Electronic Supplementary Material (ESI) for Chemical Communications.

Binding Modes of High Stoichiometry Guest Complexes with a Co_8L_{12} Cage Uncovered by Mass Spectrometry

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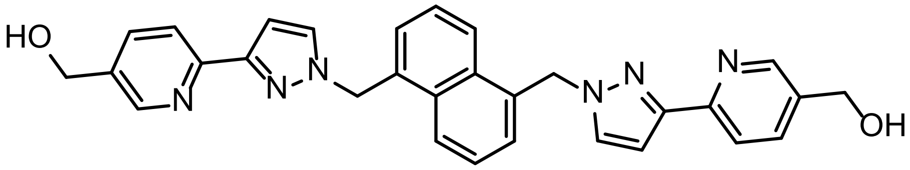
Experimental section

The solvents and guests were purchased from commercial sources. The **H^{W}** cage was synthesised according to published procedures.[1]

L^{w} ligand



Chemical formula: $C_{30}H_{26}N_6O_2$

H^{w}Co: [Co_8**L^{w}**$_{12}$]$(BF_4)_{16}$

Chemical formula: $Co_8C_{360}H_{312}N_{72}O_{24}B_{16}F_{64}$

Sample Preparation

A 100 µM stock solution of **H^{W}$_{Co}$** in H_2O was prepared by heating and vigorously stirring the solution for 2 h at 80 °C. The resulting solution was used to prepare a 1:10 diluted host solution in H_2O (10 µM), which was used in the experiments.

A 100 µM stock solution of **MAC** in 10% CH_3OH / H_2O was prepared. This solution together with the 100 µM **H^{W}$_{Co}$** were used to prepare the solution of 10 µM **H^{W}$_{Co}$** / 50 µM **MAC** in 5% CH_3OH / H_2O, by mixing the following: 100 µL of 100 µM **H^{W}$_{Co}$** + 500 µL of 100 µM **MAC** + 400 µL H_2O.

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A 100 µM stock solution of **CUD** in 10% DMSO / H_2O was prepared. This solution together with the 100 µM **H^{W}$_{Co}$** were used to prepare the solution of 10 µM **H^{W}$_{Co}$** / 50 µM **CUD** in 5% DMSO / H_2O, by mixing the following: 100 µL of 100 µM **H^{W}$_{Co}$** + 500 µL of 100 µM **CUD** + 400 µL H_2O.

Prior to their injection in the MS equipment, all solutions were centrifuged. All used solvents were of LC-MS grade.

Mass spectrometer instrumental parameters

Electrospray ionisation quadrupole-time-of-flight mass spectrometric (ESI-Q-TOF-MS) experiments were performed using a Synapt G2-S HDMS (Waters Co., Milford, MA, USA) instrument. ESI-HRMS and CID experiments were done using the following instrumental parameters: flow rate 5 µL/min, capillary voltage 1.63 kV, sample cone voltage 25 V, source offset 30 V, source temperature 85 °C, desolvation temperature 200 °C, nebulizer gas 4 bar, desolvation gas flow 180 Lh^{-1}. CID experiments employed N_2 as buffer gas and were performed in the transfer cell of the MS instrument, at collision voltages of 2–15 V with a 1 V increment. IMS measurements were done using an IMS wave velocity of 600 ms^{-1} and IMS wave height of 18 V. MassLynx^{TM} (version 4.1) software was used for data acquisition and processing. Origin pro 2023 (OriginLab corporation) was used to plot graphs.

Computational and $^{TM}CCS_{N2}$ calculations

Energy minimised structures were calculated using the universal force field (UFF) level of theory implemented in Avogadro.[2] Structures were initially generated from crystal structures by deleting solvent molecules and performing a minimisation for gas-phase structures. For the $\mathbf{H^{W}_{Co}}^{\mathbf{10+}}$ the counterions in the portal were retained and the others deleted. The respective guests were added and structures minimised again at UFF level. Theoretical $^{TM}CCS_{N2}$ values were calculated using the trajectory method implemented in IMoS software (Larriba Lab).[3] figures were generated using Scigress (Fujitsu software). Corner structure with MAC bound was optimised at the B97-3c level of theory implemented in the ORCA software. [4-6]

