

Supplementary Information.

Experimental Method

A detailed description of the instrumentation used for generation, resolution and detection of the cluster beam has been provided in previous publications.^{1,2} Briefly, the apparatus combines a supersonic cluster and pick-up source with a high resolution double focusing mass spectrometer (VG ZAB-E). Argon carrier gas at a pressure of between 30 and 40 psi was passed through a reservoir containing water at room temperature. The resultant mixture of argon and water vapour then underwent supersonic expansion through a pulsed 200 μm diameter conical nozzle, followed by collimation 2 cm downstream by a 1 mm-diameter skimmer. Midway between the expansion chamber and the mass spectrometer, the cluster beam passed over the mouth of a high temperature effusion cell (DCA Instruments, EC-40-63-21) equipped with a crucible of pyrolytic boron nitride. Metal vapour from each of the nine metals discussed here was allowed to diffuse into the flight tube in order to create a region where the vapour and the cluster beam could interact. Previous experiments using the 'pick-up' technique have shown that the presence of clusters in the beam of the form Ar_nL_m , where L is water, is essential for the successful generation of neutral ML_k complexes.¹

Signal intensities recorded on the apparatus over a series of experiments have suggested that the optimal partial pressure of metal vapour is between 10^{-1} and 10^{-2} torr. Above this pressure, disruption of the cluster beam results in reduced signal intensity, and at lower pressures the signal metal/solvent clusters decreases. For each of the metals, the above partial pressure was estimated from published temperature/vapour pressure observations and the effusion cell was held at the appropriate temperature as measured with a standard C-type thermocouple. Once the complexes had been detected in the mass spectrometer, the conditions of expansion pressure and oven temperature were fine-tuned to maximise signal

intensity. A shutter at the exit of the effusion cell was used to confirm the identity of clusters containing each metal.

The neutral metal/solvent clusters were ionised by 100 eV electrons within the ion source of the mass spectrometer and were then accelerated at a potential of +5kV. After passing through a field free region, individual $[M(L)_n]^{2+}$ ions were selected according to their mass/charge ratio in a magnetic sector. A second field free region (*2ffr*) separated the magnetic sector from an electrostatic analyser (ESA), and together they were operated in a linked-scan mode to give a MIKE (Mass-analysed Ion Kinetic Energy) spectrum³ of any singly charge products produced as a result of reaction (3) taking place in the *2ffr*. These reactions take place against a background pressure of $< 10^{-7}$ mbar and they arise because dications can undergo unimolecular decay from a metastable state that lies behind a barrier to proton transfer⁴ that is created by Coulomb repulsion between the reaction products as they undergo charge separation. With the ion source potential set at 5 kV the initial laboratory-frame kinetic energy of the dications was 10 keV; therefore, the ESA could be scanned to transmit any fragment ions with kinetic energies of between 5 and 10 keV without any background interference from underlying singly charged ions that may pass through the magnet. Final ion detection took place at a Daly detector, where phase sensitive detection was facilitated by a Stanford Research Systems SR850 lock-in amplifier.

Figures S1 and S2 shows examples of Coulomb fission where laboratory-frame kinetic energy profiles have been recorded for metal-containing fragments ions arising from the ions $[Mn(H_2O)_4]^{2+}$ and $[Sn(H_2O)_{17}]^{2+}$ ion. Each profile exhibits the characteristic shape of a reaction that is accompanied by the high kinetic energy release that results from Coulomb repulsion between the two singly charged ions as they separate.⁴ Profiles similar to those given in figures S1 and S2 have been recorded for all of the systems discussed here,⁵ and

further examples of Coulomb explosion in Cu^{2+} , Zn^{2+} and Pb^{2+} complexes with water are to be found in preliminary publications.⁶⁻⁸

Table S1 Summary of previous measurements of the minimum number of water molecules required to stabilise the metal dications listed. The comparison is between n_s , which has been identified in these experiments as the minimum number of water molecules required to stabilise a metal ion, and n_{crit} , which has been measured in experiments by others as being the number at which or below Coulomb fission or charge separation is observed. If all of the measurements gave similar results then $n_{\text{crit}}=n_s-1$.

Metal	$n_s - 1^a$	n_{crit}	n_{crit}^d	2 nd ion. energy of M / eV
Sr^{2+}	0	2^b	2	11.02
Ca^{2+}	0	2^b	2	11.86
Mg^{2+}	3	3^b	4	15.02
Mn^{2+}	4	3^b	4	15.63
Zn^{2+}	7	5^b	6	17.95
Cr^{2+}	6	-	-	16.47
Pb^{2+}	10	-	-	15.02
Cu^{2+}	7	6^c	6	20.27
Sn^{2+}	25	-	-	14.51

^a This work together with data taken from refs. 6-8

^b Kebarle and co-workers, refs. 9-12.

