

Supplementary Information

Examining interactions of uranyl(VI) ions with amino acids in the gas phase

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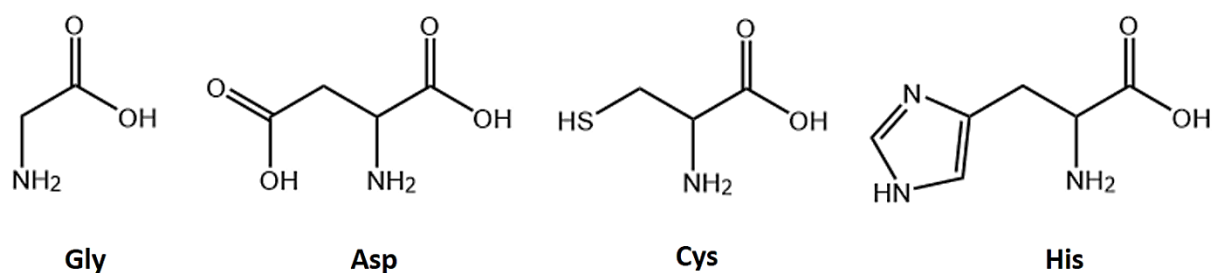
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Scheme S1. Canonical structures of the studied amino acids: glycine, aspartic acid, cysteine, and histidine.

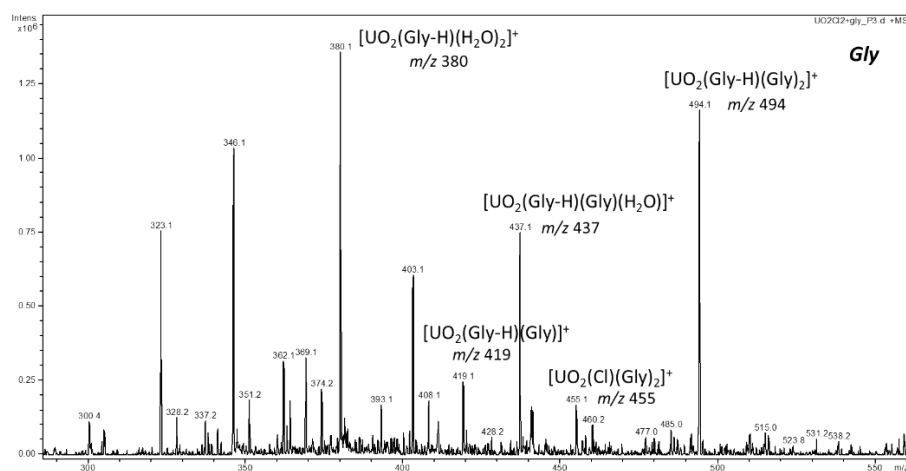


Figure S1. ESI-MS of a uranyl chloride + glycine solution (1:4) in positive ion mode.

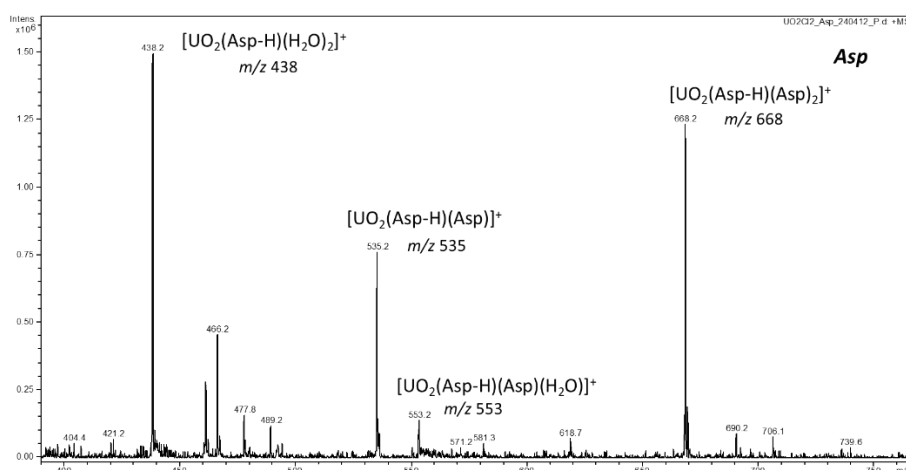


Figure S2. ESI-MS of a uranyl chloride + aspartic acid solution (1:4) in positive ion mode.

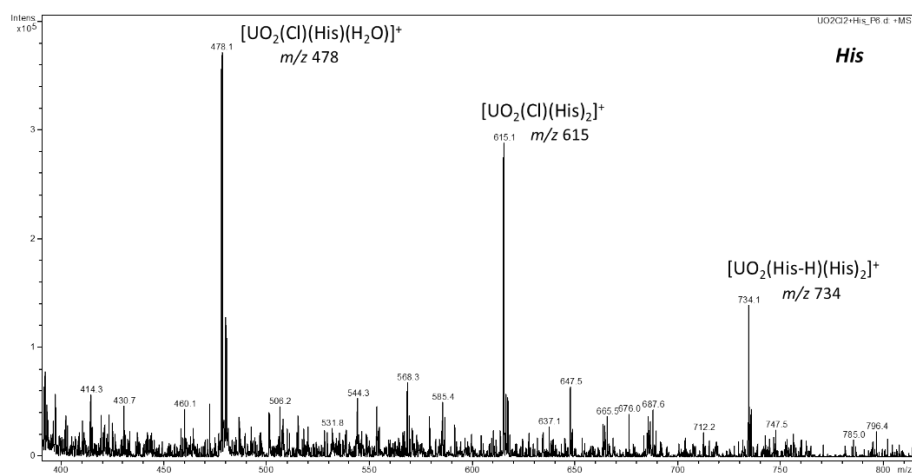


Figure S3. ESI-MS of a uranyl chloride + histidine solution (1:4) in positive ion mode.

