

Electrospray mass and tandem mass spectrometry of homologous and isomeric singly, doubly, triply and quadruply charged cationic ruthenated *meso*-(phenyl)_m-(*meta*- and *para*-pyridyl)_n ($m + n = 4$) macrocyclic porphyrin complexes

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Ten homologous or isomeric singly, doubly, triply and quadruply charged cationic macrocyclic complexes I–Va, bⁿ⁺ ($n = 1–4$) formed by the coordination of [Ru(bipy)₂Cl]⁺ to the pyridyl N-atoms of a series of *meso*-(phenyl)_m-(*meta* or *para*-pyridyl)_n-porphyrins ($m + n = 4$) were transferred to the gas phase and structurally characterized by electrospray ionization (ESI) mass (MS) and tandem mass (MS/MS) spectrometry. Previously known to be stable in solution and in the solid state, I–Va, bⁿ⁺ are found to constitute also a new class of stable, long-lived multiply charged gas-phase ions with spatially separated charge sites. Increasing intramolecular electrostatic repulsion from Ia, b⁺ to IVa, b³⁺ facilitates in-source and tandem collision-induced dissociation (CID). However, for the quadruply charged ions Va, b⁴⁺, electrostatic repulsion is alleviated mainly by ion pairing with the CF₃SO₃[−] counterion forming the salt clusters [Va, b/CF₃SO₃]³⁺ and [Va, b/(CF₃SO₃)₂]²⁺ with reduced charge states. Ion-pairing that yields [IVa, b/CF₃SO₃]²⁺ is also observed as a minor ESI process for the triply charged ions IVa, b³⁺. The gaseous ions I–Va, bⁿ⁺ ($n = 2, 3$ or 4) dissociate by sequential ‘charge partitioning’ with the formation of *two* cationic fragments by the release of [Ru(bipy)₂Cl]⁺. The *meta* (a) and *para* (b) isomers and the positional isomers II²⁺ and III²⁺ display nearly identical ESI-MS and ESI-MS/MS spectra. ESI-MS/MS of I–Va, bⁿ⁺ shows that the Ru—py(P) is, intrinsically, the weakest bond since this bond breaks preferentially upon CID. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: ruthenated macrocyclic porphyrins; tandem mass spectrometry; electrospray ionization; gas-phase ion chemistry

INTRODUCTION

Electrospray ionization (ESI) has greatly revolutionized the way in which molecules are ionized and transferred as gaseous ions to mass spectrometers,¹ and has expanded the applications of mass spectrometry (MS) to a variety of new classes of molecules, supermolecules and supramolecules² including a variety of organic, inorganic and organometallic species³ and transient reaction intermediates.⁴

Porphyrins and metalloporphyrins are of great importance in many areas such as biology, catalysis, geology

and photochemistry, and ESI-MS(/MS) has been increasingly used for the previously challenging MS structural characterization of these thermally labile and/or polar molecules.⁵ We have synthesized a series of *meso*-tetra(4-pyridyl)porphyrins coordinated to ruthenium polypyridine complexes, and found that they exhibit enhanced catalytic, electrocatalytic and photochemical properties.⁶ The macrocycle 5,10,15,20-tetra(4-pyridyl)porphyrin and 5,10,15,20-tetra(3-pyridyl)porphyrin complexes can be used as convenient ligands, such as to [Ru(bipy)₂Cl]⁺, to obtain many coordinating transition metal complexes.

