Adduct Ions as Diagnostic Probes of Metallosupramolecular Complexes using Ion Mobility Mass Spectrometry

Niklas Geue¹, Tom S. Bennett², Lennart A. I. Ramakers¹, Grigore A. Timco², Eric. J. L. McInnes², Neil A. Burton², P. B. Armentrout³, Richard E. P. Winpenny² and Perdita E. Barran¹,*

¹Michael Barber Centre for Collaborative Mass Spectrometry, Manchester Institute of Biotechnology, Department of Chemistry, The University of Manchester, 131 Princess Street, Manchester, M1 7DN, UK. ²Department of Chemistry, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK. ³Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, USA.

*Corresponding Author: perdita.barran@manchester.ac.uk

Abstract

Following electrospray ionization (ESI), it is common for analytes to enter the gas phase accompanied by an additional small ion or molecule. Although these may not be influential in solution, they often determine the charge of the entire complex and can markedly tune their properties in the gas phase. Therefore, measuring their relative influence can be used to assist our understanding of the structure and stability of the target molecule. Because these adducts are usually distinguishable by their mass, differences in the behaviour of the analyte resulting from these added species can be extracted readily. Here, we use ion mobility mass spectrometry (IM-MS), supported by density functional theory (DFT), to investigate how different charge carriers (H⁺, Na⁺, K⁺, Cs⁺) as well as water influence the disassembly, stability, and conformational landscape of the homometallic ring [Cr₈F₈(O₂C'Bu)₁₆] and different heterometallic rotaxanes [NH₂RR'][Cr₇MF₈(O₂C'Bu)₁₆], where M = Mn, Fe, Co, Ni, Cu, Zn, and Cd. The results yield new insights on their disassembly mechanisms and support previously reported trends in cavity size and transition metal properties, demonstrating the potential of adduct ion studies for characterising metallosupramolecular complexes in general.
Introduction

Mass spectrometry (MS) allows the investigation of ions in the gas phase and, in combination with advanced fragmentation techniques, enables the investigation of their stability and disassembly. The most common fragmentation method is collision-induced dissociation (CID), by which ions are activated via collisions with a stationary target gas at user-defined kinetic energies. This gives rise to fragment ions, whose nature as well as energy of appearance can provide information regarding the stability and disassembly of the precursor ion. Another powerful addition to mass spectrometry is ion mobility (IM-MS), which separates ions based on their time to traverse a gas-filled drift cell. Here, structural information is provided in the form of collisional cross sections (CCS), which correspond to the size and shape of a given ion and can be compared to values computed from candidate geometries.

For MS and IM-MS experiments, neutral sample molecules require added charge-carrying species, $A^+/A^-$, in order to be studied. The occurrence of different adduct ions $[M + A]^+$ and $[M + A]^{-}$ can be tuned by using $A^+/A^-$ containing solutions and/or by changing ion source conditions.\(^1\) These charge carrying species can also affect intrinsic properties of the sample molecules, as previously reported for a range of compound classes such as carbohydrates,\(^2\) steroids,\(^3\) fullerenes,\(^4\) and macrocycles.\(^5,6\) For example, Kellner et al. showed that the formation, disassembly, and stability of crown ether fullerene dimers depend on the size of the alkali metal cations used, which was attributed to different adduction sites.\(^4\) Rister et al. used IM-MS to separate isobaric steroids and reported varying CCS resolutions for different $A^+$, highlighting the relevance of choosing the most suitable charge-carrying species.\(^3\)