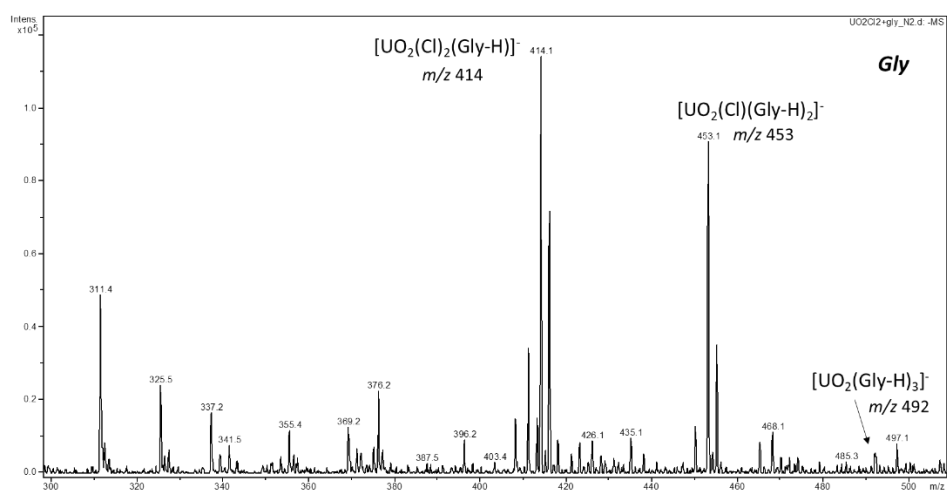


Figure S4. ESI-MS of a uranyl chloride + glycine solution (1:4) in negative ion mode.

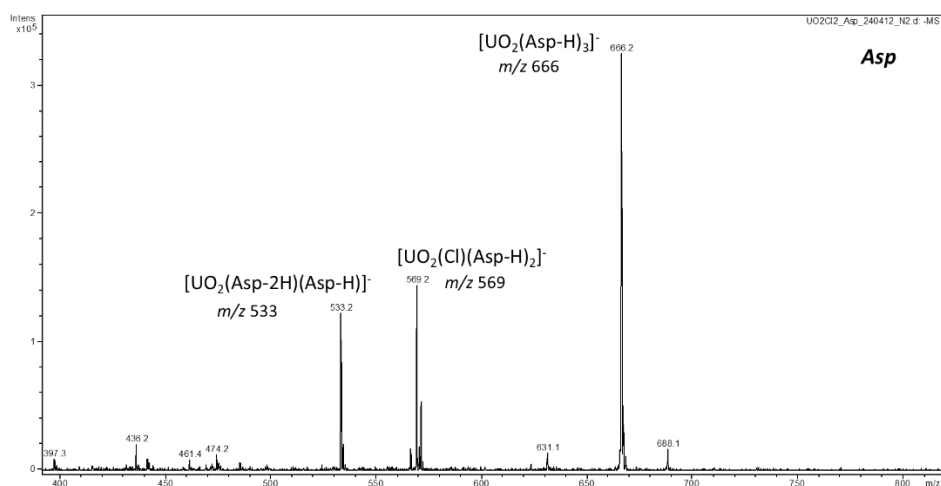


Figure S5. ESI-MS of a uranyl chloride + aspartic acid solution (1:4) in negative ion mode.

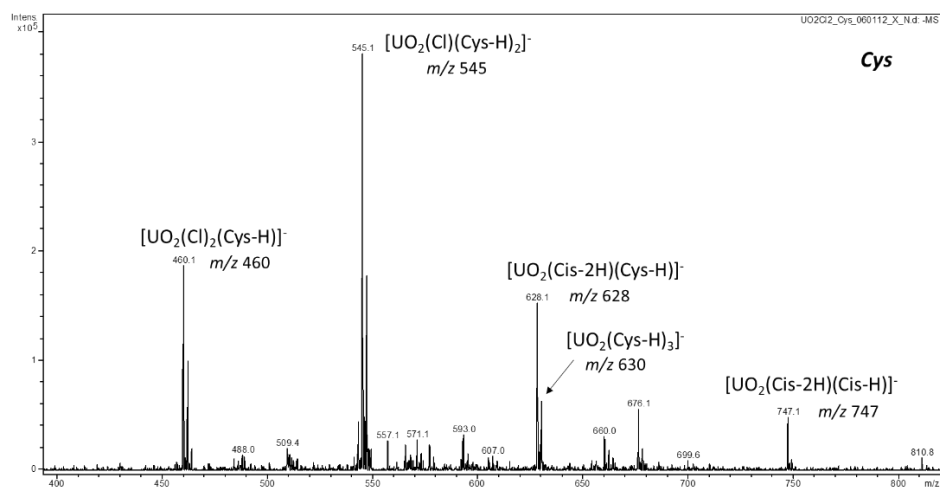


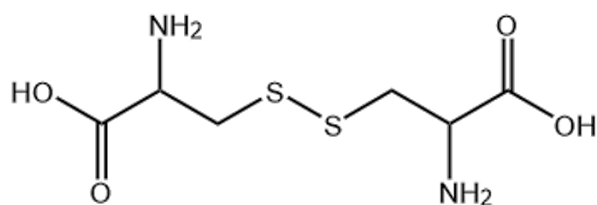
Figure S6. ESI-MS of a uranyl chloride + cysteine solution (1:4) in negative ion mode.

Table S1. Main uranyl-amino acid complexes observed by ESI-MS in positive ion mode.

Amino acid	Complex	Calculated m/z	Observed m/z
Glycine	$[\text{UO}_2(\text{Cl})(\text{Gly})]^+$	380.041	-
	$[\text{UO}_2(\text{Gly-H})(\text{Gly})]^+$	419.096	419.1
	$[\text{UO}_2(\text{Cl})(\text{Gly})_2]^+$	455.073	455.1
	$[\text{UO}_2(\text{Gly-H})(\text{Gly})_2]^+$	494.128	494.1
Aspartic acid	$[\text{UO}_2(\text{Cl})(\text{Asp})]^+$	438.046	-
	$[\text{UO}_2(\text{Asp-H})(\text{Asp})]^+$	535.107	535.2
	$[\text{UO}_2(\text{Cl})(\text{Asp})_2]^+$	571.084	571.2
	$[\text{UO}_2(\text{Asp-H})(\text{Asp})_2]^+$	668.145	668.2
Cysteine	$[\text{UO}_2(\text{Cl})(\text{Cys})]^+$	426.029	426.2
	$[\text{UO}_2(\text{Cys-H})(\text{Cys})]^+$	511.072	511.2
	$[\text{UO}_2(\text{Cl})(\text{Cys})_2]^+$	547.048	547.1
	$[\text{UO}_2(\text{Cys-H})(\text{Cys})_2]^+$	632.091	632.2
Histidine	$[\text{UO}_2(\text{Cl})(\text{His})]^+$	460.078	-
	$[\text{UO}_2(\text{His-H})(\text{His})]^+$	579.171	-
	$[\text{UO}_2(\text{Cl})(\text{His})_2]^+$	615.148	615.1
	$[\text{UO}_2(\text{His-H})(\text{His})_2]^+$	734.241	734.1

Table S2. Main uranyl-amino acid complexes observed by ESI-MS in negative ion mode.

