp signals are detected at room temperature, the cooling of the solution results in broad resonance bands, both on the coordinated thioethers and pyrazolyl environments, which are interpreted as a system in rapid change, that is, the apparent magnetic equivalence of the solution does not imply a simultaneous k^3-[9]aneS$_3$ and k^3-HCpz$_3$ coordination. The coalescence is still observed on the lower temperature limit of the study, which means that the inversion is still fast on the proton NMR time scale.

3.2. *ESIMS spectra of the solutions of the synthesized complexes*

At lower cone voltages, the mass spectra of both fresh and aged solutions of the complexes $[Ru^{II}([9]aneS_3)(HCpz_3)Cl]Cl$ and $[Ru^{II}([9]aneS_3)(HCpz_3)]Cl(PF_6)$ (Table 1) present an abundant doubly charged ion, at *m/z* 248, which was assigned to the $[Ru^{II}([9]aneS_3)(HCpz_3)]^{2+}$ ion, or $[M–Cl]^{2+}$. The monocharged ion at *m/z* 531, ascribed to the inner sphere complex ion $[Ru^{II}([9]aneS_3)(HCpz_3)Cl]^+$, M^+ ion, was also observed, but with a lower relative abundance. Another monocharged species, at *m/z* 495, corresponds to the $[Ru^{II}([9]aneS_3\text{-}H)(HCpz_3)]^+$ ion, or $[M–HCl]^+$.

Table 1
Formulae and nominal masses of the complexes studied.

Complexes	Formulae	Nominal mass (Da)
1	$[Ru^{II}([9]aneS_3)(HCpz_3)Cl]Cl$	566
2	$[Ru^{II}([9]aneS_3)(HCpz_3)]ClPF_6$	676
3	$[Ru^{II}([9]aneS_3)(HCpz)](PF_6)_2$	786
4	$[Ru^{II}([9]aneS_3)(dppz)Cl]$ Cl	634
5	$[Ru^{II}([9]aneS_3)(dmso)Cl_2]$	430

As the cone voltage increases, doubly charged ions formed by fragmentation of the thioether are observed, such as the $[M–Cl–CH_2CH_2]^{2+}$ and the $[M–Cl–CH_2CH_2–H_2S]^{2+}$ ions, *m/z* 234 and *m/z* 217 respectively. As the cone voltage further increases the doubly charged species became less abundant and monocharged species such as $[M–HCl–CH_2CH_2]^+$, *m/z* 467, $[M–HCl–2CH_2CH_2]^+$, *m/z* 439 and $[M–HCl–2CH_2CH_2–Hpz]^+$, *m/z* 371 are observed. The signal of the $[M–Cl]^{2+}$ ions decreases with the cone voltage increase, until it disappears around 60 V.

The mass spectra of a 50:50 methanol/water solution of $[Ru^{II}([9]aneS_3)(k^2\text{-}HCpz_3)Cl]Cl$, at cone voltages of 20 and 50 V, are shown in Fig. 2.

The above described behavior contrasts with the general fragmentation pattern of the complexes with the general formula $[Ru^{II}([9]aneS_3)(N–N)Cl]X$, (where N–N are bidentate diimines, such as dipyrido[3,2-a:2′,3′-c]phenazine (dppz), Scheme 1, and $X = Cl^-$ or PF_6^-), which have a inner sphere similar to the $[Ru^{II}([9]aneS_3)(k^2\text{-}HCpz_3)Cl]^+$ ion. The mass spectra of these complexes show predominantly the inner sphere monocharged cation $[Ru^{II}([9]aneS_3)(N–N)Cl]^+$, M^+, and no doubly charged species are observed, even at voltages as low as 10 V. At higher voltages the main signals detected are from the monocharged ions formed by losses 64 and 92 Da from the thioether $[M–HCl–CH_2CH_2]^+$ and $[M–HCl–2CH_2CH_2]^+$, respectively [54].