Light and highly charged species such as the pentacyano- and hexacyanoferrates are considerably unstable in the gas phase owing to the high concentration of charge formally on the metal center.⁷ The positive charges in the isomeric I–Va, bⁿ⁺ are, however, spatially separated and dispersed in relatively high volumes and masses, thus greatly increasing the prospect for gas-phase stability. The porphyrins are stable

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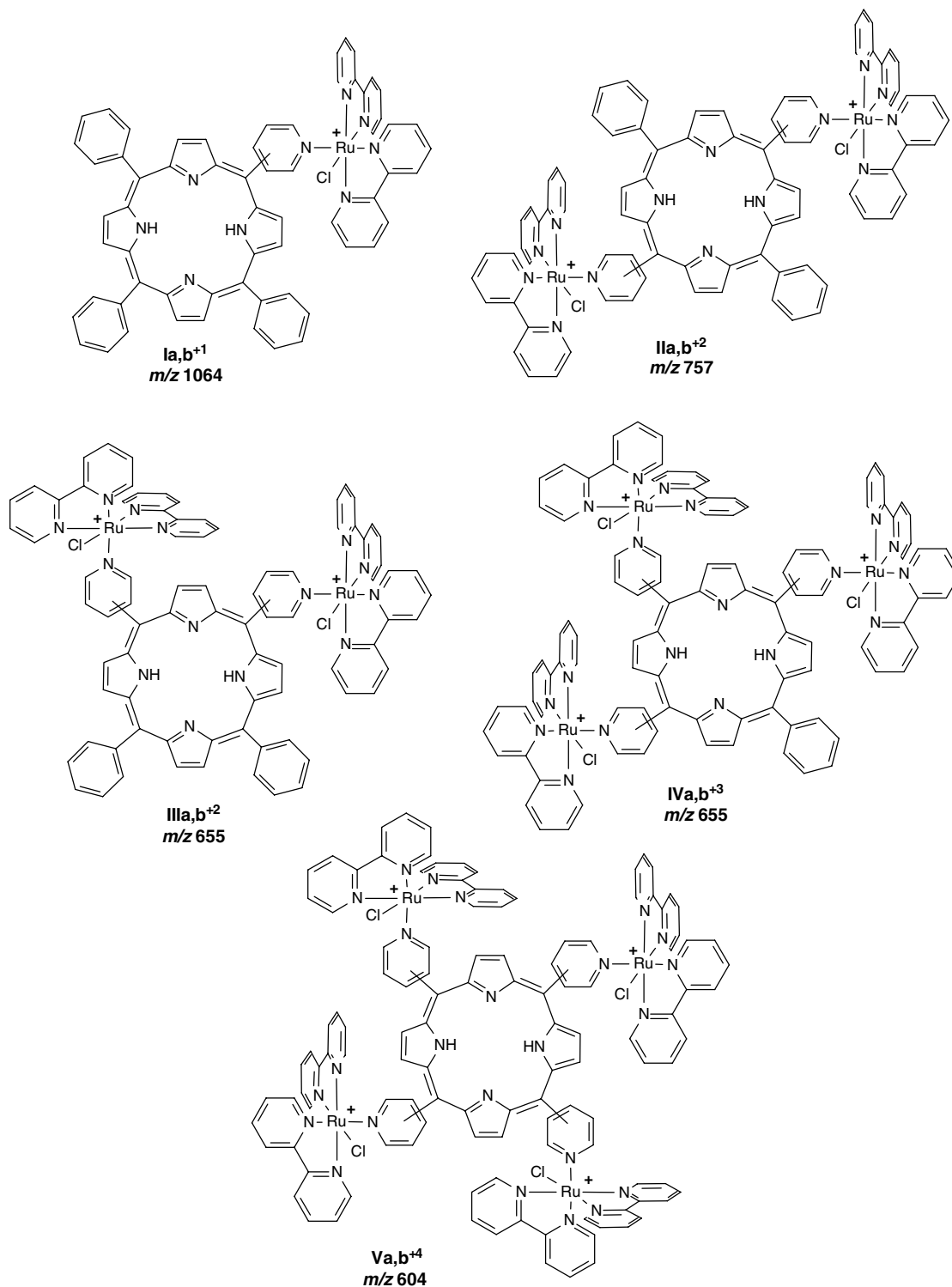
condensed-phase aromatic macrocycles suitable for vapor deposition⁸ and Ru—bipy bonds are also highly stabilized by the chelate effect.⁹ The Ru—py(P) bond (py(P) = the pyridyl porphyrin ligand) is, however, relatively weak in solution⁶ (weaker than Ru—Cl) and the most susceptible to cleavage.