Amino acid	Complex	Calculated m/z	Observed m/z
Glycine	$[\text{UO}_2(\text{Cl})_2(\text{Gly-H})]^-$	414.002	414.1
	$[\text{UO}_2(\text{Cl})(\text{Gly-H})_2]^-$	453.057	453.1
	$[\text{UO}_2(\text{Gly-H})_3]^-$	492.113	492.2
Aspartic acid	$[\text{UO}_2(\text{Cl})_2(\text{Asp-H})]^-$	472.007	472.1
	$[\text{UO}_2(\text{Cl})(\text{Asp-H})_2]^-$	569.068	569.2
	$[\text{UO}_2(\text{Asp-H})_3]^-$	666.129	666.2
Cysteine	$[\text{UO}_2(\text{Cl})_2(\text{Cys-H})]^-$	459.990	460.1
	$[\text{UO}_2(\text{Cl})(\text{Cys-H})_2]^-$	545.033	545.1
	$[\text{UO}_2(\text{Cys-H})_3]^-$	630.076	630.1
Histidine	$[\text{UO}_2(\text{Cl})_2(\text{His-H})]^-$	494.039	494.1
	$[\text{UO}_2(\text{Cl})(\text{His-H})_2]^-$	613.132	613.2
	$[\text{UO}_2(\text{His-H})_3]^-$	732.225	732.2

**Cis****Scheme S2.** Canonical structure of cystine.**Table S3.** Gas-phase data for the studied amino acids.

Amino acid	Symbol	Gas-phase acidity (GA) ¹ [kJ/mol]	Proton affinity (PA) ² [kJ/mol]	Gas-phase basicity (GB) ² [kJ/mol]
Glycine	Gly	1434	886.5	852.2
Aspartic acid	Asp	1345	908.9	875.0
Cysteine	Cys	1395	903.2	869.3
Histidine	His	1375	988.0	950.2

1. Jones, C.M.; Bernier, M.; Carson, E.; Colyer, K.E.; Metz, R.; Pawlow, A.; Wischow, E.D.; Webb, I.; Andriole, E.J.; Poutsma, J.C., Gas-phase Acidities of the 20 Protein Amino Acids. *Int. J. Mass Spectrom.* 2007, 267, 54-62. <https://doi.org/10.1016/j.ijms.2007.02.018>.

2. Hunter, E.P.; Lias, S.G., Evaluated Gas Phase Basicities and Proton Affinities of Molecules: An Update. *J. Phys. Chem. Ref. Data* 1998, 27, 413-656. <https://doi.org/10.1063/1.556018>.

Table S4. Solution data for the studied amino acids.¹

Amino acid	Symbol	pK_a	pK_b	pK_c
Glycine	Gly	2.34	9.58	-
Aspartic acid	Asp	1.95	9.66	3.71
Cysteine	Cys	1.91	10.28	8.14
Histidine	His	1.70	9.09	6.04

1. Haynes, W.M.; Lide, D.R.; Bruno, T.J. (Eds.), *CRC Handbook of Chemistry and Physics*, 97th edition, CRC Press, Boca Raton, FL, USA, 2017.

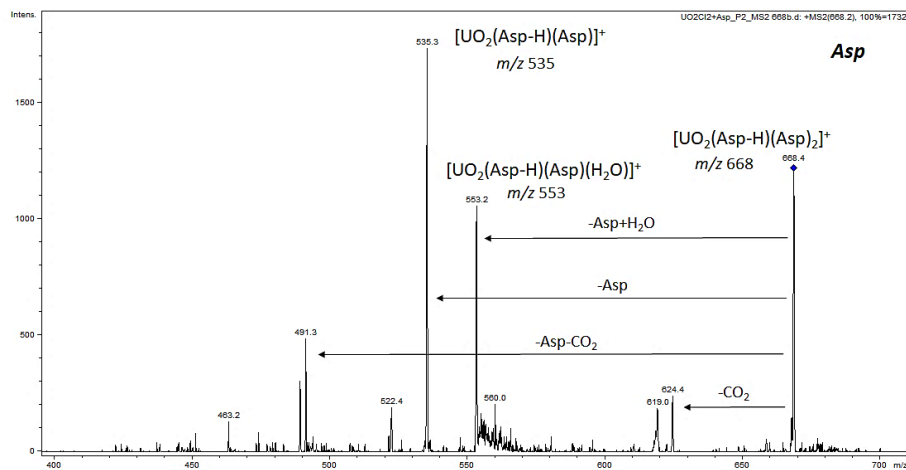


Figure S7. CID mass spectrum of $[\text{UO}_2(\text{Asp-H})(\text{Asp})_2]^+$.

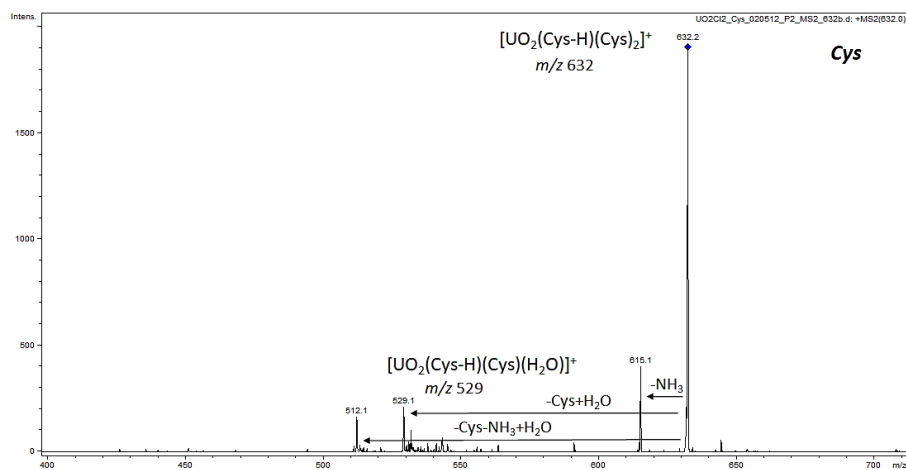


Figure S8. CID mass spectrum of $[\text{UO}_2(\text{Cys-H})(\text{Cys})_2]^+$.