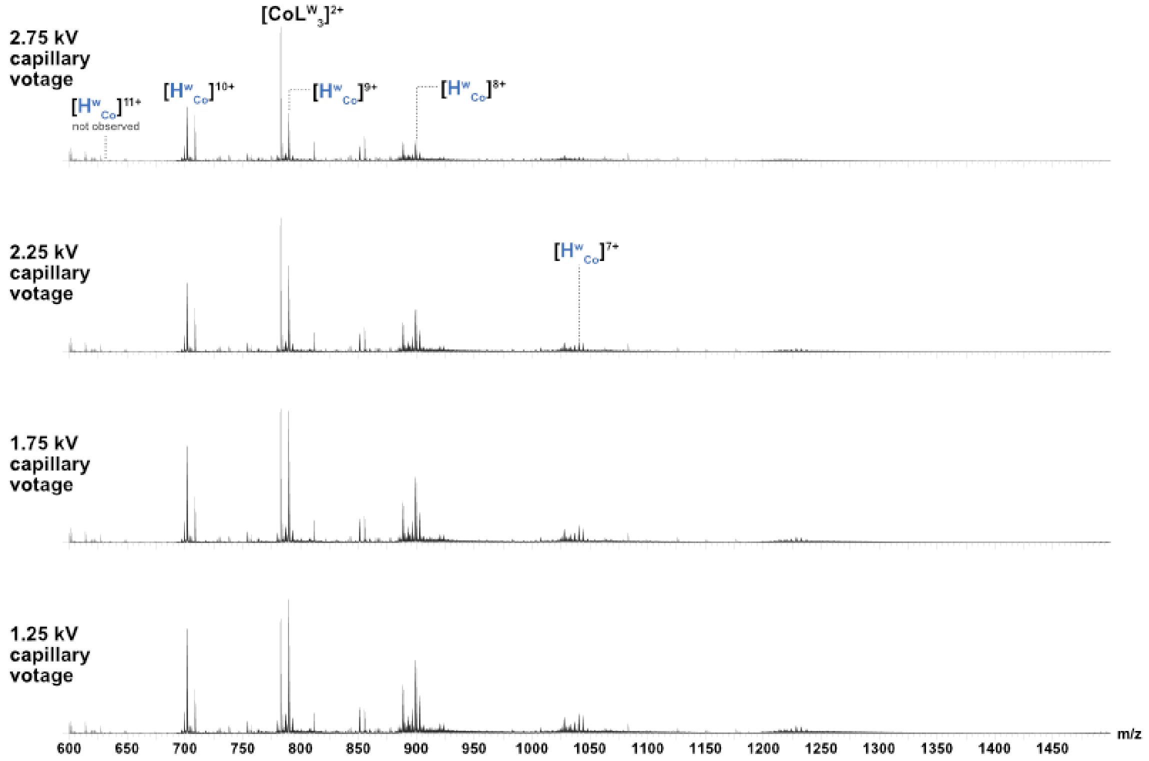


Fig. S1: ESI-MS of 10 µM $\mathbf{H^{W}_{Co}}$ in H_2O at different capillary voltages. The ratio between the different charge states changes and cage fragmentation dominates at higher capillary voltages likely as a result of the increased charged repulsion at higher charge states. $\mathbf{H^{W}_{Co}}^{11+}$ was never observed.

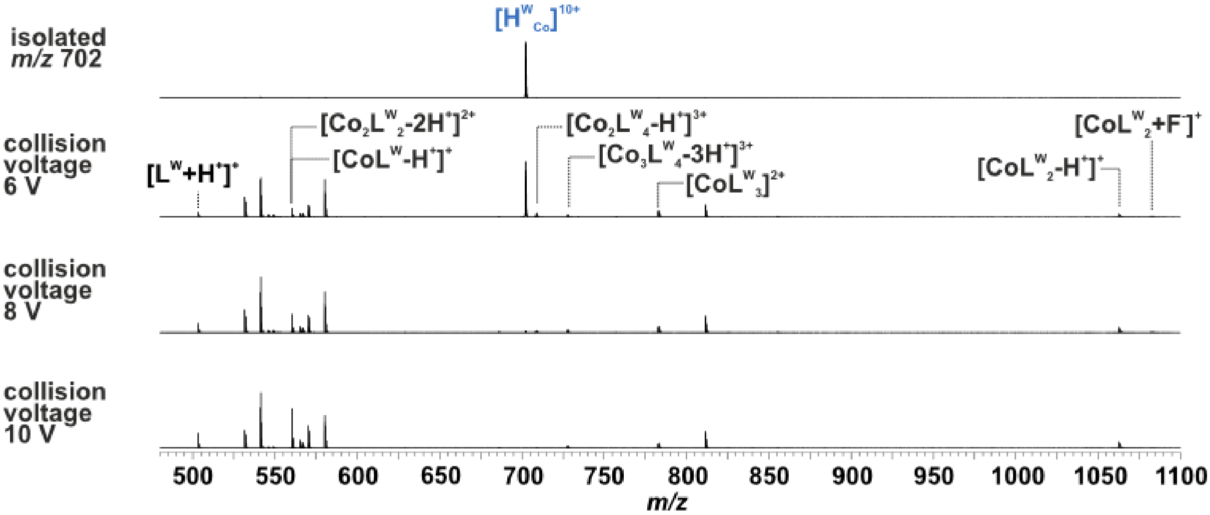


Fig. S2: Stacked MS/MS spectra of $\mathbf{H^{W}_{Co}}^{10+}$ ion (blue) at collision voltages 2–12 V. The $\mathbf{H^{W}_{Co}}^{10+}$ ion was fragmented completely at 8 V.