In Fig. 3 the mass spectra of $[Ru^{II}([9]aneS_3)(k^2\text{-}HCpz_3)Cl]Cl$ and $[Ru^{II}([9]aneS_3)(dppz)Cl]Cl$ at a cone voltage of 30 V are shown. As it can be seen for the latter, no doubly charged ions $[M–Cl]^{2+}$, at *m/z* 282, are observed at this voltage.

The presence of the M^{2+} ions in the mass spectra of $[Ru^{II}([9]aneS_3)(k^2\text{-}HCpz_3)Cl]Cl$, which are absent in the mass spectra of $[Ru^{II}([9]aneS_3)(dppz)Cl]Cl$ and related complexes,[7] points to a rapidly exchangeable Cl ligand in the former. This was unexpected, since in the solid state structure the Cl atom and the non-coordinated pendant pyrazolyl are positioned on oppo-

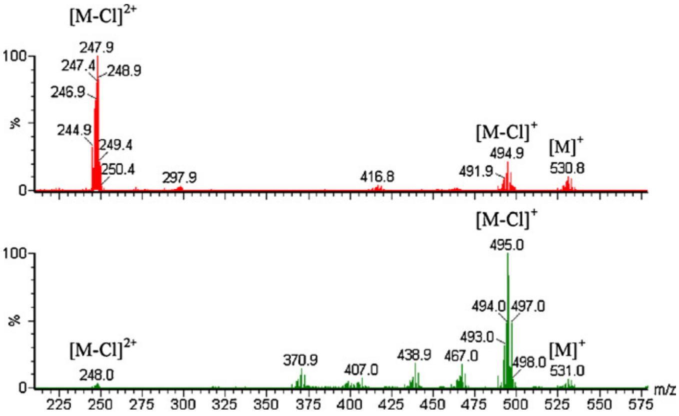

Fig. 2. Mass spectrum of $[Ru^{II}([9]aneS_3)(k^2\text{-}HCpz_3)Cl]Cl$. (A) Cone voltage 10 V and (B) cone voltage 50 V.