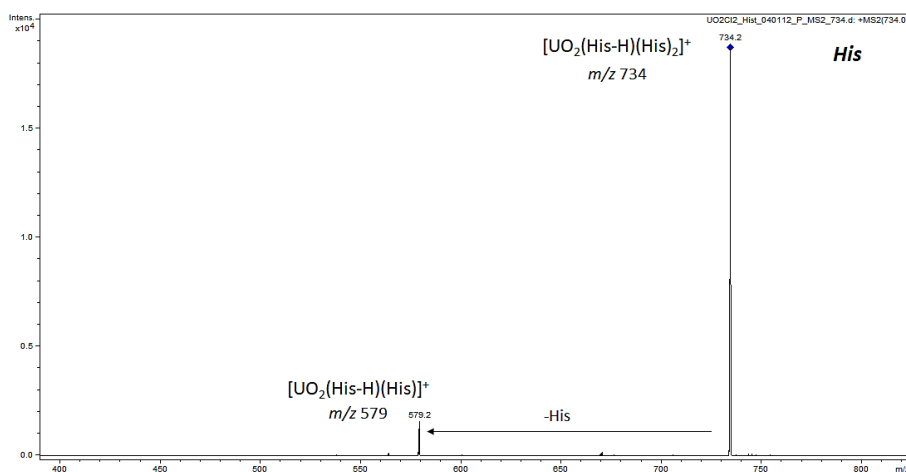


Figure S9. CID mass spectrum of $[\text{UO}_2(\text{His-H})(\text{His})_2]^+$.

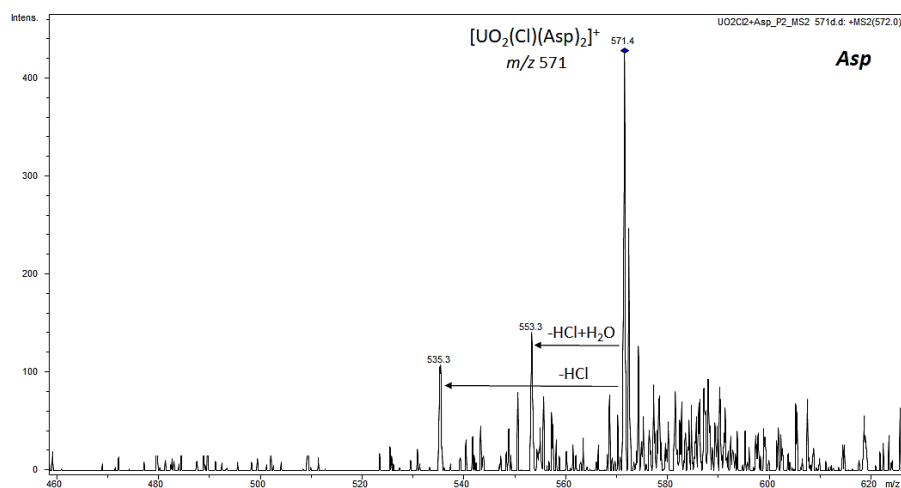


Figure S10. CID mass spectrum of $[\text{UO}_2(\text{Cl})(\text{Asp})_2]^+$.

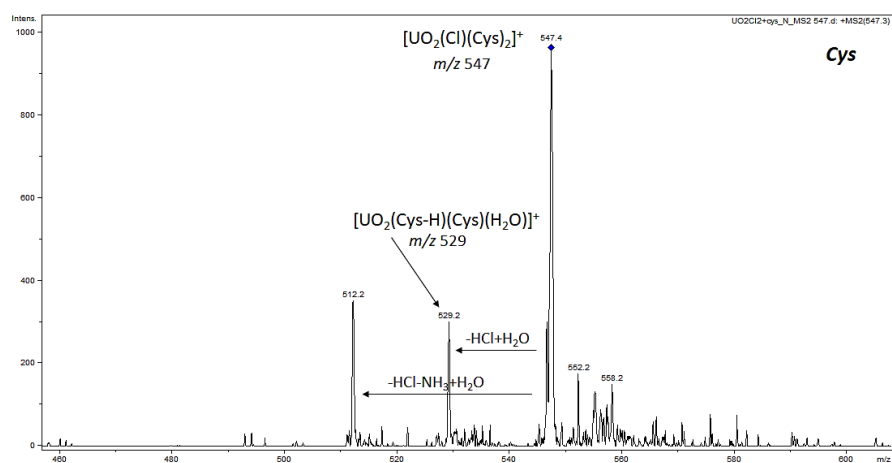


Figure S11. CID mass spectrum of $[\text{UO}_2(\text{Cl})(\text{Cys})_2]^+$.

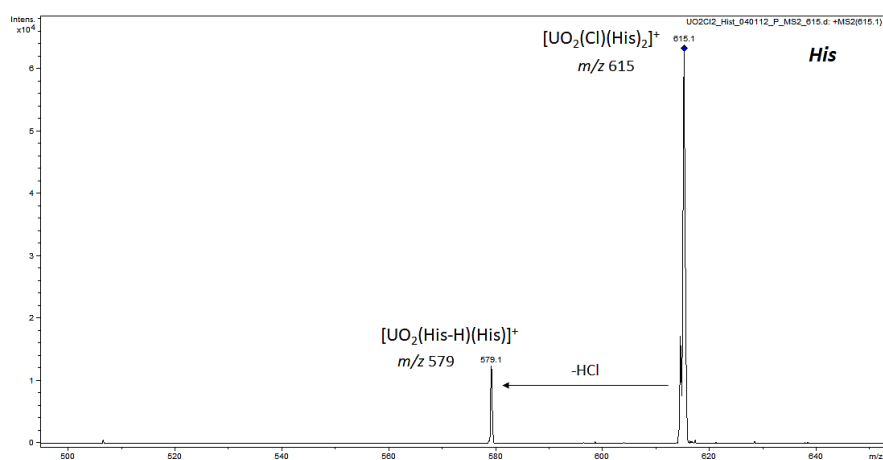


Figure S12. CID mass spectrum of $[\text{UO}_2(\text{Cl})(\text{His})_2]^+$.