In this work, we investigate the influence of different cations $A^+$ ($A^+ = H^+, Na^+, K^+, Cs^+$), and $H_2O$, on the disassembly, stability, and conformational landscape of metallosupramolecular complexes, namely the homometallic ring $[\text{Cr}_8\text{F}_6(\text{O}_2\text{C}^\text{t}\text{Bu})_{16}]$ = “$\text{RingCr}$,” and the rotaxane families $\text{Ph}_\text{M}$ and $\text{Am}_\text{M}$, $[\text{NH}_2\text{RR}'][\text{Cr}_7\text{MF}_6(\text{O}_2\text{C}^\text{t}\text{Bu})_{16}]$, where for $\text{Ph}_\text{M}$ the thread $[\text{NH}_2\text{RR}'^+]$ is $[\text{NH}_2(\text{CH}_2\text{Ph})(\text{CH}_2\text{CH}_2\text{Ph})]^+$ (“$\text{TPh}^+$”) and for $\text{Am}_\text{M}$ the thread $[\text{NH}_2\text{RR}'^+]$ is $[\text{NH}_2(\text{CsH}_{12}\text{NHC}(\text{O})^\text{t}\text{Bu})_2]^+$ (“$\text{TAm}^+$”), with $M = \text{Mn}^{\text{II}}$, $\text{Fe}^{\text{II}}$, $\text{Co}^{\text{II}}$, $\text{Ni}^{\text{II}}$, $\text{Cu}^{\text{II}}$, $\text{Zn}^{\text{II}}$, $\text{Cd}^{\text{II}}$. Our results show that the presence of different charge carriers and small molecules can inform about structural trends of the studied polymetallic complexes. Experimental and computational details can be found in the Supporting Information.
Results and Discussion

**Encapsulating Charge Carriers and Small Molecules in Ring**. The neutral, homometallic wheel **Ring** contains a Cr\(_8\) octagon, in which each edge is bridged by one fluoride inside the ring and two pivalate ligands outside (O\(_2\)C\(\text{Bu}\) = Piv\(^-\), Figure 1 Inset).\(^6\) In previous studies, we showed that **Ring** can encapsulate both small neutral and cationic species, making this compound an ideal example to investigate adduct ion formation.\(^7,8\) **Ring** was transferred to the gas phase from solutions of the iodides Al (A\(^+\) = Na\(^+\), K\(^+\), Cs\(^+\); Figure S1 for NaI) or by adding formic acid. We observed various cationic adducts [**Ring** + A\(^+\)]\(^+\) (A\(^+\) = Na\(^+\), Na\(^+\) + H\(_2\)O, K\(^+\), Cs\(^+\)) as well as the oxidised [**Ring** + H\(_2\)O\(^+\)] (Figure S2 for Isotopic Distribution, which excludes an additional proton as the source of the positive charge). The adducts were isolated, activated via collisions with nitrogen gas, and the fractions of precursor ions that did not fragment (“survival yield”) were derived for different centre-of-mass energies \(E_{\text{com}}\) (Figure 1a including fragmentation pathways). The \(E_{\text{com}}\) at which 50% of the precursor ion fragments (“\(E_{50}\)”) is known as a relative measure of ion stability and was enumerated for all species.

As shown in Figure 1a and Table 1, [**Ring** + Cs\(^+\)]\(^+\) is the most stable of the studied adducts. A significantly lower \(E_{50}\) value was observed for the alkali metal cation [**Ring** + K\(^+\)]\(^+\) and lower still for [**Ring** + Na\(^+\)]\(^+\), showing that the stability trend correlates with alkali metal size. To rationalise this behaviour, DFT optimised structures were generated for [**Ring** + A\(^+\)]\(^+\) (A\(^+\) = Na\(^+\), K\(^+\), Cs\(^+\)). In these geometries, Cs\(^+\) is located in the centre of the ring, whereas K\(^+\), and more strongly pronounced Na\(^+\), are closer to the edge of the interior (Figures S3-S5 including atomic distances). The stability of the entire adduct likely depends on the A-F ion-dipole interactions, which are more abundant for Cs\(^+\) > K\(^+\) > Na\(^+\) because of their size. The calculated structures are also in agreement with our previous findings from crystal structures, where Cs\(^+\) was shown to fill the cavity of the similar heterometallic [**Ring**\(_\text{Co}\)]\(^-\) (discussed further below), binding to eight fluorides,\(^9\) whereas the smaller Na\(^+\) does not bind to all fluorides.\(^10\)