Here we report high-resolution ESI-MS and ESI-MS/MS isolation, mass measuring, structural characterization and gas-phase stability evaluation of the isomeric series of both *meta* (**a**) and *para* (**b**) singly, doubly, triply, and quadruply charged gaseous cationic poly(mono to

tetra)-ruthenated *meso*-(phenyl)_{*m*}-(*meta*- and *para*-pyridyl)_{*n*} macrocyclic coordinating porphyrin complexes ($m + n = 4$) **I–Va, bⁿ⁺** (Scheme 1).

EXPERIMENTAL

The syntheses and characterization of **I–Va, bⁿ⁺** as their corresponding CF₃SO₃[−] salts have been published elsewhere.⁶ Briefly, these salts are obtained by reacting neutral *meso*-(phenyl)_{*m*}-(*meta*- and *para*-pyridyl)_{*n*}-porphyrins ($m + n = 4$)



Scheme 1

with $[\text{Ru}(\text{bipy})_2\text{C}_2]^+$ or $[\text{Ru}(\text{bipy})_2\text{Cl}(\text{H}_2\text{O})]^{2+}$, and have been characterized as pure materials by UV-visible, ^1H NMR and luminescence spectroscopy, and also by electrochemical, spectroelectrochemical and flash photolysis methods. Figure 1 displays a three-dimensional structure representation of the quadruply charged macrocyclic complex Va^{4+} with the central porphyrin ligands coordinated to the four $[\text{Ru}(\text{bipy})_2\text{Cl}]^+$ groups.

ESI-MS and ESI-MS/MS measurements were made in the positive ion mode (m/z 50–3000 range) on a Q-ToF (Waters-Micromass, UK) mass spectrometer with a quadrupole (Qq) and high-resolution (7000) orthogonal time-of-flight (o-TOF) configuration. Sample introduction was performed using a syringe pump (Harvard Apparatus, Pump 11) set to $10\ \mu\text{l}\ \text{min}^{-1}$, pumped through an uncoated fused-silica capillary. All samples were dissolved in pure methanol at concentrations ranging from 10^{-7} to $10^{-6}\ \text{mol}\ \text{l}^{-1}$. ESI mass spectra were acquired using an ESI capillary voltage of 3 kV and a cone voltage of 10 V. This relatively low ESI ion accelerating cone voltage was used to minimize in-source collision-induced dissociation (CID). Isotopic patterns were calculated using MassLynx software.

RESULTS AND DISCUSSION

ESI-MS structural characterization

Figure 2(a) shows the mass spectrum acquired in the positive ion mode after ESI of a methanolic solution of the $\text{Ia}/\text{CF}_3\text{SO}_3$ salt. Via ESI, the singly charged complex Ia^+ is gently and

efficiently transferred from the solution to the gas phase, and detected by MS as a very abundant cluster of singly charged isotopologue ions. In this cluster, the most abundant ion is that of m/z 1064. Because both ruthenium (^{96}Ru (5.52%), ^{98}Ru (1.88%), ^{99}Ru (12.7%), ^{100}Ru (12.6%), ^{101}Ru (17.0%), ^{102}Ru (31.6%), ^{104}Ru (18.7%)) and chlorine (^{35}Cl (75.8%), ^{37}Cl (24.2%)) are multiple isotope elements, the isotopic pattern of the isotopologue cluster 'of m/z 1064' firmly establishes the Ru_1Cl_1 composition of Ia^+ . Only a few very minor fragment ions probably resulting from in-source CID of Ia^+ are also detected in the mass spectrum in Fig. 2(a), which indicates that Ia^+ is a stable, long-lived gaseous species. The richness of the ESI-MS (and also ESI-MS/MS, see below) mass, isotopic and structural characterization of such complex compared with other classical techniques of metalloporphyrin analysis is noteworthy.⁶