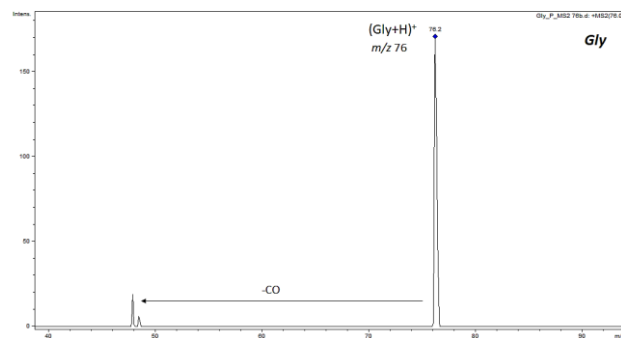


Figure S13. CID mass spectrum of (Gly+H)⁺. Loss of H₂O+CO could not be observed due to a low *m/z* cut-off of 50.

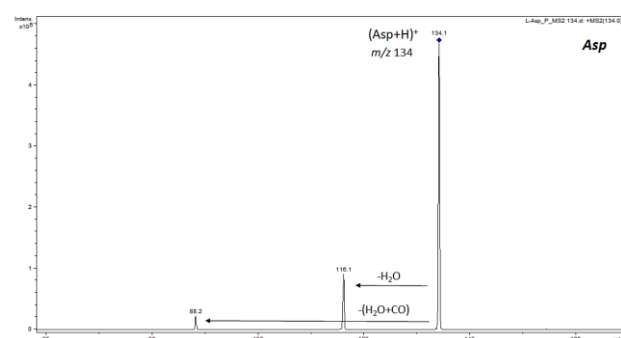


Figure S14. CID mass spectrum of (Asp+H)⁺.

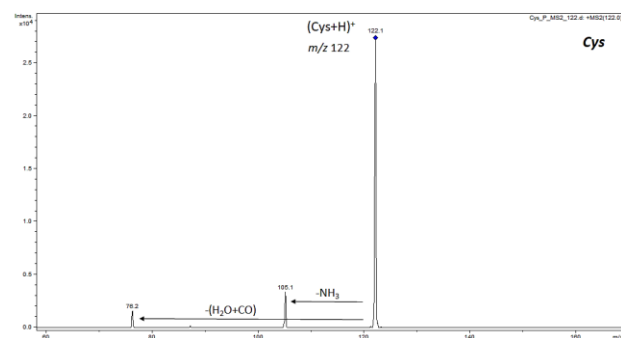


Figure S15. CID mass spectrum of (Cys+H)⁺.

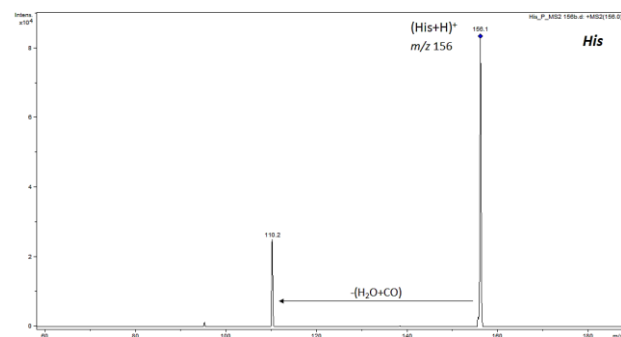


Figure S16. CID mass spectrum of (His+H)⁺.

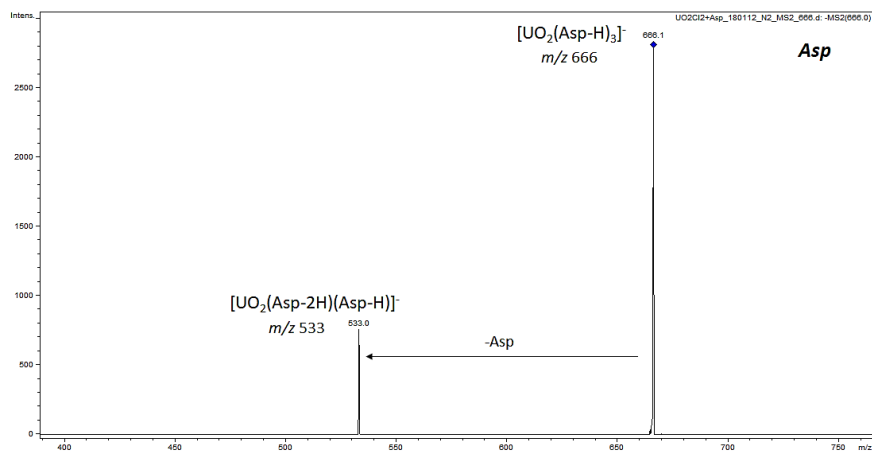


Figure S17. CID mass spectrum of $[\text{UO}_2(\text{Asp-H})_3]^-$.

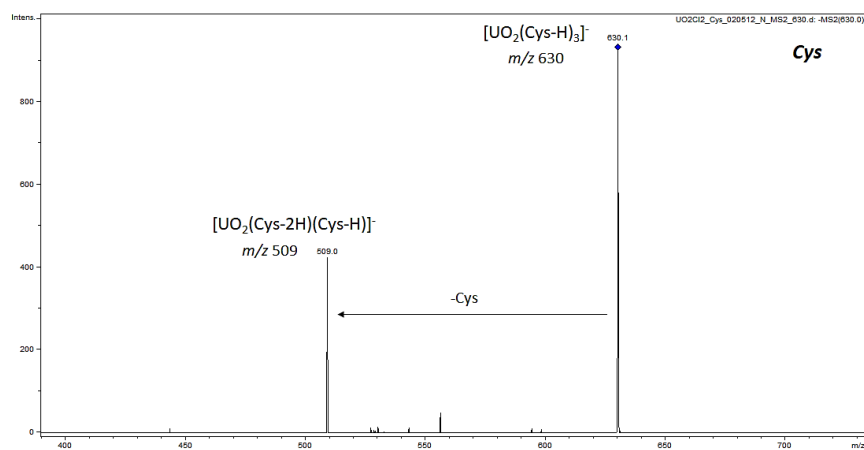


Figure S18. CID mass spectrum of $[\text{UO}_2(\text{Cys-H})_3]^-$.