[**Ring** + Na\(^+\)]\(^+\) was observed in the mass spectrum of **Ring** in a solution of NaI, but could not be isolated in the quadrupole mass filter (Figure S1, S2). However, the MS\(^2\) spectrum of the sodiated water adduct [**Ring** + Na + H\(_2\)O\(^+\)]\(^+\) yielded both product ions [**Ring** + A\(^+\)]\(^+\) (A\(^+\) = Na\(^+\), Na\(^+\) + H\(_2\)O) without further collisional activation (Figure S6), indicating a small energy barrier for the loss of water. This was confirmed by highly similar \(E_{50}\) values of [**Ring** + Na\(^+\)] and
[\textit{Ring}_{\text{Cr}} + \text{Na} + \text{H}_2\text{O}]^+$, although the latter was found to be slightly more stable (Figure 1a, Table 1), consistent with stable inclusion of water.

\textbf{Table 1:} $E_{50}$ and $^{TW}CCS_{N2}$ ($TW =$ “Traveling Waves”) values of the cations $[\textit{Ring}_{\text{Cr}} + A]^+$ ($A^+ = \text{Na}^+$, $\text{Na}^+ + \text{H}_2\text{O}$, $\text{K}^+$, $\text{Cs}^+$) and $[\textit{Ring}_{\text{Cr}} + \text{H}_2\text{O}]^+$ including experimental error. The $^{TW}CCS_{N2}$ value of $[\textit{Ring}_{\text{Cr}} + \text{Na}]^+$ is very close to that found for $[\textit{Ring}_{\text{Cr}} + \text{Na} + \text{H}_2\text{O}]^+$, which may be attributed to metastable loss of water post the drift region.

\begin{center}
\begin{tabular}{l|c|c}
\hline
Cation & $E_{50}$ (eV) & $^{TW}CCS_{N2}$ (Å$^2$) \\
\hline
$[\textit{Ring}_{\text{Cr}} + \text{H}_2\text{O}]^+$ & 1.364 ± 0.004 & 426.1 ± 1.4 \\
$[\textit{Ring}_{\text{Cr}} + \text{Na}]^+$ & 1.822 ± 0.004 & 429.7 ± 0.3 \\
$[\textit{Ring}_{\text{Cr}} + \text{Na} + \text{H}_2\text{O}]^+$ & 1.860 ± 0.003 & 429.4 ± 0.4 \\
$[\textit{Ring}_{\text{Cr}} + \text{K}]^+$ & 2.045 ± 0.008 & 428.1 ± 0.6 \\
$[\textit{Ring}_{\text{Cr}} + \text{Cs}]^+$ & 2.239 ± 0.005 & 429.6 ± 1.0 \\
\hline
\end{tabular}
\end{center}
Figure 1: a) Normalised survival yield vs. $E_{\text{com}}$ for [Ring$_{\text{Cr}}$ + A]$^+$ (A$^+$ = Na$^+$, Na$^+$ + H$_2$O, K$^+$, Cs$^+$) as well as [Ring$_{\text{Cr}}$ + H$_2$O]$^+$. The main dissociation reactions are presented. b) CCS$_{N2}$ distributions of [Ring$_{\text{Cr}}$ + H$_2$O]$^+$, [Ring$_{\text{Cr}}$ + Na + H$_2$O]$^+$ and [Ring$_{\text{Cr}}$ + Cs]$^+$. One dataset each is shown and all experimental errors are smaller than 0.5% (Table 1). Data for [Ring$_{\text{Cr}}$ + Na]$^+$ and [Ring$_{\text{Cr}}$ + K]$^+$ are similar and were omitted for clarity. Inset: Structure of the chromium-wheel complex Ring$_{\text{Cr}}$ (green: chromium, yellow: fluorine, red: oxygen, grey: carbon). Hydrogen atoms were omitted for clarity at the tert-butyl groups.
Different disassembly channels were observed for the ions $[\text{Ring}_\text{Cr} + A]^+$ (A$^+$ = Na$^+$, Na$^+$ + H$_2$O, K$^+$, Cs$^+$) and the oxidized species $[\text{Ring}_\text{Cr} + \text{H}_2\text{O}]^+$ (Figure 1a). Although the alkali metal cations show the loss of one chromium centre and three anionic ligands (predominantly three pivalates, Figure S7a), $[\text{Ring}_\text{Cr} + \text{H}_2\text{O}]^+$ fragments via the loss of water and one, likely neutral pivalate (see discussion below) as the main dissociation channel (Figure S7b). $[\text{Ring}_\text{Cr} + \text{H}_2\text{O}]^+$ was found to have the smallest $E_{50}$ value of all studied adducts, which we attribute to a thermodynamically favourable reduction during fragmentation. The DFT optimised structure of $[\text{Ring}_\text{Cr} + \text{H}_2\text{O}]^+$ was computed (Figure S8) and, to investigate which part of this unusual cation is oxidised, we analysed the corresponding spin-density (Supplementary Dataset). This analysis suggests that all Cr$^{\text{III}}$ centres are maintained and the electron is removed from the pivalates on the opposite side of the water binding sites.