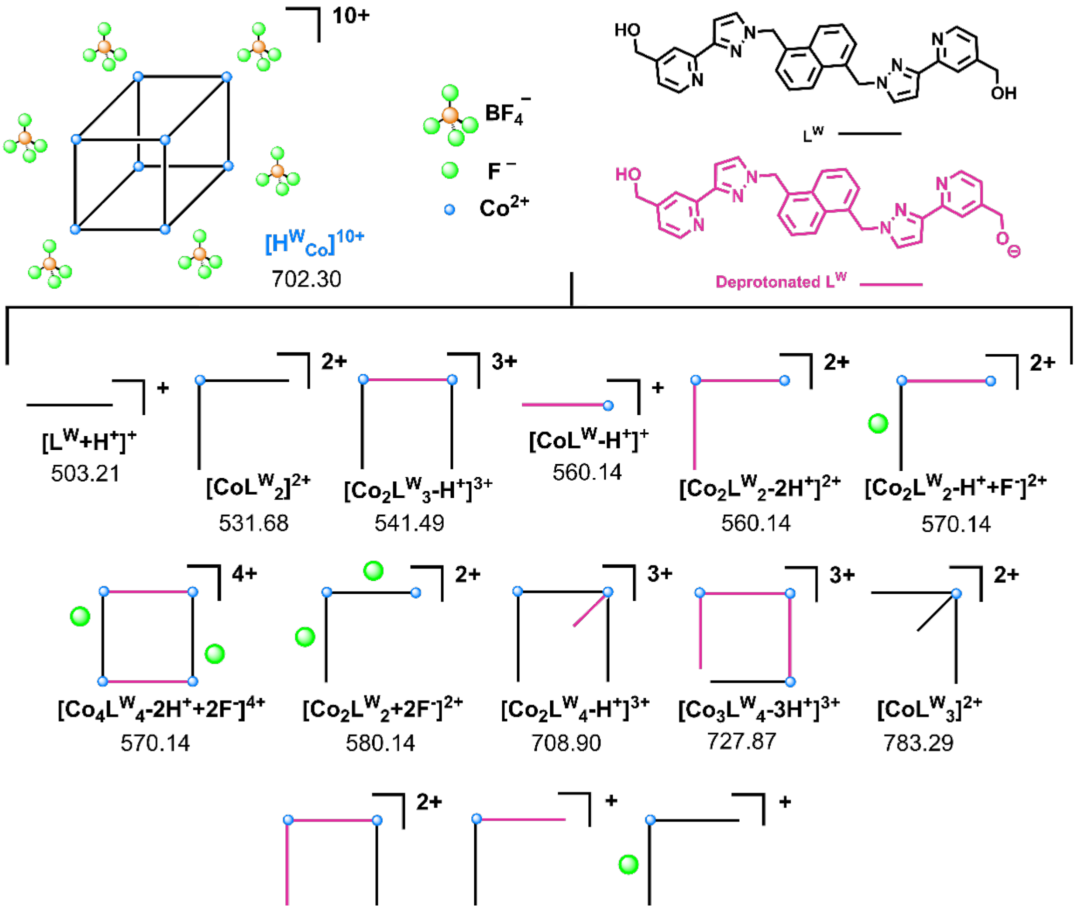


Fig. S3: Representation of the fragments of $[\mathbf{H}^{\mathbf{W}}{}_{\mathbf{Co}}]^{10+}$, their labels and *m/z* values. The deprotonated ligand $\mathbf{L}^{\mathbf{W}}$ (pink) was chosen arbitrarily. The BF_4^- and F^- anions were also placed arbitrarily.