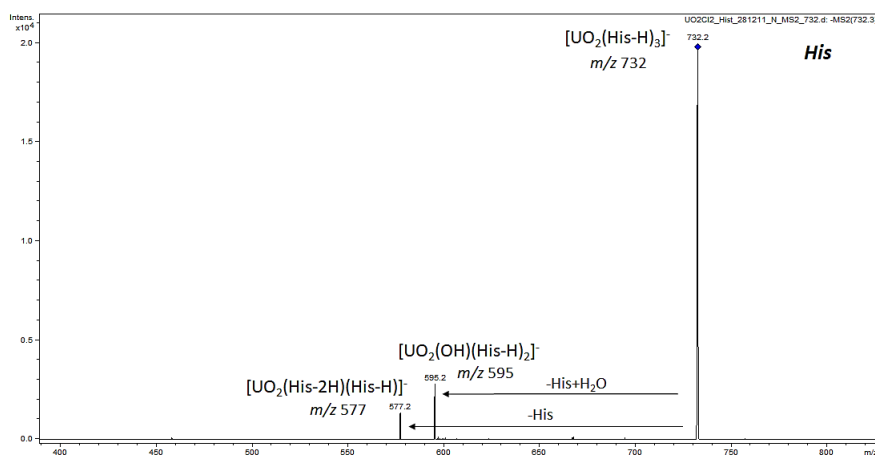


Figure S19. CID mass spectrum of $[\text{UO}_2(\text{His-H})_3]^-$.

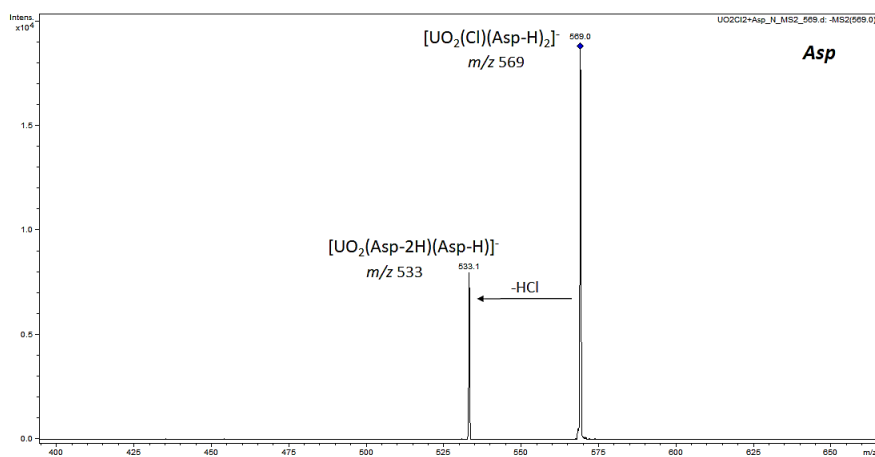


Figure S20. CID mass spectrum of $[\text{UO}_2(\text{Cl})(\text{Asp-H})_2]^-$.

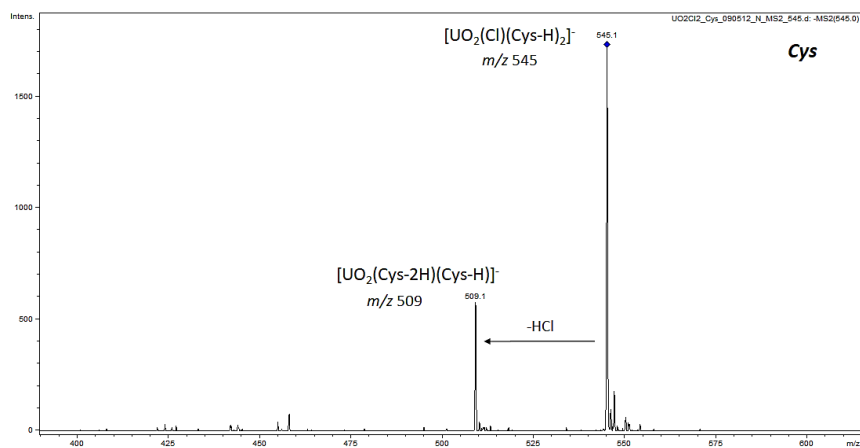


Figure S21. CID mass spectrum of $[\text{UO}_2(\text{Cl})(\text{Cys-H})_2]^-$.

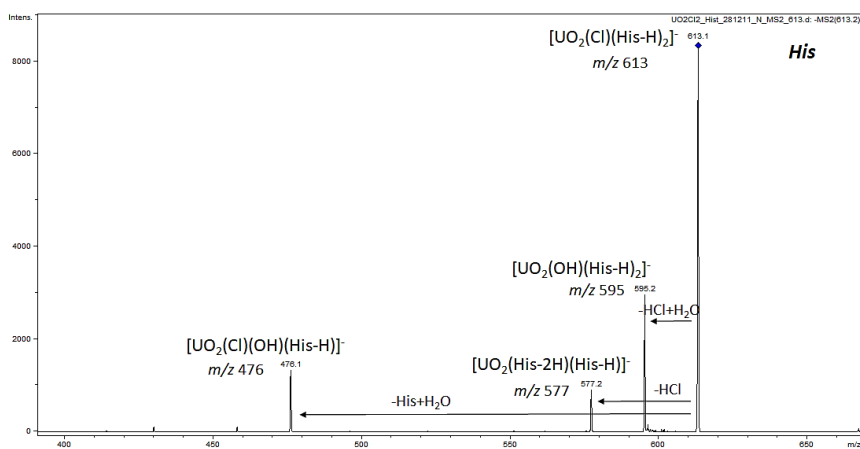


Figure S22. CID mass spectrum of $[\text{UO}_2(\text{Cl})(\text{His-H})_2]^-$.

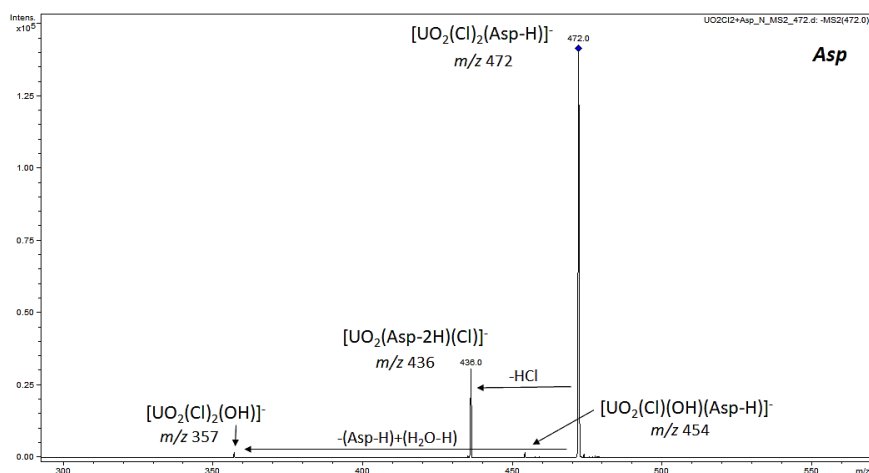


Figure S23. CID mass spectrum of $[\text{UO}_2(\text{Cl})_2(\text{Asp-H})]^-$.