ESI-MS of the doubly charged complexes $\text{IIa}, \text{b}^{2+}$ (Fig. 2(b) for IIa^{2+}) detects, under the same conditions, mainly a cluster of isotopologue ions of m/z 757 with a peak separation of $0.5\ m/z$ unit and a characteristic isotopic pattern characteristic of the doubly charged Ru_2Cl_2 -containing species $\text{IIa}, \text{b}^{2+}$. Moreover, minor clusters of singly charged isotopologue ions of m/z 1065 and 449 are also observed, which indicates in-source CID of $\text{IIa}, \text{b}^{2+}$ by 'charge partitioning' that yields *two* singly charged species: the monoruthenated biphenylbipyridylporphyrin cation of m/z 1065 and $[\text{Ru}(\text{bipy})_2\text{Cl}]^+$ of m/z 449. Note that in the *meso*-(bipyridylbiphenyl)porphyrins of $\text{IIa}, \text{b}^{2+}$, in comparison with those of Ia, b^+ , one of the phenyl groups has been

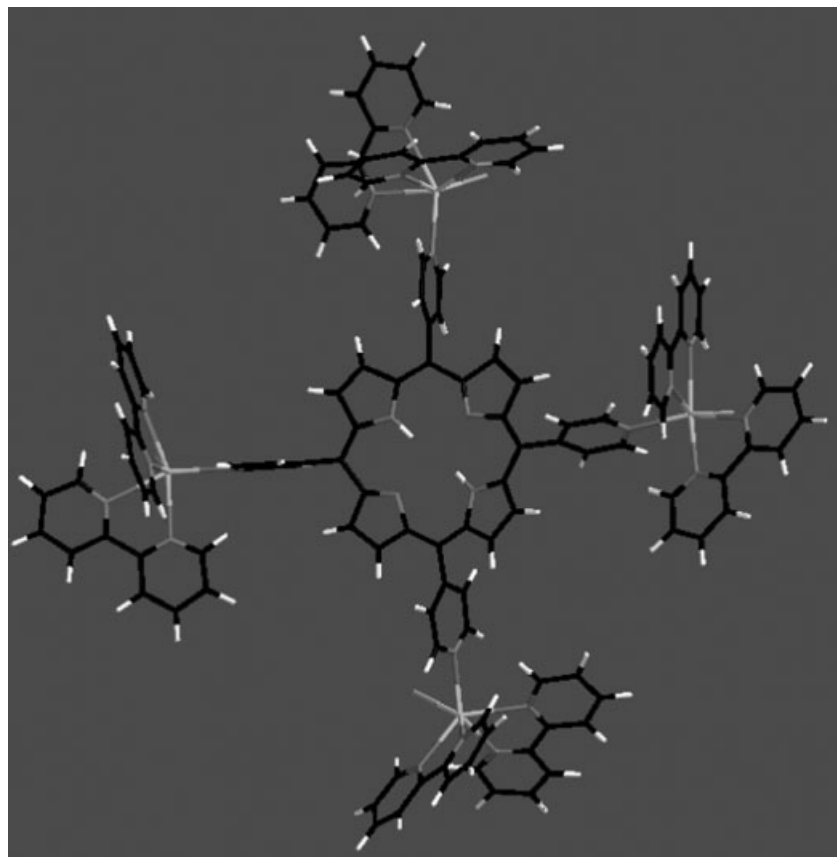


Figure 1. Three-dimensional representation of the gaseous structure of the quadruply charged cationic metalloporphyrin complex Va^{4+} .