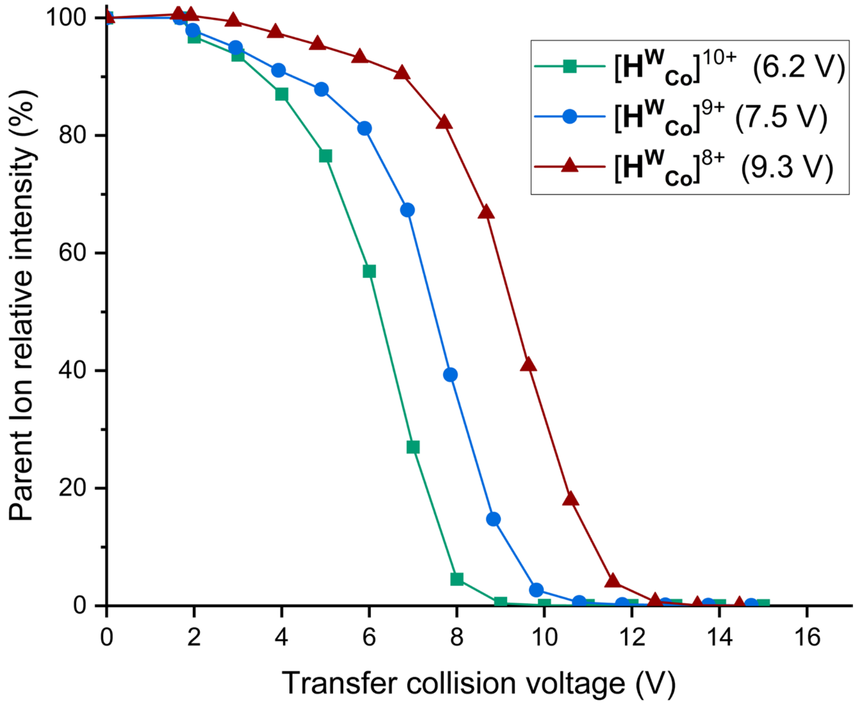


Fig. S4: Parent ion relative intensity versus transfer collision voltage for $\mathbf{H}^{\mathbf{w}}{}_{\mathbf{Co}}{}^{10+}$, $\mathbf{H}^{\mathbf{w}}{}_{\mathbf{Co}}{}^{9+}$; $\mathbf{H}^{\mathbf{w}}{}_{\mathbf{Co}}{}^{8+}$. The inflection point of the curves, which can be used to compare relative stabilities, is shown in parentheses

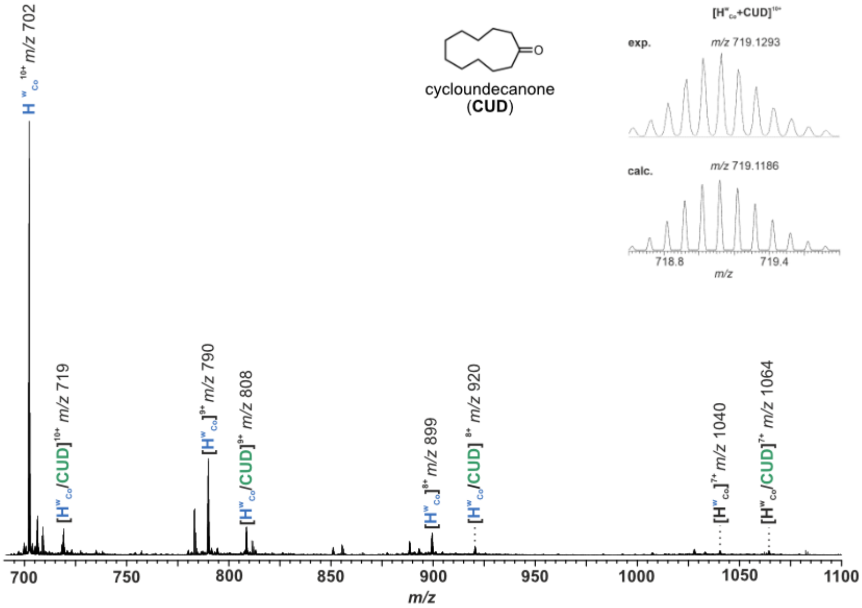


Fig. S5: ESI-HRMS spectrum of $\mathbf{H^{W}_{Co}/CUD}$ (10 µM / 50 µM) in 5% DMSO/H_2O. The inset Fig. represents the calculated *vs* experimental isotopic patterns and *m/z* values for the $\mathbf{H^{W}_{Co}/CUD^{10+}}$ ion.