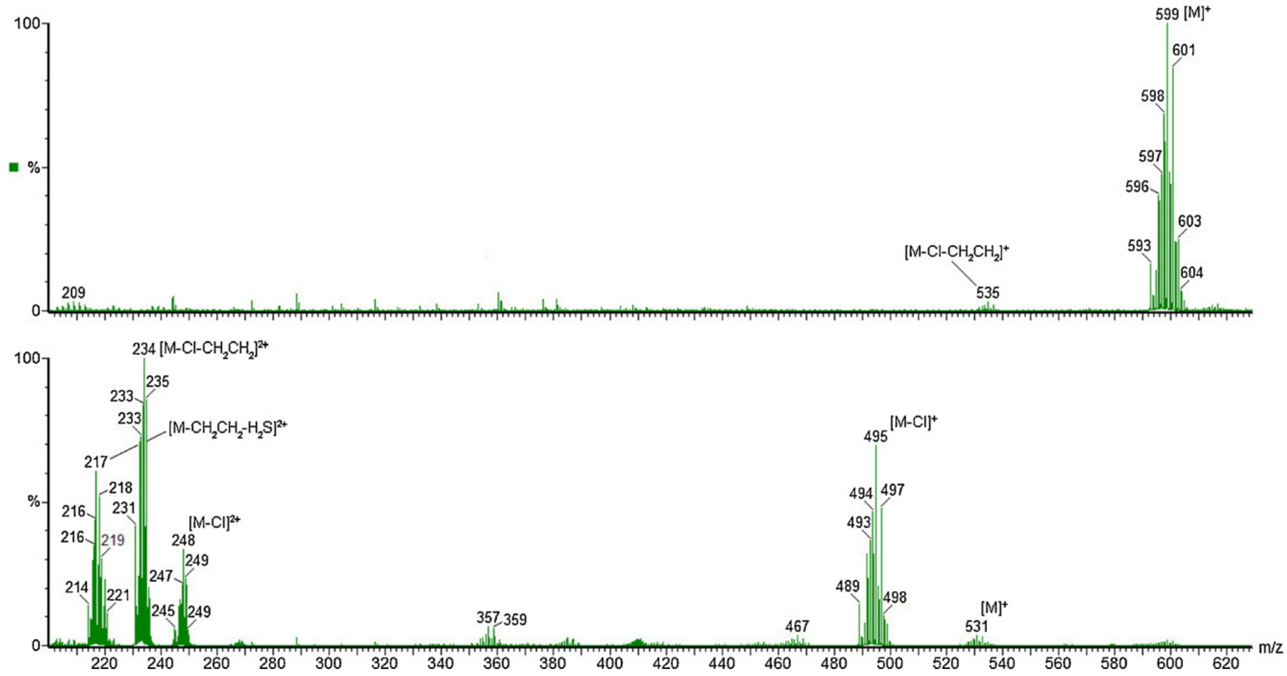

Fig. 3. Mass spectra at a cone voltage of 30 V of (A) $[Ru^{II}([9]aneS_3)(dppz)Cl]Cl$ and (B) $[Ru^{II}([9]aneS_3)(k^2\text{-}HCpz_3)Cl]Cl$.

site sides (Fig. 1A). A rapid loss of a Cl atom (formation of the M^{2+} ions) was observed only in the case of $[Ru^{II}([9]aneS_3)(k^2\text{-}terpy)Cl]PF_6$ (terpy = 2,2′:6′,2″-terppyridine) which possesses a non-coordinated pendant pyridyl positioned near the Cl ligand [12,54].

The nominal masses of the ligands and solvents used are presented in Table 2.

3.3. Breakdown graphs

We drew breakdown graphs by plotting ion abundances vs. cone voltages. This approach can be useful in the present case as there is only one dominant ion at low cone voltages, i.e. the $[Ru^{II}([9]aneS_3)(HCpz_3)]^{2+}$, $[M–Cl]^{2+}$ ion [55].

We observed that in fresh solutions of the $[Ru^{II}([9]aneS_3)(k^2\text{-}HCpz_3)Cl]Cl$ complex the abundance of the *m/z* 531 ion, M^+, does not change significantly with the cone voltage, whereas the abundance of the doubly charged ions, *m/z* 248, $[M–Cl]^{2+}$ decreases (no significant signal was detected for cone voltages above 60 V). However the abundance of the ion at *m/z* 495, $[M–HCl]^+$ increases (Fig. 4A). The breakdown graph for the $[Ru^{II}([9]aneS_3)(k^3\text{-}HCpz_3)]Cl(PF_6)$ complex shows a similar behavior, except for the formation of an ion at *m/z* 641, assigned to the ion pair $[Ru^{II}([9]aneS_3)(HCpz_3)\text{+ }PF_6]^+$ (Fig. 4B).

Similar experiments were done for solutions kept overnight and showed an overall similar behavior for both complexes. However, for the $[Ru^{II}([9]aneS_3)(k^3\text{-}HCpz_3)]Cl(PF_6)$ complex, the ion pair $[Ru^{II}([9]aneS_3)(HCpz_3) + PF_6]^+$ is much more abundant than in the case of the fresh solutions (Fig. 4C).

Table 2
Nominal masses of the ligands and relevant molecules.

Ligand/solvent	Name	Nominal mass (Da)
$[9]aneS_3$	1,4,6-Trithiacyclononane	180
$HCpz_3$	Tris(pyrazolyl)methane	214
dppz	Dipyrido[3,2-a:2′,3′-c]phenazine	282
dmso	Dimethylsulfoxide	78
Hpz	Pyrazole	68
CH_3OH	Methanol	32
CH_3CN	Acetonitrile	41

These results, suggest that the *m/z* 531 ion is formed by two different isomers, one with the Cl atom coordinated to the metal center, that is the original k^2 complex, and another where the Cl atom is part of an ion pair, $[Ru^{II}([9]aneS_3)(HCpz_3) + Cl]^+$.