^c Stone and Vukomanovic, ref. 13

^d Shvartsburg and Siu, ref. 14

Table S1 Summary of Coulomb fission events recorded for $[M(H_2O)_N]^{2+}$ complexes together with kinetic energy releases, $\langle \epsilon_t \rangle$, measured from the peak profiles .

n in $[M(H_2O)_n]^{2+}$	MOH ⁺ fragment	Counter ion	$\langle \epsilon_t \rangle$ / kJ mol ⁻¹
M = Mg			
3	MgOH ⁺ (H ₂ O)	H ₃ O ⁺	209
M = Ca			
M = Sr			
M = Mn			
3	MnOH ⁺ (H ₂ O)	H ₃ O ⁺	252
4	MnOH ⁺ (H ₂ O) ₂	H ₃ O ⁺	201
M = Cu			
6	CuOH ⁺ (H ₂ O) ₃	H ₃ O ⁺ (H ₂ O)	174
7	CuOH ⁺ (H ₂ O) ₃	H ₃ O ⁺ (H ₂ O) ₂	150
M = Zn ^a			
4	ZnOH ⁺ (H ₂ O) ₂	H ₃ O ⁺	172
5	ZnOH ⁺ (H ₂ O) ₂	H ₃ O ⁺ (H ₂ O)	161
6	ZnOH ⁺ (H ₂ O) ₃	H ₃ O ⁺ (H ₂ O)	158
7	ZnOH ⁺ (H ₂ O) ₃	H ₃ O ⁺ (H ₂ O) ₂	145
M = Cr			
6	[Cr(OH)(H ₂ O) ₃] ⁺	H ₃ O ⁺ (H ₂ O)	211
M = Pb ^b			
4	PbOH ⁺ (H ₂ O)	H ₃ O ⁺ (H ₂ O)	191
7	PbOH ⁺ (H ₂ O) ₂	H ₃ O ⁺ (H ₂ O) ₃	178
8	PbOH ⁺ (H ₂ O) ₄	H ₃ O ⁺ (H ₂ O) ₂	160
9	PbOH ⁺ (H ₂ O) ₄	H ₃ O ⁺ (H ₂ O) ₃	157
10	PbOH ⁺ (H ₂ O) ₅	H ₃ O ⁺ (H ₂ O) ₃	152
M = Sn			
15	SnOH ⁺ (H ₂ O) ₈	H ₃ O ⁺ (H ₂ O) ₅	140
16	SnOH ⁺ (H ₂ O) ₉	H ₃ O ⁺ (H ₂ O) ₅	129
17	SnOH ⁺ (H ₂ O) ₉	H ₃ O ⁺ (H ₂ O) ₆	125
	SnOH ⁺ (H ₂ O) ₁₀	H ₃ O ⁺ (H ₂ O) ₅	96
18	SnOH ⁺ (H ₂ O) ₁₀	H ₃ O ⁺ (H ₂ O) ₆	97
19	SnOH ⁺ (H ₂ O) ₁₂	H ₃ O ⁺ (H ₂ O) ₅	92
20	SnOH ⁺ (H ₂ O) ₁₃	H ₃ O ⁺ (H ₂ O) ₅	72
21	SnOH ⁺ (H ₂ O) ₁₄	H ₃ O ⁺ (H ₂ O) ₅	97

22	$\text{SnOH}^+(\text{H}_2\text{O})_{14}$	$\text{H}_3\text{O}^+(\text{H}_2\text{O})_6$	97
23	$\text{SnOH}^+(\text{H}_2\text{O})_{15}$	$\text{H}_3\text{O}^+(\text{H}_2\text{O})_6$	120
24	$\text{SnOH}^+(\text{H}_2\text{O})_{16}$	$\text{H}_3\text{O}^+(\text{H}_2\text{O})_6$	104
25	$\text{SnOH}^+(\text{H}_2\text{O})_{17}$	$\text{H}_3\text{O}^+(\text{H}_2\text{O})_6$	80

^a Some of these reactions were reported in ref. 8

^b Some of these reactions were reported in ref. 7.