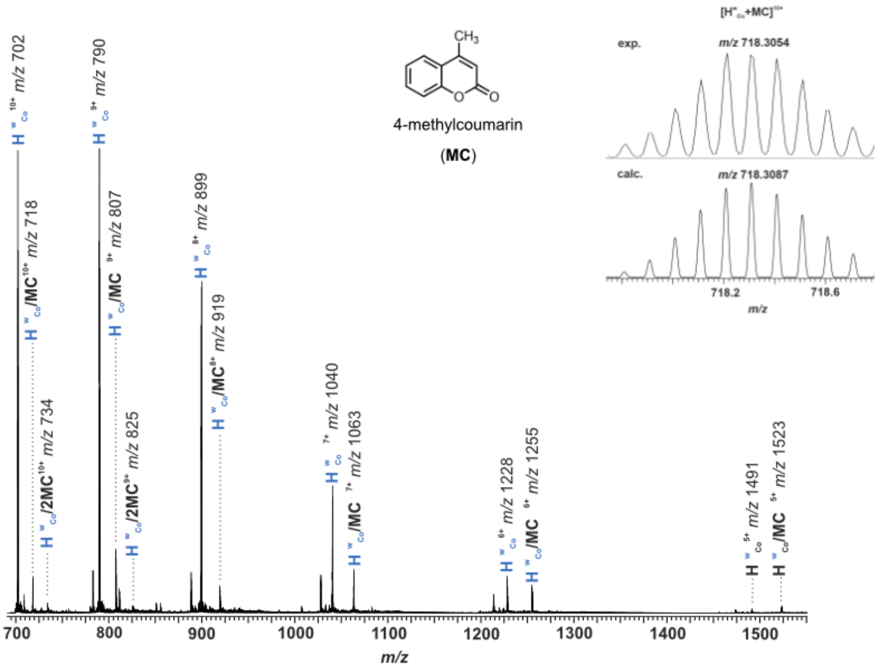


Fig. S6: ESI-HRMS spectrum of $\mathbf{H^{W}_{Co}/MC}$ (10 µM / 50 µM) in 5% CH_3OH/H_2O.

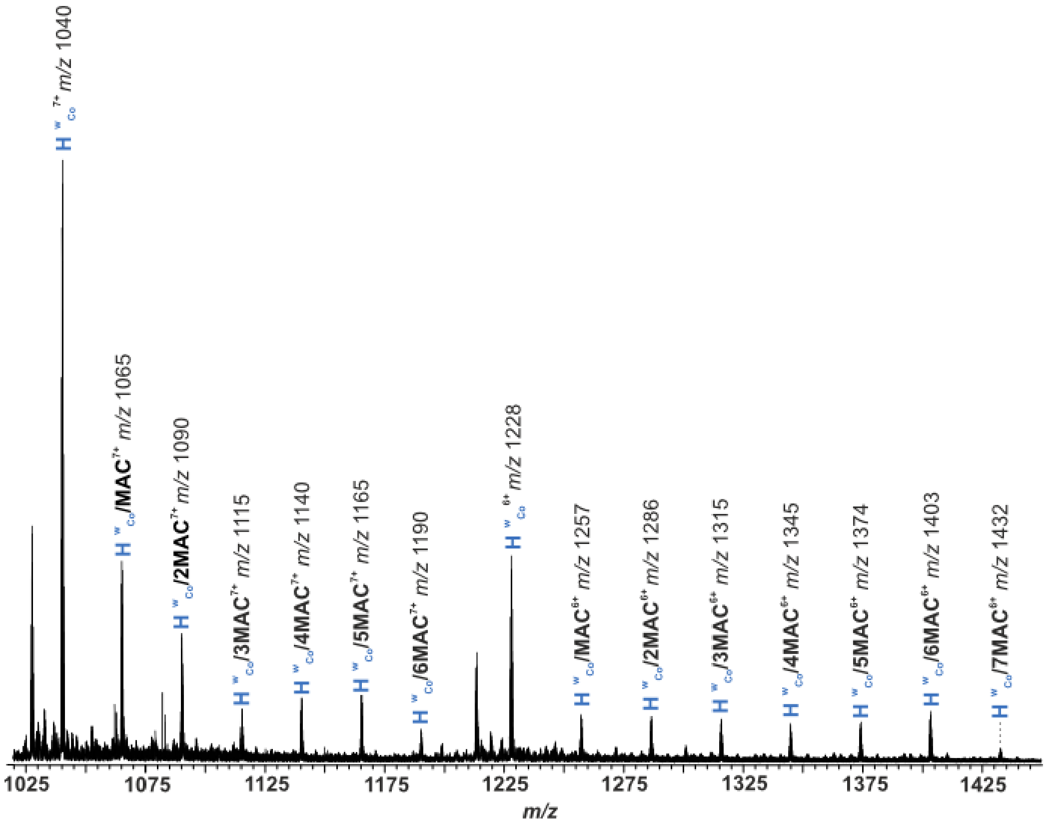


Fig. S7: 1025-1425 *m/z* region of ESI-HRMS spectrum of $\mathbf{H^{W}_{Co}}$ with **MAC** (10 µM / 50 µM) in 5% CH_3OH/H_2O. Stoichiometry with 7 **MAC** are observed albeit at low signal intensity.