Formation of the ion pair $[Ru^{II}([9]aneS_3)(HCpz_3) + PF_6]^+$ in much higher abundance for solutions kept overnight indicates that the loss of the Cl ligand and the formation of the hexafluorophosphate ion pair are time-dependent. Besides the coulombic attraction between cation and anion, additional space-oriented connections are needed to assure favored positions of the atoms in the ions. These may include partial coordination (sharing of electron density) and hydrogen bond formation [56]. Such space-oriented binding is more probable in a slow kinetic process.

If we consider a $k^3\text{-}HCpz_3$ coordination mode to the metal center, only the carbon atoms and three non-coordinated nitrogen atoms remain available. As it can be seen in Fig. 1B, the non-coordinated nitrogen atoms are closer to the metal center and much less accessible for further bond formation, than the carbon atoms. C–H···F hydrogen bonds between PF_6^- anions and Ru^{II} complexes with polypyridyls have been observed in their crystal structures [12]. Also a similar type of binding has been observed in ionic liquids [57]. It is thus possible that C–H···F bonds may be formed in solution between a F atom of the PF_6^- and the more acidic carbon-bonded hydrogens of the pyrazolyl rings, specially as the formation of these bonds is probably charge assisted,[58] that is, preceded by a coulombic attraction between the hexafluorophosphate anion and the inner sphere complex cation.

In a series of studies on ruthenium(II) polypyrazolyl methanes or borates, Macchioni et al. have clearly established the presence of stabilizing ion pairs by NOESY NMR solution spectroscopy and theoretical studies [24,26].

While the formation of organometallic ion pairs typically occurs in low polarity solvents, our studies indicate that they can also exist in high relative permittivity solvents, such as the methanol/water mixtures used. During its synthesis and crystallization, $[Ru^{II}([9]aneS_3)(k^2\text{-}HCpz_3)Cl]Cl$ stays in boiling ethanol for a large time and has a long crystallization period. If we consider these data together with the stability at high cone voltages of the *m/z* 531, [M^+] and *m/z* 641, [(M–Cl) + PF_6]$^+$ ions, we may suggest that they are *inner sphere ion pairs* (ISIPs).

The choice mechanism for intermediate formation in octahedral Ru(II) complexes is through substitution, not addition, reactions [59]. This preference is related to the rarity of hepta coordination in Ru(II) (only observed in transient species or when very special conditions are fulfilled to allow their formation) [60,61]. Based on this, a proposal of ISIP formation requires that one of the potentially tridentate ligands is present in a k^2 coordination mode.

Further support to the ISIP hypothesis is given by the mass spectrum of [Ru^{II}(k^3-[9]aneS_3)(k^3-HCpz_3)]Cl(PF_6) in the coordinating solvent acetonitrile, which shows a moderately abundant ion at *m/z* 268.5, which corresponds to the association of a solvent molecule, [(M–Cl) + CH_3CN]$^{2+}$. Since the corresponding ions are not observed in methanol (and methanol/water) solutions, this indicates the presence of a temporarily free position, accessible only to coordinating solvents like acetonitrile.

With a stable k^3-[9]aneS_3/k^3-HCpz_3 coordination mode there would be no reason for the observation of the fast dynamic interchange in NMR spectra at low temperatures. Also the formation of an *outer sphere ion pair* {[Ru^{II}(k^3-[9]aneS_3)(k^3-HCpz_3)]Cl}$^+$ at high cone voltages and in aged solutions is unlikely. Furthermore, DFT theoretical calculations indicate that {[Ru^{II}(k^3-[9]aneS_3)(k^3-HCpz_3)]Cl}$^+$ optimized structure is higher in energy than [Ru^{II}(k^3-[9]aneS_3)(k^2-HCpz_3) + Cl]$^+$ [14].

ESIMS and NMR data indicate that a k^2-HCpz_3 ligand may change its coordination mode to k^3 by displacing the axial ligand which offers less stereochemical hindrance and lacks the possibility of π retro-donation [24,26] which, in the present case, is Cl and not S. The loss of the Cl ligand requires another coordinating ligand close by, such as previous ESIMS studies have demonstrated [54].