The identity of the added species had no major impact on the adduct size, as measured by IM-MS, and only small differences were observed in their CCS$_{N2}$ distributions (Figure 1b, Table 1). All species appear with a slightly asymmetric peak shape, and the extent of the asymmetry varies from sample to sample. This suggests the occurrence of different, potentially interconverting ring adduct conformers, attributable to varying locations of A$^+$ or H$_2$O in $\text{Ring}_\text{Cr}$. The asymmetry is most strongly pronounced for $[\text{Ring}_\text{Cr} + \text{H}_2\text{O}]^+$, which is also slightly smaller than the alkali metal adducts. This behaviour could be a result of the different charge distribution in the oxidized $[\text{Ring}_\text{Cr} + \text{H}_2\text{O}]^+$. Theoretical CCS$_{N2}$ values were predicted for all five cations from their DFT optimised structures (Figures S3-S5, S8, S9) using the trajectory method of IMoS (Table S1).$^{11}$ These were found to be $\approx 9\%$ larger than experiment, which we previously observed for the similar heterometallic rings $[\text{Ring}_\text{M}]^+$ and discussed there in detail.$^{12}$ In agreement with the experimental values, only minor differences in the calculated CCS$_{N2}$ values were found for different A$^+$.

*Stability of the Rotaxane Ions $[\text{Am}_\text{M} + A]^+$ and $[\text{Ph}_\text{M} + A]^+$ ($A^+ = \text{Na}^+, \text{K}^+, \text{Cs}^+$).* The rotaxane families $\text{Am}_\text{M}$ and $\text{Ph}_\text{M}$ involve a secondary ammonium cation $[\text{NH}_2\text{RR'}]^+$ (“Thread”) surrounded by a heterometallic ring $[\text{Ring}_\text{M}]^+$ ($M = \text{Mn}^{\text{II}}, \text{Fe}^{\text{II}}, \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Cu}^{\text{II}}, \text{Zn}^{\text{II}}, \text{Cd}^{\text{II}}$; Figure 2a). These rings are similar to $\text{Ring}_\text{Cr}$, but with one Cr$^{\text{III}}$ centre exchanged for a divalent metal M$^{\text{II}}$, leading to an overall negative charge.$^{13,14}$ Previously, we have extensively studied the disassembly of $[\text{Ring}_\text{M}]^+$, $[\text{Am}_\text{M} + A]^+$, and $[\text{Ph}_\text{M} + A]^+$ ($A^+ = \text{H}^+, \text{Na}^+$), using IM-MS, and demonstrated that the d-metal present and the thread strongly influence the $E_{50}$ value and
disassembly mechanism of these cations. Major differences were also observed between protonated and sodiated forms, showing that the charge-carrying species is an important factor when considering the disassembly of these complexes (Table 2, Figure S10). Here, we extend this work by enumerating the $E_{50}$ values of the potassium and caesium adducts, $[\text{Am}_M + A]^+$ and $[\text{Ph}_M + A]^+$ ($A^+ = K^+, \text{Cs}^+$), and compare them to the data of the sodiated forms (Table 2, Figure 2b including dissociation reactions). In addition to the influence of the divalent metal, the data show notable differences with respect to the alkali metal.