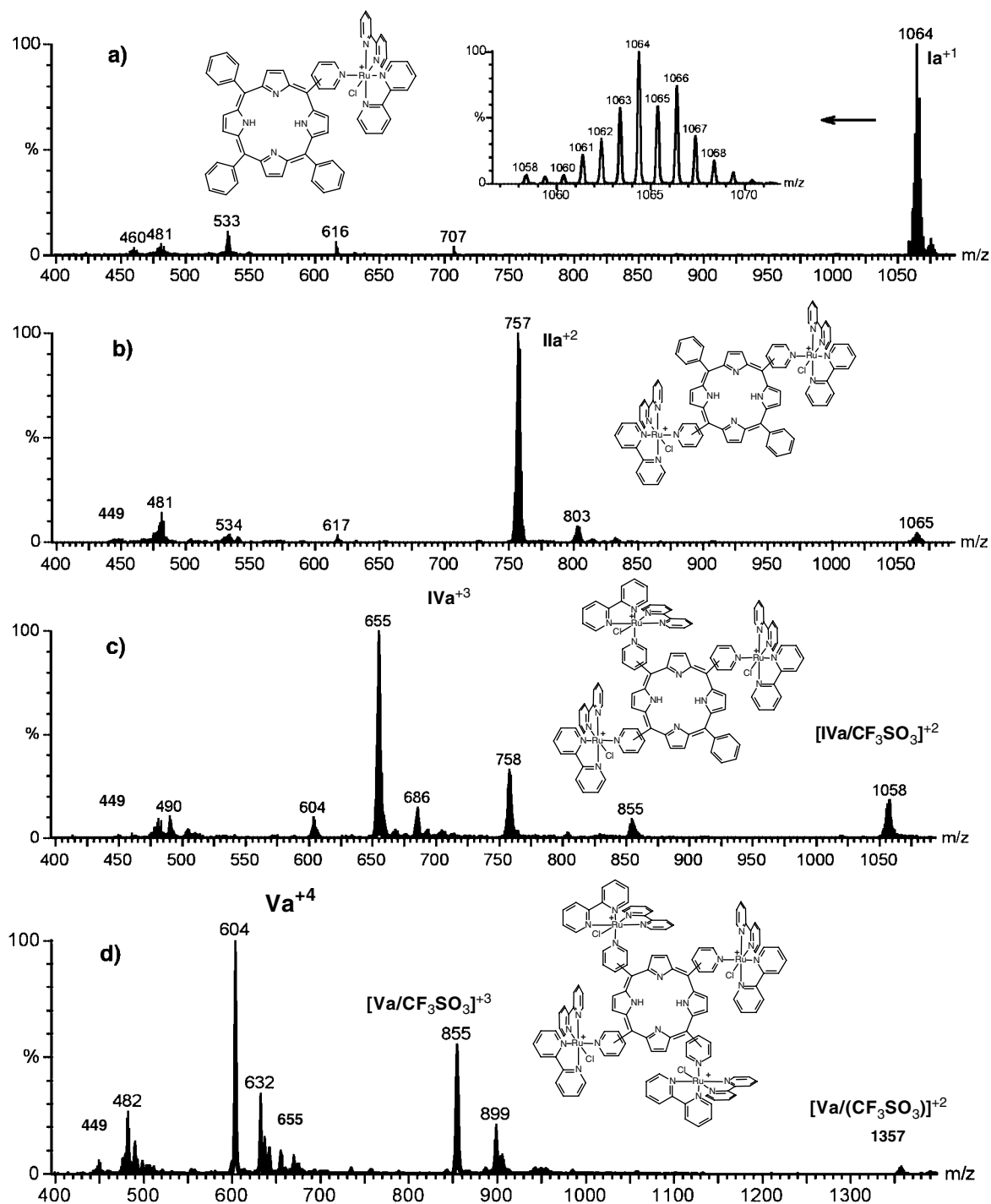