The crystal structure of *trans*-[Ru^{II}(PMe)$_2$(CO)(COMe)-(k^2-HCpz_3)]BPh_4 shows a HCpz_3 positioning which is very similar to the one observed in Fig. 1A. However, in the case of the former, a fast exchange process is known to occur as result of an interconversion between the coordinated and free pyrazolyl groups [24]. If a rotation of HCpz_3 also occurs for [Ru(k^3-[9]aneS_3)(k^2-HCpz_3)Cl]$^+$, the positioning of a free pyrazolyl near the Cl would justify the loss of the Cl group. Other possibilities however have to be considered. A k^2-[9]aneS_3 coordination mode, while unusual, can result from competition between the two tridentate ligands. In these circumstances the polythioether would switch fast between the two non-occupied positions, in a similar mode as reported for five-coordinated [Pt([9]aneS_3)(phen)]$^{2+}$ (phen = 1,10-phenanthroline) [9]. During the switching process the sulfur could come closer the Cl atom. The existence of an ion at *m/z* 417 (tentatively assigned to [(M-SCH_2–Hpz)]$^+$ (Hpz = pyrazole) in the mass spectra of a methanolic solution of [Ru(k^3-[9]aneS_3)(k^2-HCpz_3)Cl]$^+$ seems to support this process.