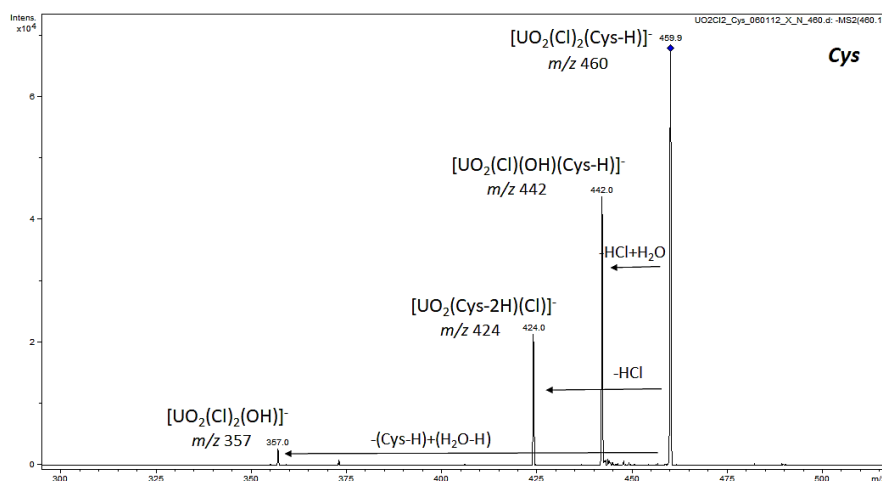


Figure S24. CID mass spectrum of $[\text{UO}_2(\text{Cl})_2(\text{Cys-H})]^-$.

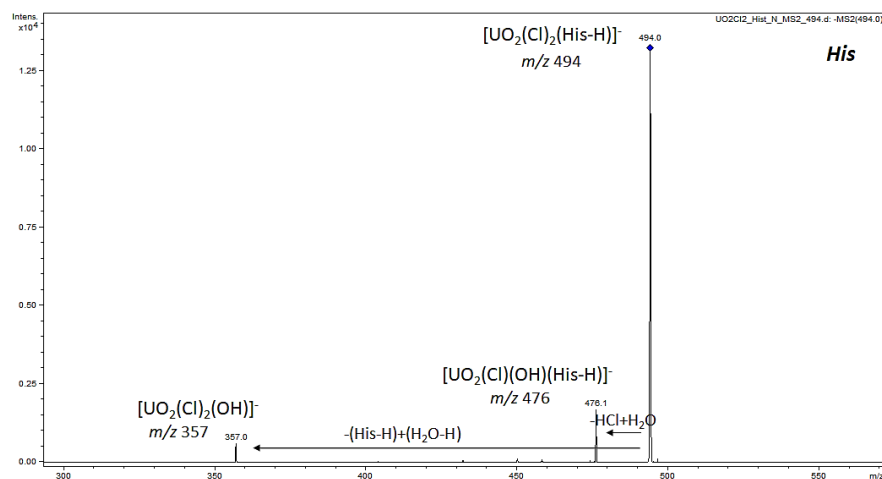


Figure S25. CID mass spectrum of $[\text{UO}_2(\text{Cl})_2(\text{His-H})]^-$.

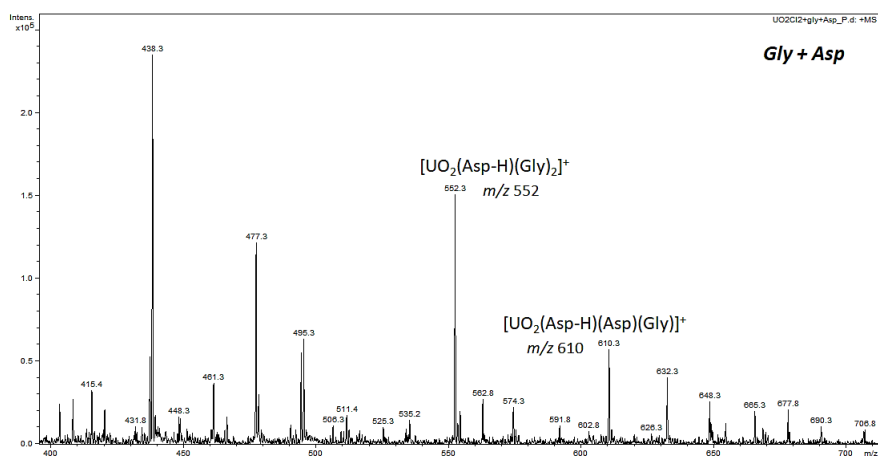


Figure S26. ESI-MS of a uranyl chloride + glycine + aspartic acid solution (1:2:2) in positive ion mode.

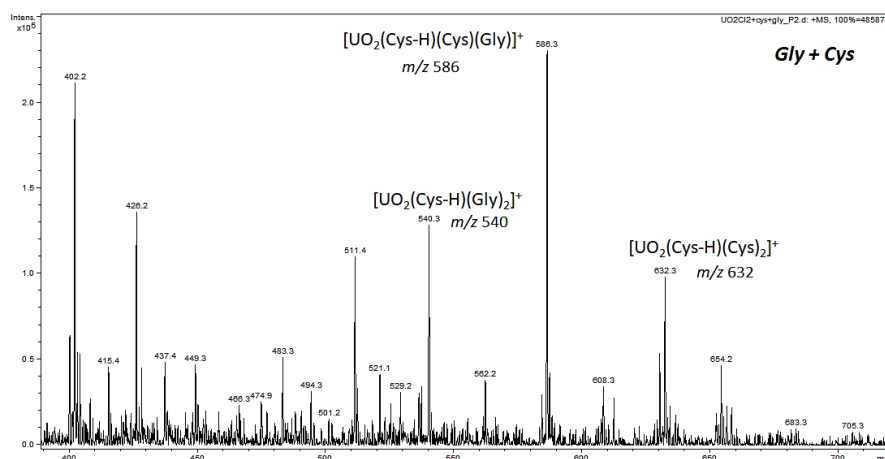


Figure S27. ESI-MS of a uranyl chloride + glycine + cysteine solution (1:2:2) in positive ion mode.