**Table 2:** $E_{50}$ values of $[\text{Ph}_M + A]^+$ and $[\text{Am}_M + A]^+$ ($A^+ = H^+, \text{Na}^+, K^+, \text{Cs}^+$) including experimental error. Data for $[\text{Ph}_M + A]^+$ and $[\text{Am}_M + A]^+$ ($A^+ = H^+, \text{Na}^+$) were obtained from our previous work.

<table>
<thead>
<tr>
<th>$E_{50}$ in eV</th>
<th>Mn$^{\text{II}}$</th>
<th>Fe$^{\text{II}}$</th>
<th>Co$^{\text{II}}$</th>
<th>Ni$^{\text{II}}$</th>
<th>Cu$^{\text{II}}$</th>
<th>Zn$^{\text{II}}$</th>
<th>Cd$^{\text{II}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ph}_M + H]^+$</td>
<td>0.283 $\pm$ 0.003</td>
<td>-</td>
<td>0.288 $\pm$ 0.005</td>
<td>0.331 $\pm$ 0.003</td>
<td>0.478 $\pm$ 0.014</td>
<td>0.377 $\pm$ 0.008</td>
<td>0.242 $\pm$ 0.002</td>
</tr>
<tr>
<td>$[\text{Ph}_M + Na]^+$</td>
<td>1.021 $\pm$ 0.001</td>
<td>0.953 $\pm$ 0.001</td>
<td>0.940 $\pm$ 0.002</td>
<td>1.066 $\pm$ 0.002</td>
<td>0.772 $\pm$ 0.002</td>
<td>0.802 $\pm$ 0.002</td>
<td>0.889 $\pm$ 0.002</td>
</tr>
<tr>
<td>$[\text{Ph}_M + K]^+$</td>
<td>0.992 $\pm$ 0.003</td>
<td>0.988 $\pm$ 0.004</td>
<td>0.970 $\pm$ 0.003</td>
<td>1.102 $\pm$ 0.004</td>
<td>0.731 $\pm$ 0.003</td>
<td>0.777 $\pm$ 0.002</td>
<td>0.862 $\pm$ 0.004</td>
</tr>
<tr>
<td>$[\text{Ph}_M + Cs]^+$</td>
<td>0.946 $\pm$ 0.002</td>
<td>0.984 $\pm$ 0.003</td>
<td>0.947 $\pm$ 0.003</td>
<td>1.071 $\pm$ 0.004</td>
<td>0.709 $\pm$ 0.002</td>
<td>0.755 $\pm$ 0.002</td>
<td>0.805 $\pm$ 0.004</td>
</tr>
<tr>
<td>$[\text{Am}_M + H]^+$</td>
<td>0.248 $\pm$ 0.003</td>
<td>-</td>
<td>0.256 $\pm$ 0.002</td>
<td>0.209 $\pm$ 0.002</td>
<td>0.450 $\pm$ 0.004</td>
<td>0.336 $\pm$ 0.002</td>
<td>0.218 $\pm$ 0.003</td>
</tr>
<tr>
<td>$[\text{Am}_M + Na]^+$</td>
<td>1.098 $\pm$ 0.005</td>
<td>1.094 $\pm$ 0.002</td>
<td>1.092 $\pm$ 0.005</td>
<td>1.221 $\pm$ 0.003</td>
<td>0.912 $\pm$ 0.004</td>
<td>0.902 $\pm$ 0.003</td>
<td>1.028 $\pm$ 0.007</td>
</tr>
<tr>
<td>$[\text{Am}_M + K]^+$</td>
<td>1.108 $\pm$ 0.004</td>
<td>1.059 $\pm$ 0.003</td>
<td>1.076 $\pm$ 0.003</td>
<td>1.207 $\pm$ 0.004</td>
<td>0.782 $\pm$ 0.007</td>
<td>0.881 $\pm$ 0.003</td>
<td>0.984 $\pm$ 0.003</td>
</tr>
<tr>
<td>$[\text{Am}_M + Cs]^+$</td>
<td>0.993 $\pm$ 0.003</td>
<td>0.968 $\pm$ 0.003</td>
<td>0.989 $\pm$ 0.003</td>
<td>1.124 $\pm$ 0.003</td>
<td>0.743 $\pm$ 0.003</td>
<td>0.802 $\pm$ 0.003</td>
<td>0.851 $\pm$ 0.003</td>
</tr>
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</table>