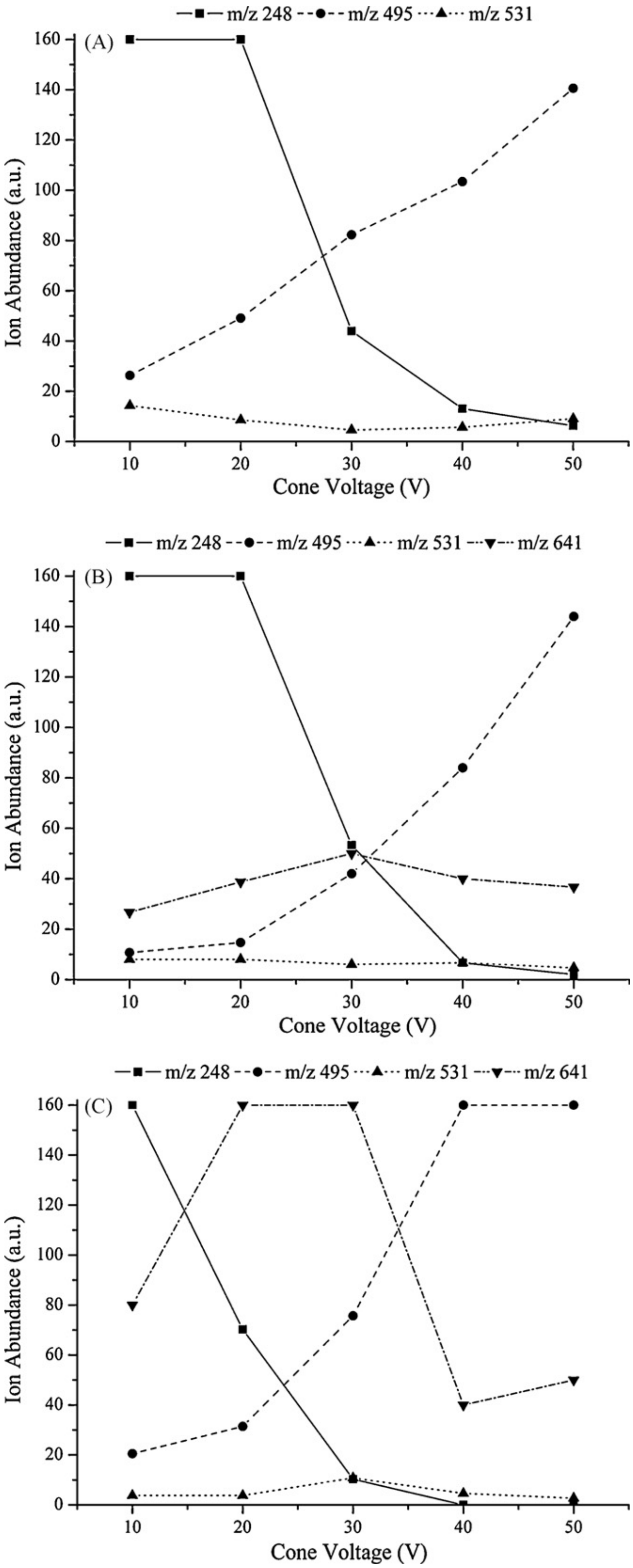

Fig. 4. Breakdown graphs (ion abundances vs. cone voltages). (A) Fresh solution of [Ru^{II}([9]aneS_3)(k^2-HCpz_3)Cl]Cl in methanol, (B) fresh solution of [Ru^{II}([9]aneS_3)(k^3-HCpz_3)]Cl(PF_6) in acetonitrile and (C) aged solution the [Ru^{II}([9]aneS_3)(k^3-HCpz_3)]Cl(PF_6) in acetonitrile.

Table 3

Formulae, nominal masses and *m/z* values of the ions formed from 50: 50 water–methanol aged solutions of [Ru^{II}([9]aneS_3)(dmso)Cl_2] and HCpz_3 at a cone voltage of 30 V.

Complex ions	Nominal mass (Da)	*m/z*
[Ru^{II}([9]aneS_3)(dmso)Cl]$^+$	395	395
[Ru^{II}([9]aneS_3)(dmso)Cl(H_2O)]$^+$	413	413
[Ru^{II}([9]aneS_3)(dmso)Cl(CH_3OH)]$^+$	427	427
[Ru^{II}([9]aneS_3)(HCpz_3)Cl]$^+$	531	531
{[Ru^{II}([9]aneS_3)(HCpz_3)(dmso)Cl](H_2O)}$^+$	627	627
[RuII([9]aneS_3)(HCpz_3)]$^{2+}$	496	248
{[Ru^{II}([9]aneS_3)(HCpz_3)(H_2O)$_2$] HCpz_3}$^{2+}$	746	373
[Ru^{II}([9]aneS_3)(HCpz_3)$_2$(H_2O)]$^{2+}$	728	364
[Ru^{II}([9]aneS_3)(HCpz_3)$_2$]$^{2+}$	710	355

Table 4
Product ion spectra of the *m/z* 248 ions at a cone voltage of 20 V and a collision energy of 150 eV.

m/z	Relative abundances according to origin (%)		
	Solid state	Solid state	Water–methanol solutions of $[Ru^{II}([9]aneS_3)(dmso)Cl_2]$ and $HCpz_3$
	$[Ru^{II}([9]aneS_3)(k^2\text{-}HCpz_3)Cl]Cl$	$[Ru^{II}([9]aneS_3)(k^3\text{-}HCpz)](PF_6)_2$	–
248	5.9	2.5	2.7
234	100.0	100.0	100.0
212	53.1	86.6	86.2

Table 5
Product ion spectra of the *m/z* 531 ions at a cone voltage of 80 V and a collision energy of 150 eV.

m/z	Relative abundances according to origin (%)	
	Solid state $[Ru^{II}([9]aneS_3)(k^2\text{-}HCpz_3)Cl]Cl$	Water–methanol solutions of $[Ru^{II}([9]aneS_3)(dmso)Cl_2]$ and $HCpz_3$ –
531	1.9	2.0
467	20.1	19.9
439	100.0	100.0

More detailed theoretical studies, taking into account the effect of the ion pairs and alternative mechanisms, are now underway.

3.4. Formation of the $[Ru^{II}([9]aneS_3)(HCpz_3)]^{2+}$ and $[Ru^{II}([9]aneS_3)(HCpz_3)Cl]^+$ ions by electrospraying $HCpz_3$ and $[Ru^{II}([9]aneS_3)(dmso)Cl_2]$ mixed solutions