References

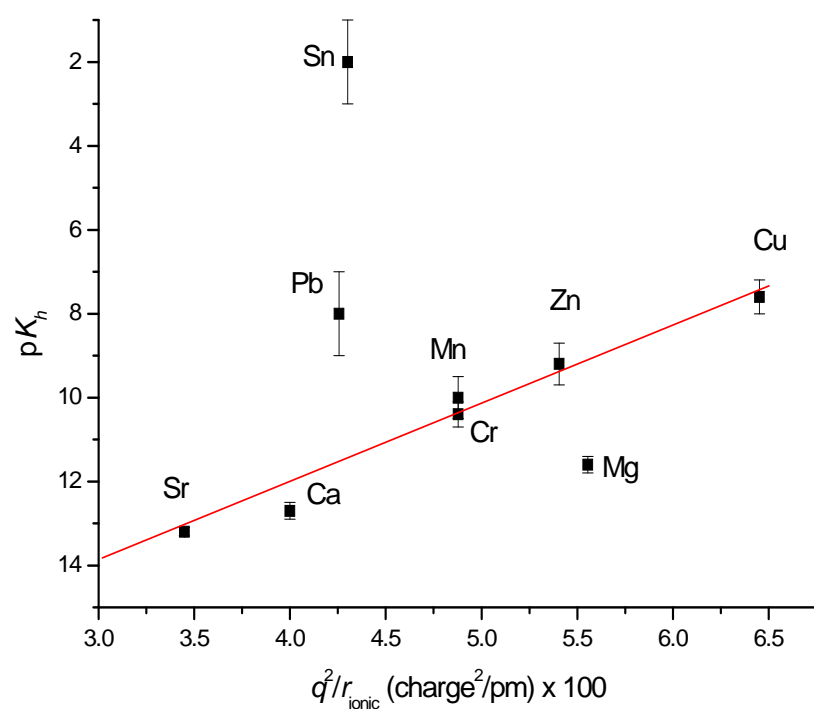
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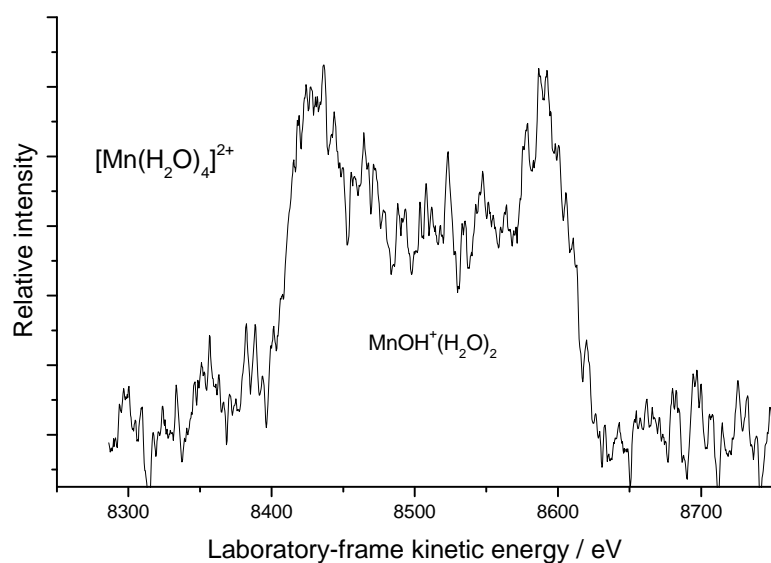
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Figure S1.



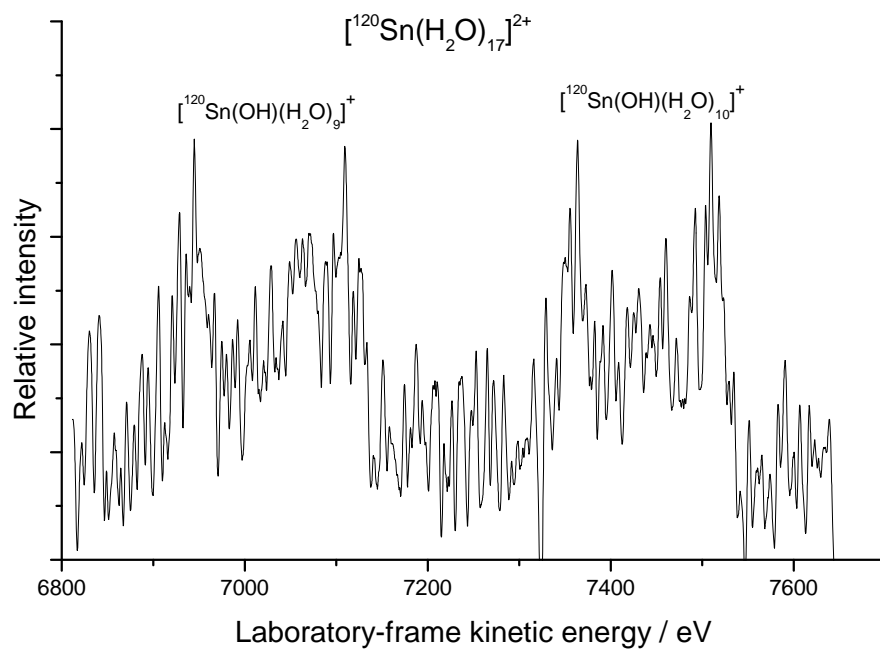
Plot of the acidity constant, pK_h for each of the metal dications shown against their charge to ionic radius ratio. The line shown does not represent a fit to the data, but is given to guide the eye. The data used are given in Table 1.

Figure S2.



Example of Coulomb fission recorded following the unimolecular decay of $[\text{Mn}(\text{H}_2\text{O})_4]^{2+}$.

Figure S3.



Examples of Coulomb fission recorded following the unimolecular decay of $[\text{Sn}(\text{H}_2\text{O})_{17}]^{2+}$.