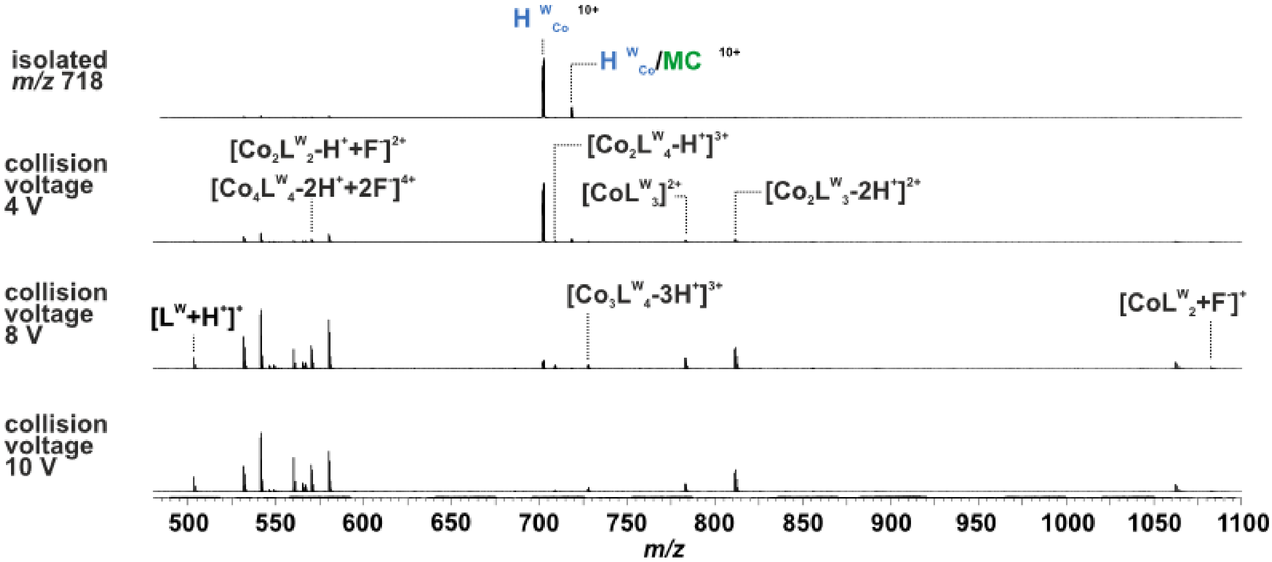


Fig. S8: Stacked CID spectra of mass selected $\mathbf{H^{W}_{Co}/CUD^{8+}}$ (10 µM / 50 µM) in 5% $DMSO/H_2O$.

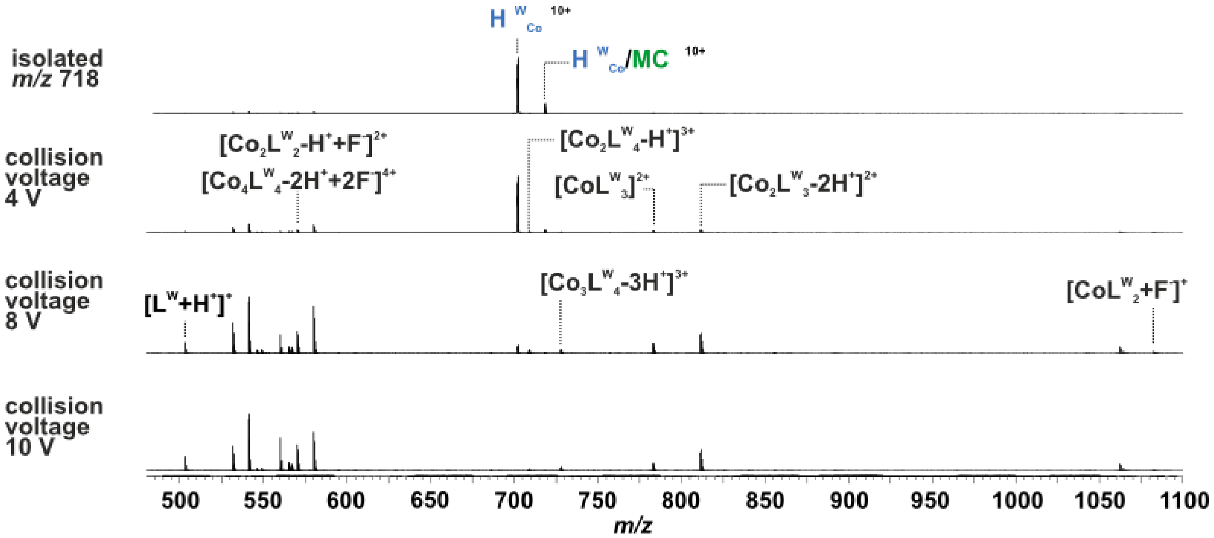


Fig. S9: Stacked CID spectra of mass-selected $\mathbf{H^{W}_{Co}/MC^{10}}$ (10 µM / 50 µM) in 5% CH_3OH/H_2O.