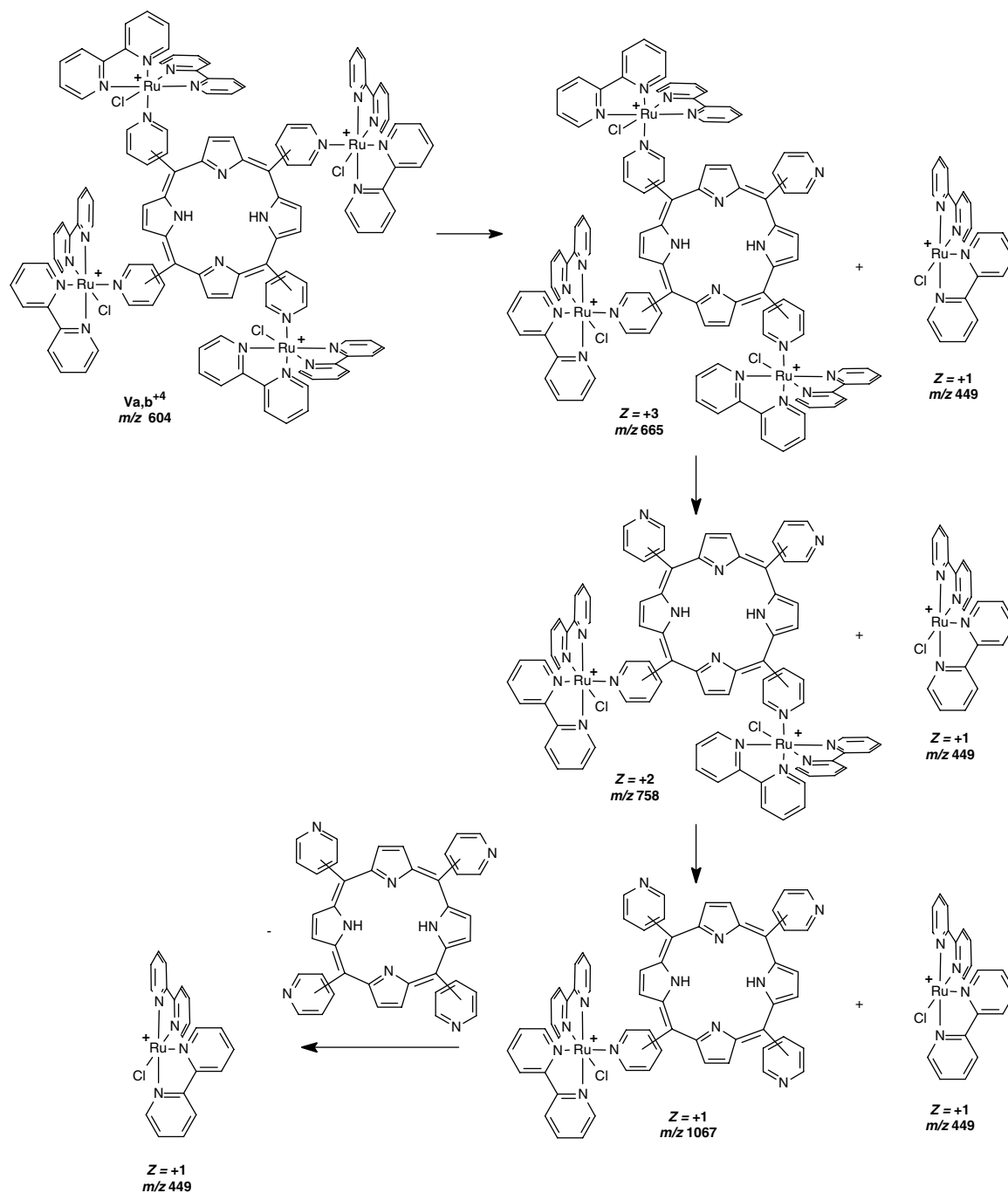