The formation of the $[Ru^{II}([9]aneS_3)(HCpz_3)Cl]^+$ and $[Ru^{II}([9]aneS_3)(HCpz_3)]^{2+}$ ions was assayed by reacting the $[Ru^{II}([9]aneS_3)(dmso)Cl_2]$ complex with $HCpz_3$ in methanol/water and acetonitrile/water. The M^+, *m/z* 531, and $[M–Cl]^{2+}$, *m/z* 248, ions were observed at low cone voltages, the latter with high relative abundances. The ratio of the $[M–Cl]^{2+}$ and M^+ abundances increases only moderately with time. For instance, for cone voltages of 20 V, $[M–Cl]^{2+}/M^+$ is 1/10 for fresh solutions and 1/13 for aged solutions. The fact that the M^+ ion is still observed for the latter indicates that this ion is stable in solution. The main ions formed by electrospraying aged solutions of the $[Ru^{II}([9]aneS_3)(dmso)Cl_2]$ complex with $HCpz_3$, at a cone voltage of 30 V are shown in Table 3.

3.5. Collision induced dissociation experiments

We have also analyzed the behavior of the $[Ru^{II}([9]aneS_3)(HCpz_3)]^{2+}$ ions, *m/z* 248, formed from water–methanol solutions of $[Ru^{II}([9]aneS_3)(dmso)Cl_2]$ and $HCpz_3$, after being mass selected and subjected to collisions in the hexapole. The ions with the same mass to charge ratio, *m/z* 248, formed from water–methanol solutions of $[Ru^{II}([9]aneS_3)(HCpz_3)Cl]Cl$ and $[Ru^{II}([9]aneS_3)(HCpz_3)]Cl(PF_6)$ were also subjected to the same type of experiments. The relative abundances (RA/%) of the precursor, *m/z* 248, and the fragment ions, obtained in the same experimental conditions, are presented in Table 4.

The main fragment ions of the *m/z* 248 precursors are in all cases, the *m/z* 234 ions, formed by loss of ethene from the thioether $[Ru^{II}([9]aneS_3\text{-}CH_2CH_2)(HCpz_3)]^{2+}$. Other losses from the macrocycle, such as the joint losses of two CH_2CH_2 molecules and one CH_2CH_2 plus one H_2S molecule, also observed for ruthenium complexes with diimines and the $[12]aneS_4$ ligand,[62] lead to the less abundant ions $[Ru^{II}([9]aneS_3\text{-}2CH_2CH_2)(HCpz_3)]^{2+}$, *m/z* 220, and $[Ru^{II}([9]aneS_3\text{-}2CH_2CH_2\text{-}H_2S)(HCpz_3)]^{2+}$, *m/z* 203 (not shown). The second most abundant ions, in all the three cases, are the *m/z* 212 ions to which may be assigned the formula $[Ru^{II}([9]aneS_3\text{-}2CH_2CH_2)(HCpz_3) + H_2O]^+$. Addition of water to precursor and product ions in collision-induced experiments, in a hexapole collision cell, with argon, has been already observed [62,63], and the source of the associated water was reported to be either the background gases or the argon itself.

The relative abundances of the $[Ru^{II}([9]aneS_3\text{-}2CH_2CH_2)(HCpz_3) + H_2O]^+$ and of the precursor $[Ru^{II}([9]aneS_3)(HCpz_3)]^{2+}$ ions point to similar precursors in the case of formation from water–methanol solutions of $[Ru^{II}([9]aneS_3)(dmso)Cl_2]$ and $HCpz_3$, and formation from the $[Ru^{II}([9]aneS_3)(k^3\text{-}HCpz_3)](PF_6)_2$ complex and thus to a k^3 coordination mode for both $[9]aneS_3$ and $HCpz_3$. A simultaneous k^3 or *bis-fac* coordination corresponds to a distorted octahedral geometry and a strained $[9]aneS_3$ crown. The opening of the crown eases the strain and allows the preservation of the k^3 coordination of $HCpz_3$.

For the electrosprayed solutions of $[Ru^{II}([9]aneS_3)(k^2\text{-}HCpz_3)Cl]Cl$ the relative abundance of the precursor ion *m/z* 248 is higher whereas that of the *m/z* 212 ion is lower; thus, the $[Ru^{II}([9]aneS_3)(HCpz_3)]^{2+}$ ions formed in this case may be not one but two isotopomers with different coordination modes.