For six of the seven divalent metals studied, $E_{50}$ values for $[\text{Am}_M + A]^+$ ($A = \text{Na}^+, K^+, \text{Cs}^+$) each show the Na$^+$ adducts to be most stable, followed by the respective K$^+$ and Cs$^+$ species; the minor exception is for M = Mn$^{\text{II}}$ (Figure 2b left). However, for the rotaxane adducts $[\text{Ph}_M + A]^+$
(A = Na⁺, K⁺, Cs⁺), the alkali metal trend varies with the divalent metal M. The stability order is Na⁺ > K⁺ > Cs⁺ for M = Mn¹¹, Cu¹°, Zn¹°, and Cd¹° (Figure 2b right). For M = Fe¹°, Co¹°, and Ni¹°, the potassium adducts are most stable, followed by [PhM + Cs]⁺ and [PhM + Na]⁺.

The observed trends can be rationalised with the binding site of the alkali metals. For AmM⁺, A⁺ (A⁺ = Na⁺, K⁺, Cs⁺) likely coordinates at the end groups of TAmp⁺, whose amides are well-known to bind alkali metals effectively in the gas phase (bond dissociation energies: 120 - 160 kJ/mol). This is unlikely for the phenyl groups in TPh⁺ and here crystal structures also suggest that the end groups are too close to the ring in order to coordinate A⁺ without major distortions. This leaves the outside of the ring as the most likely location of A⁺ in [PhM + A]⁺ (A⁺ = Na⁺, K⁺, Cs⁺), presumably close to M¹° as the charge density there is lower than adjacent to Cr¹°.

The disassembly mechanism of [AmM + A]⁺ and [PhM + A]⁺ involve the release of the thread via slipping through the ring (and the loss of an anionic pivalate), however the data indicate that A⁺ remains on the product [(RingM − Piv) + A]⁺ after fragmentation. For [AmM + A]⁺, we suggest an alkali metal transfer from the thread to the ring during thread release (Figure S11), which leads to the coordination of A⁺ in the centre of the ring, similar to the alkali metal adducts of RingCr (Figure 1) and our previously reported complexes [RingCo + A]⁺ (A⁺ = Na⁺, Cs⁺). Na⁺ is the smallest of the three studied alkali metal cations, with the highest charge density, leading to stronger bonds with the thread end groups than for K⁺ and even less for Cs⁺. Additionally, the disassembly products [(RingM − Piv) + A]⁺ are similar to [RingCr + A]⁺ and presumably also most stabilised with Cs⁺ > K⁺ > Na⁺ (Table 1, Figure 1). Both trends would lead to the loss of the thread and transfer of A⁺ to the ring being most favoured for Cs⁺ and least favoured for Na⁺, which results in the highest E₅₀ values for Na⁺ as observed for [AmM + A]⁺.