Figure 2. ESI-MS in the positive ion mode of the *meta*-substituted series (a) of cationic polyruthenated porphyrin complexes (a) Ia^+ , (b) IIa^{2+} , (c) IVa^{3+} and (d) Va^{4+} (see Scheme 1 for structures). The *para*-substituted (b) series display spectra nearly identical with those of the a series. ESI-MS of the isomeric IIIa^{2+} (not shown) is also nearly identical with that of IIa^{2+} . The inset in (a) is an expansion for the cluster of isotopologue ions Ia^+ .

replaced by a pyridyl group, which causes an increase of 1 Da for such species (m/z 1065 for the singly charged fragment ion of IIa , b^{2+} as compared with m/z 1064 for Ia , b^+). The isomeric porphyrin complexes IIIa , b^{2+} exhibit ESI-MS (not shown) nearly identical with those of IIa , b^{2+} .

ESI-MS of the triply charged complexes IVa , b^{3+} (Fig. 2(c) for IVa^{3+}) detects mainly a cluster of isotopologue ions of m/z 655 with peak separation of one-third of an m/z unit and an isotopic pattern characteristic of the triply charged

Ru_3Cl_3 -containing species IVa , b^{3+} . Compared with its singly and doubly charged analogs, IVa , b^{3+} undergo in-source CID to a greater extent. Charge partitioning breaks the weakest $[\text{Ru}(\text{bipy})_2\text{Cl}]^+ - \text{py}(\text{P})$ bond of IVa , b^{3+} to form both a doubly (m/z 758) and a singly charged (m/z 449) isotopologue cluster of fragment ions (in the ESI mass spectra, the relative abundance of the fragment ion of m/z 449 seems to have been depleted by further dissociation or by coordination with solvent). Interestingly, ion pairing with



CF_3SO_3^- also occurs to a considerable extent for IVa^{3+} during ESI, as indicated by the MS detection of the cluster of doubly charged ions of m/z 1058: $[\text{IVa, b}/\text{CF}_3\text{SO}_3]^{2+}$.

ESI-MS of the quadruply charged complexes Va, b^{4+} (Fig. 2(d) for Va^{4+}) shows an isotopologue cluster of ions of m/z 604 with one-quarter of an m/z unit peak separation and characteristic isotopic pattern fully consistent with the detection of the quadruply charged Ru_4Cl_4 -containing species Va, b^{4+} . Compared with that of IVa, b^{3+} , ESI-MS of Va, b^{4+} reveals less pronounced in-source CID (see Scheme 2) that forms minor ionic clusters of triply charged (m/z 655) and singly charged ions (m/z 449). CID is not so pronounced because electrostatic repulsion of Va, b^{4+} seems to be alleviated mainly by ion pairing that forms the relatively

abundant clusters of triply charged ions $[\text{Va, b}/\text{CF}_3\text{SO}_3]^{3+}$ of m/z 855 and doubly charged ions $[\text{Va, b}/(\text{CF}_3\text{SO}_3)_2]^{2+}$ of m/z 1357.

ESI-MS/MS structural characterization

The isotopologue gaseous and stable I-Va, b^{4+} ions detected by ESI-MS (Fig. 2) were then isolated via mass selection for ESI-MS/MS structural characterization. As Fig. 3 shows, the long-lived isotopologue Va^{4+} ions 'of m/z 604' dissociate promptly upon 15 eV collisions with argon by sequential loss of the singly charged isotopologue $[\text{Ru}(\text{bipy})_2\text{Cl}]^+$ ions 'of m/z 449' to yield, by charge partitioning, the triply, then the doubly and finally the singly charged isotopologue fragment ions 'of m/z 655, 758 and 1067', respectively (Scheme 2). The