A similar procedure was applied to the ions with *m/z* 531 $[Ru^{II}([9]aneS_3)(HCpz_3)Cl]^+$, formed from water–methanol solutions of $[Ru^{II}([9]aneS_3)(dmso)Cl_2]$ and $HCpz_3$ and from water–methanol solutions of the $[Ru^{II}([9]aneS_3)(HCpz_3)Cl]Cl$ solid. The relative abundances (RA/%) of the precursor, *m/z* 531, and fragment ions, obtained in the same experimental conditions are presented in Table 5.

The product ion spectra of the two *m/z* 531 precursors are practically identical. The second most abundant ions are the *m/z* 439 ions ($[M–HCl–2CH_2CH_2] = [M–92]^+$, the most abundant being the *m/z* 467 ions ($[M–HCl–CH_2CH_2]^+ = [M–64]^+$). These fragment ions formed by losses of 92 and 64 Da are characteristic of the $[Ru^{II}([9]aneS_3)(k^2\text{-}N–N)Cl]^+$ series already mentioned where N–N are diimines such as dppz (Scheme 1) and 1,10-phenanthroline [54].

4. Conclusions

The higher abundances of the $[Ru([9]aneS_3)(HCpz_3)]^{2+}$ ions, *m/z* 248, when compared with the abundances of the $[Ru([9]aneS_3)(HCpz_3)Cl]^+$, *m/z* 531 at lower cone voltages suggest a rapid exchangeable Cl ligand in $[Ru(k^3\text{-}[9]aneS_3)(k^2\text{-}HCpz3)Cl]Cl$. Additional evidence is gathered from ^1H NMR studies and from comparison with the mass spectral behavior of previously studied $[Ru(k^3\text{-}[9]aneS_3)(k^2\text{-}N–N)Cl]X$ ($X = Cl, PF_6$) complexes. This rapid exchange may be caused by a fast rotation of the $HCpz_3$ ligand, positioning a non-coordinated pyrazol near the Cl ligand, but competition between [9]aneS$_3$ and HCpz$_3$ for a k^3 coordination mode, with a pendant tioether located near the Cl atom cannot be excluded. However, the evolution with time of the ions present in solution shows only a small increment of the abundances of the *m/z* 248 ions, when compared with the abundances of the *m/z* 531 ions (*ca* 1/3 increase in 16 h) at low cone voltages, indicating that the two ions coexist in solution for long time intervals.

The collision induced fragmentation of the *m/z* 248 ions by ethene elimination and other losses from the macrocycle indicates a strained simultaneous k^3 coordination of [9]aneS$_3$ and HCpz$_3$. On the other hand, the fragmentation of the *m/z* 531 ion shows the characteristic losses of the [Ru(k^3-[9]aneS$_3$)(k^2-N–N)Cl]$^+$ series, suggestive of a less strained complex, but the Cl ligand was shown to be very labile. This apparent contradiction can be explained by the formation of ion pairs, the *m/z* 531 ions probably being both the [Ru([9]aneS$_3$)k^2-(HCpz$_3$)Cl]$^+$ ion, with a fully coordinated Cl, and the [Ru([9]aneS$_3$)(HCpz$_3$) + Cl]$^+$ ion pair.

Support for ion pair formation is also found in the strong increase of the abundance of the [Ru([9]aneS$_3$)(HCpz$_3$)+ PF$_6$]$^+$ species, *m/z* 641, in the mass spectra of aged [Ru(k^3-[9]aneS$_3$)(k^3-HCpz$_3$)](Cl)PF$_6$ and [Ru(k^3-[9]aneS$_3$)(k^3-HCpz$_3$)](PF$_6$)$_2$ solutions.

The fact that both species assigned to ion pairs are much more resistant to fragmentation than the *m/z* 248 indicates that they are *inner sphere ion pairs* and that one of the potential tridentate ligands has a k^2coordination. ESIMS and NMR data point to an equilibrium in solution, of a full k^3-[9]aneS$_3$/k^3-HCpz$_3$ complex and a $k^2 + k^3$ ISIP with Cl or PF$_6$.

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