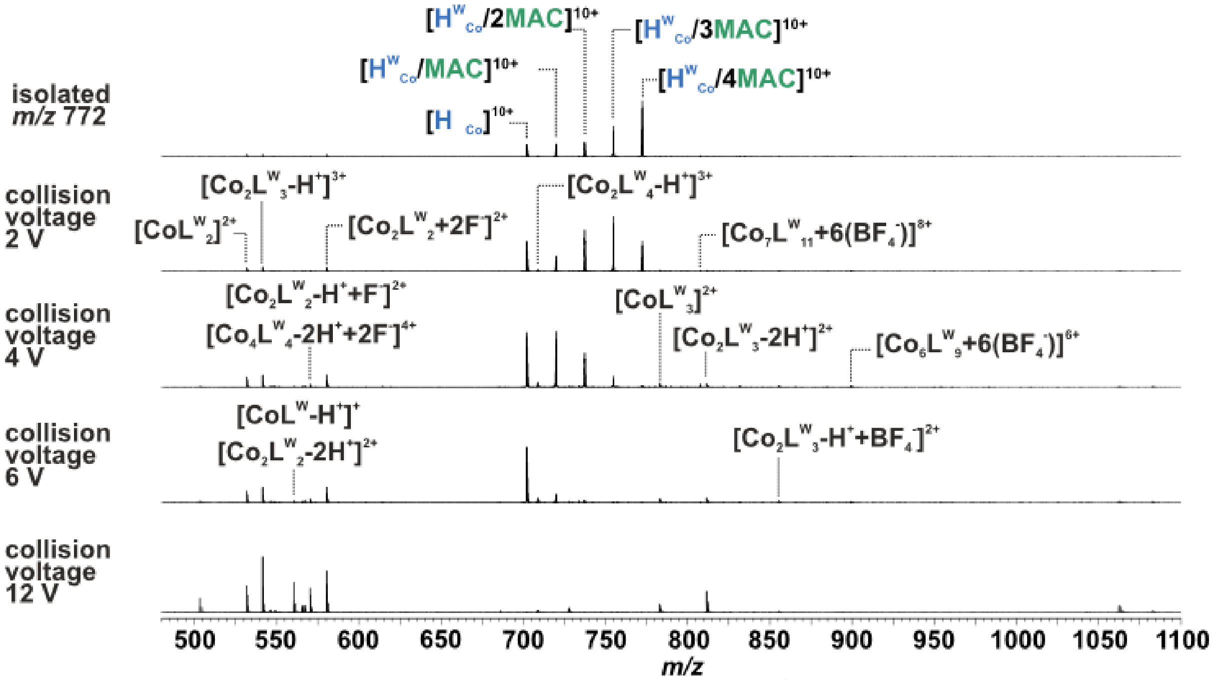


Fig. S10: Stacked CID MS/MS spectra of mass-selected ions $\mathbf{H^{W}_{Co}}$/4**MAC**$^{10+}$ A gradual loss of the **MAC** is observed when increasing the CID voltage.