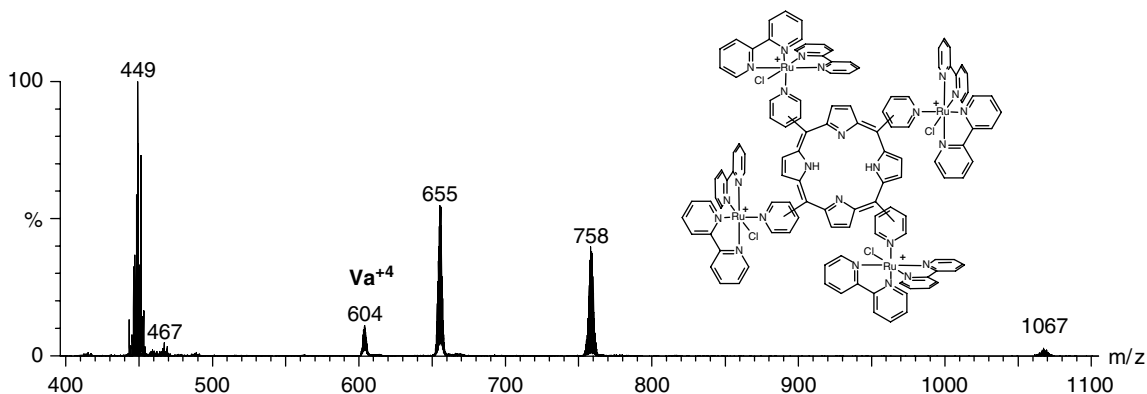


Figure 3. ESI-MS/MS in the positive ion mode for 15 eV CID of the cluster of *meta*-substituted isotopomeric ions Va^{4+} 'of m/z 604'. See Scheme 2 for the dissociation route.

singly charged fragment ions 'of m/z 1067' dissociate in turn by the loss of the neutral porphyrin to form $[Ru(bipy)_2Cl]^+$ 'of m/z 449'.

Similarly upon CID, the triply charged isotopologue complexes IVa, b^{3+} of m/z 655 lose $[Ru(bipy)_2Cl]^+$ in a stepwise fashion (spectrum not shown), forming first a cluster of doubly (m/z 758) and then singly charged ions (m/z 1066), and then $[Ru(bipy)_2Cl]^+$ of m/z 449 by the loss of the neutral porphyrin. The doubly charged complexes IIa, b^{2+} of m/z 757 dissociate, yielding the two expected clusters of singly charged ions of m/z 1065 and 449. ESI-MS/MS of the singly charged complexes Ia, b^+ of m/z 1064 shows the common 'neutral molecule plus ionic fragment' dissociation, that is, the loss of the neutral porphyrin that yields $[Ru(bipy)_2Cl]^+$ of m/z 449.

CONCLUSION

ESI is an efficient and sufficiently mild ionization technique able to transfer from solution to the gas phase the series of homologous and isomeric singly, doubly, triply and quadruply charged cationic polyruthenated macrocyclic porphyrin complexes $I-Va, b^{n+}$ ($n = 1-4$) for MS analysis. ESI-MS shows that $I-Va, b^{n+}$ constitute a new class of stable, long-lived, multiply charged gas-phase ions with spatially separated charge sites. ESI-MS shows also that increasing intramolecular electrostatic repulsion from Ia, b^+ to IVa, b^{3+} reduces the intrinsic stability, thus facilitating in-source and tandem CID. For the quadruply charged ion Va, b^{4+} , however, strong electrostatic repulsion is alleviated during ESI mainly by ion-pairing with the $CF_3SO_3^-$ counterion, which forms $[Va, b/CF_3SO_3]^{3+}$ and $[Va, b/(CF_3SO_3)_2]^{2+}$ salt clusters with reduced charge states. Ion pairing that yields $[IVa, b/CF_3SO_3]^{2+}$ is also observed as a minor ESI process for IVa, b^{3+} . Dissociation of the gaseous ions $II-Va, b^{n+}$ ($n = 2, 3$ or 4) occurs by sequential charge partitioning with the formation of *two* cationic fragments by the release of $[Ru(bipy)_2Cl]^+$. The singly charged gaseous ions Ia, b^+ dissociates by the loss of the neutral porphyrin to form solely $[Ru(bipy)_2Cl]^+$. The *meta* (a) or *para* (b) arrangement of $[Ru(bipy)_2Cl]^+$ for the isomeric $I-Va, b^{n+}$ does not affect the ESI-MS and ESI-MS/MS results. The positional isomers

II^{2+} and III^{2+} also display nearly identical ESI-MS and ESI-MS/MS results. ESI-MS and ESI-MS/MS also confirmed the expectation that $[Ru(bipy)_2Cl]^+ - py(P)$ is, intrinsically, the weakest bond for $I-Va, b^{n+}$ since this bond breaks preferentially upon CID. Very refined structural and binding information is therefore provided by ESI-MS and ESI-MS/MS analysis of $I-Va, b^{n+}$. This chemical information greatly complements and extends that provided by other classical techniques for organometallic complex analysis.⁶

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