For [PhM + A]⁺, where A⁺ is presumably located outside of the ring and close to M, we observed the same trend for the divalent metals with larger covalent radii (Cd¹°, Mn¹°, Cu¹°, and Zn¹°, Figure 2b) as for [AmM + A]⁺. This could be explained with the better fit of the smaller A⁺ into the space between the tert-butyl groups, resulting in stabilities of the order Na⁺ > K⁺ > Cs⁺. Conversely, the species with the smaller covalent radii (M = Fe¹°, Co¹°, and Ni¹°) follow the E₅₀ trend K⁺ > Cs⁺ > Na⁺ (Figure 2b right). Because of the reduced space at the outside of the ring caused by the smaller M, A⁺ cannot bind as closely to M and the precursor ion stability is likely a less significant factor for the determination of E₅₀. However, the product ions [(RingM − Piv)
+ A]⁺ are more spacious after the loss of the thread and one anionic pivalate ligand. Assuming that A⁺ remains outside the ring, these species are also likely to be most stabilised in the order Na⁺ > K⁺ > Cs⁺, which would lead to the reverse trend for the $E_{50}$ values of the precursor ions [Ph⁺ + A]⁺. The experimental data could hence be the overlap of precursor and product ion stability, which is shifted towards product ions for [Ph⁺ + A]⁺ with smaller M. A similar trend is found with the ionic radii of M, which produced a slightly worse correlation than the covalent radii.¹⁷

Figure 2: a) Schematic structure of [Ph⁺ + A]⁺ and [Am⁺ + A]⁺. b) $E_{50}$ values of [Am⁺ + A]⁺ (left) and [Ph⁺ + A]⁺ (right, A⁺ = Na⁺, K⁺, Cs⁺; M = MnⅡ, FeⅡ, CoⅡ, NiⅡ, CuⅡ, ZnⅡ, CdⅡ) with respect to M. The main dissociation reactions are presented. For [AmCu + Na]⁺, the main dissociation pathway is the loss of copper and two anionic pivalates. Error bars are shown but, in all cases, are smaller than the symbol size. Data for the series [Ph⁺ + Na]⁺ were obtained from our previous work.¹²

Conformational Flexibility of the Rotaxane Ions [Am⁺ + A]⁺ and [Ph⁺ + A]⁺ (A⁺ = H⁺, Na⁺). The conformational landscape of the studied rotaxanes can also depend on A⁺. This effect was
most prominently shown for \([\text{Am}_M + \text{Na}]^+\) and \([\text{Am}_M + \text{H}]^+\) (Figure 3 left, Table S2). The series of sodiated species shows only minor differences in \(\text{CCS}_{N2}\) \((\Delta \text{CCS}_{N2} = 5.7 \, \text{Å}^2)\). The distributions of \([\text{Am}_M + \text{H}]^+\) are spread over a much broader range \((\Delta \text{CCS}_{N2} = 12.9 \, \text{Å}^2)\), with complexes of \(M = \text{Cd}^{II}\), \(\text{Mn}^{II}\), and \(\text{Ni}^{II}\) being smaller than those of \(M = \text{Co}^{II}\), which is smaller than those for \(M = \text{Zn}^{II}\) and \(\text{Cu}^{II}\). In contrast, this larger spread was not observed for \([\text{Ph}_M + \text{H}]^+\) \((\Delta \text{CCS}_{N2} = 3.3 \, \text{Å}^2)\) nor \([\text{Ph}_M + \text{Na}]^+\) \((\Delta \text{CCS}_{N2} = 4.5 \, \text{Å}^2\), Figure 3 right, Table S2).

The variation in the \(\text{CCS}_{N2}\) data of \([\text{Am}_M + \text{H}]^+\) can be rationalized with the binding site of \(\text{H}^+\) and the covalent radii of \(M\). As shown in our previous work,\(^{12}\) the protonated species \([\text{Am}_M + \text{H}]^+\) and \([\text{Ph}_M + \text{H}]^+\) dissociate via the loss of pivalic acid (HPiv), indicating that the proton is located at the ring and likely close to \(M^{II}\) because of the lower charge density there compared to the \(\text{Cr}^{III}\) sites. For the complexes with the largest \(d\)-metals, \(\text{Cd}^{II}\) and \(\text{Mn}^{II}\), protons presumably are located between the anionic pivalate ligands, coordinated to the -O or possibly -F atoms. This will draw the complex together to a more compact conformation. Conversely, the smaller metals \((M = \text{Co}^{II}, \text{Cu}^{II}, \text{Zn}^{II})\) might not provide enough inter-ligand space, making protonation only possible at the outside of the ring. This would result in an extended ring conformation with higher \(\text{CCS}_{N2}\) (Figure 3 top left), in which the proton pulls the ligands towards the ring exterior. The \(M = \text{Ni}^{II}\) species appears more compact than the \(\text{Co}^{II}\) compound and is more difficult to rationalise.