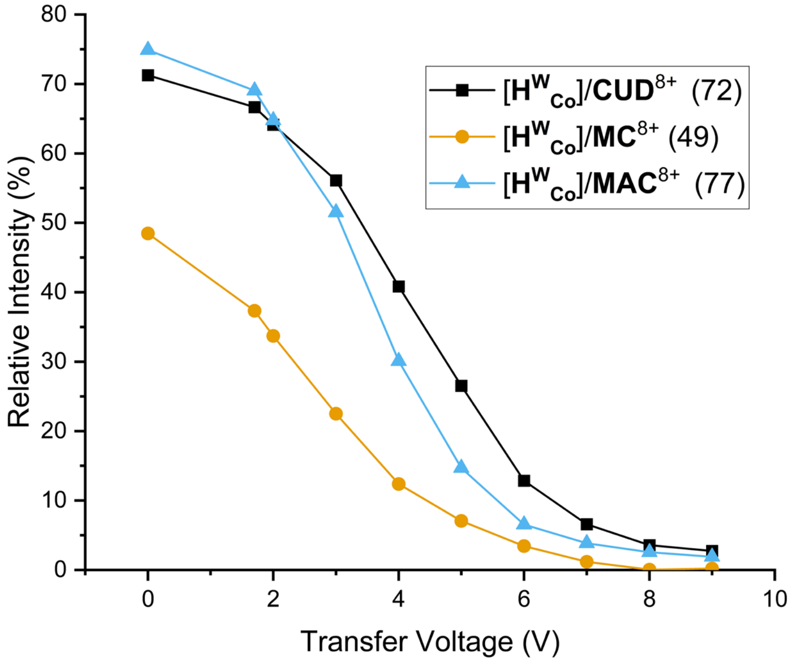
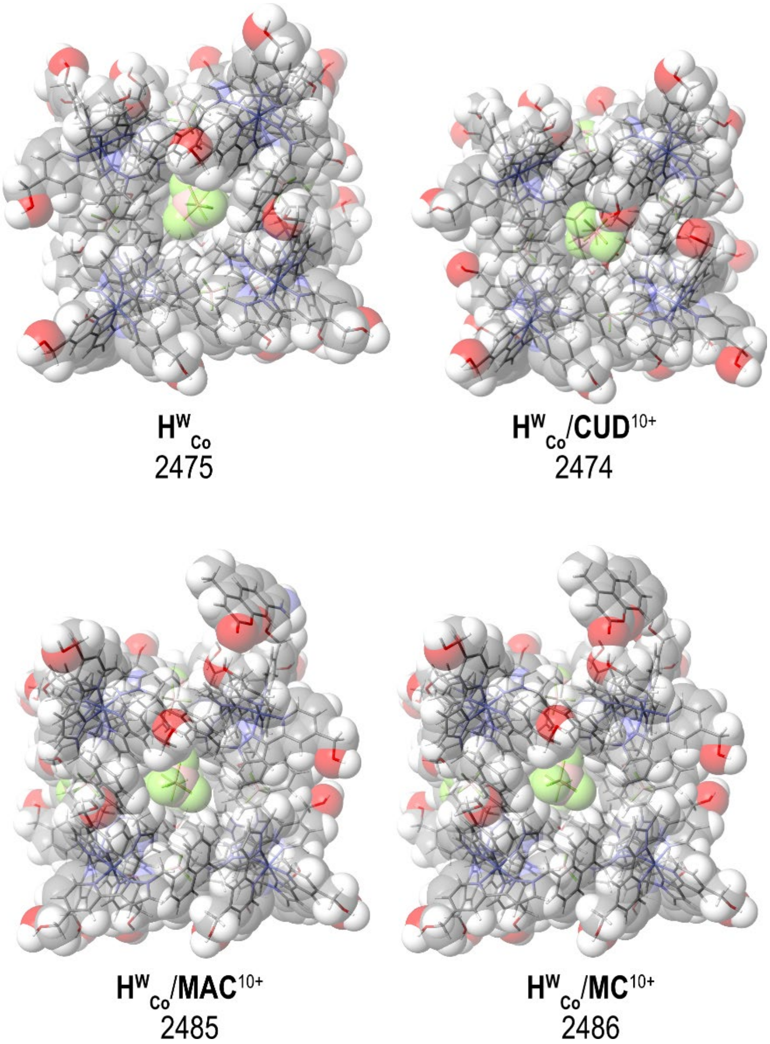


Fig. S11: Relative ion intensity versus transfer collision voltage for the $\mathbf{H^{W}{}_{Co}/G^{8+}}$ with the different guests.



$H^{W}{}_{Co}$
2475

$H^{W}{}_{Co}/CUD^{10+}$
2474

$H^{W}{}_{Co}/MAC^{10+}$
2485

$H^{W}{}_{Co}/MC^{10+}$
2486

Fig. S12: UFF structures of $\mathbf{H^{W}{}_{Co}{}^{10+}}$ (top left) $\mathbf{H^{W}{}_{Co}/CUD^{10+}}$ (top right) $\mathbf{H^{W}{}_{Co}/MAC^{10+}}$ (bottom left) $\mathbf{H^{W}{}_{Co}/MC^{10+}}$ (bottom right) used for $^{TM}CCS_{N2}$ calculations. The $^{TM}CCS_{N2}$ (Å^{2}) is shown underneath the structures.

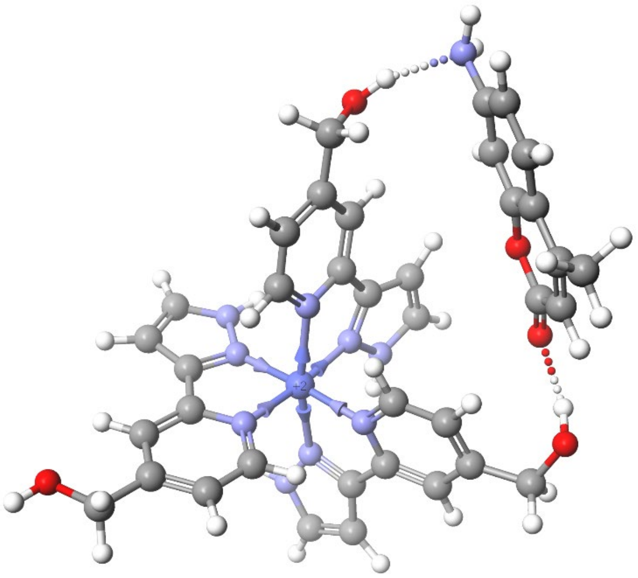


Fig. S13: Binding mode of **MAC** with two $\mathbf{L^{w}}$ in a *fac* corner of $\mathbf{H^{W}_{Co}}$. Structure was optimised at the B97-3c level of theory.

References

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