The absence of this spread for the sodiated ions \([\text{Am}_M + \text{Na}]^+\) and \([\text{Ph}_M + \text{Na}]^+\) (Figure 3 bottom) can be explained by the different binding sites of \(\text{Na}^+\), as discussed above, and the lower charge density of \(\text{Na}^+\), which possibly minimises the distortions induced by \(A^+\). The different behaviour of \([\text{Ph}_M + \text{H}]^+\) (Figure 3 top right) is presumably a result of the proximity of the phenyl end groups, limiting the binding sites of \(\text{H}^+\) at the ring and hence the conformational flexibility of \([\text{Ph}_M + \text{H}]^+\).
**Figure 3:** CCS$_{N2}$ distributions of [Am$_M$ + A]$^+$ (left) and [Ph$_M$ + A]$^+$ (A = H$^+$, Na$^+$; right). One dataset is shown each and all experimental errors are smaller than 0.5% (Table S2). For each plot, legends are arranged from highest to lowest CCS$_{N2}$ maximum as presented in the figure. The distribution for [Am$_{Fe}$ + H]$^+$ and [Ph$_M$ + H]$^+$ (M = Fe$^{II}$, Cu$^{II}$, Zn$^{II}$) could not be obtained because of overlapping signals.

We quantified the full width at half maximum of the CCS$_{N2}$ distribution for each rotaxane ion [Am$_M$ + A]$^+$ and [Ph$_M$ + A]$^+$ (A$^+$ = H$^+$, Na$^+$) as a measure of their conformational flexibility (Table S3). Significant differences in FWHM (CCS$_{N2}$) were observed, although the ions involving the large metal Cd$^{II}$ and to a lesser extent Mn$^{II}$, yield in almost all cases narrower distributions than the related species with smaller M. This suggests more rigidity for the ions with Cd$^{II}$ and Mn$^{II}$, most likely because of an enlarged and asymmetric ring shape.

Comparison of the alkali metal adducts for the two selected ions [Ph$_{Mn}$ + A]$^+$ and [Am$_{Co}$ + A]$^+$ (A$^+$ = Na$^+$, K$^+$, Cs$^+$) shows that both CCS$_{N2}$ and FWHM (CCS$_{N2}$) increase as the size of the alkali metal cations increases (Cs$^+$ > K$^+$ > Na$^+$; Tables S2, S3). This can be rationalised with the larger size of A$^+$ and their weaker bonding, which slightly increases the size and flexibility of the entire rotaxane complex.
In conclusion, we demonstrate how variation of adduct ions can be used to investigate molecular properties of metallosupramolecular complexes using IM-MS and collision-induced dissociation. Different structural trends were derived for a series of polymetallic rings and rotaxanes, correlating with previous data obtained from crystal structures. This agreement makes the presented methodology interesting for larger metallosupramolecular complexes, for which X-Ray crystallography is often not feasible. The present study demonstrates that the use of different charge-carrying species in IM-MS can contribute valuable structural information.

**Conflict of Interests**

There are no conflicts to declare.

**Supplementary Data**

Supporting data referred to in this manuscript is contained within a supplementary information document and in a supplementary data set available on Figshare 10.6084/m9.figshare.21333786. The latter contains the raw data of ion mobility mass spectrometry and mass spectrometry measurements as well as the outputs from DFT calculations.

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References


Using ion mobility mass spectrometry, we show how different charge carrying ions and small molecules can tune the stability and conformational landscape of metallosupramolecular complexes and aid their structural characterisation.