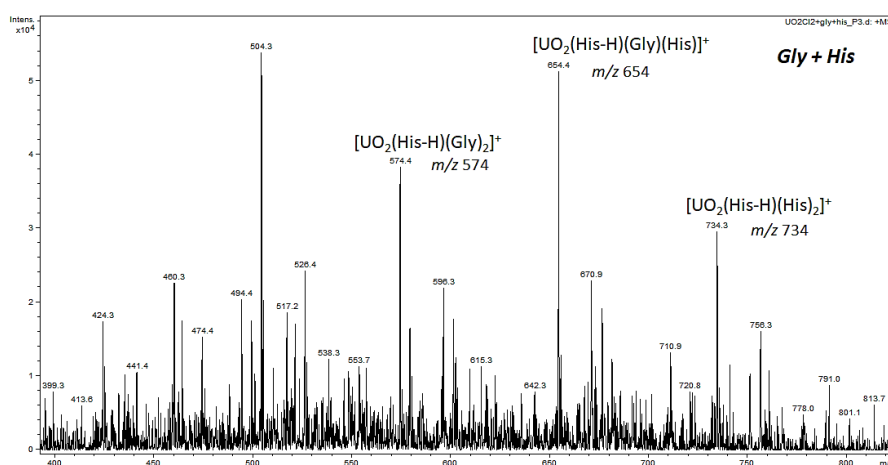


Figure S28. ESI-MS of a uranyl chloride + glycine + histidine solution (1:2:2) in positive ion mode.

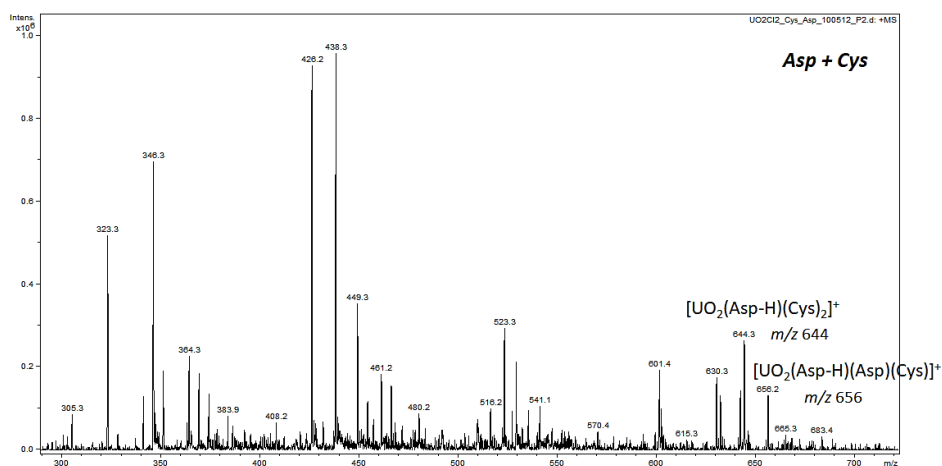


Figure S29. ESI-MS of a uranyl chloride + aspartic acid + cysteine solution (1:2:2) in positive ion mode.

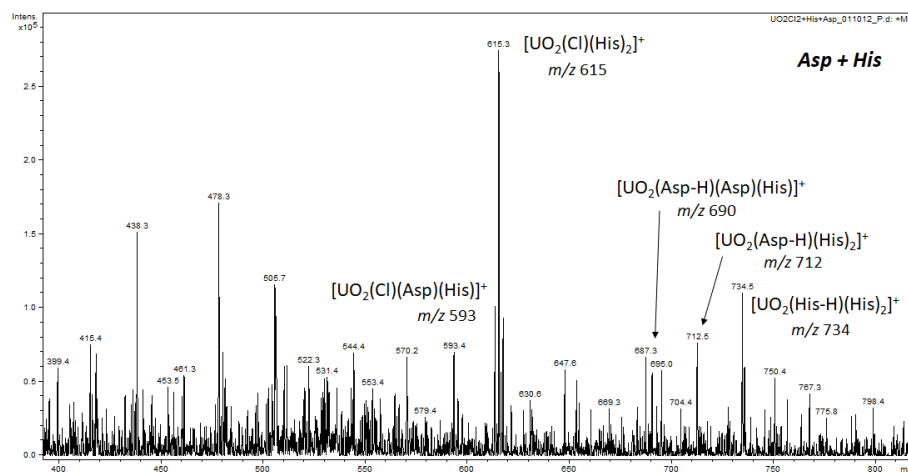


Figure S30. ESI-MS of a uranyl chloride + aspartic acid + histidine solution (1:2:2) in positive ion mode.

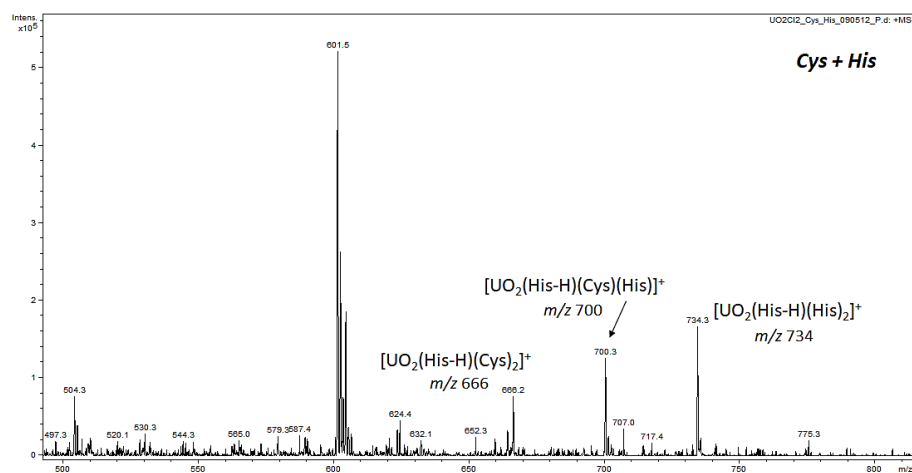


Figure S31. ESI-MS of a uranyl chloride + cysteine + histidine solution (1:2:2) in positive ion mode.

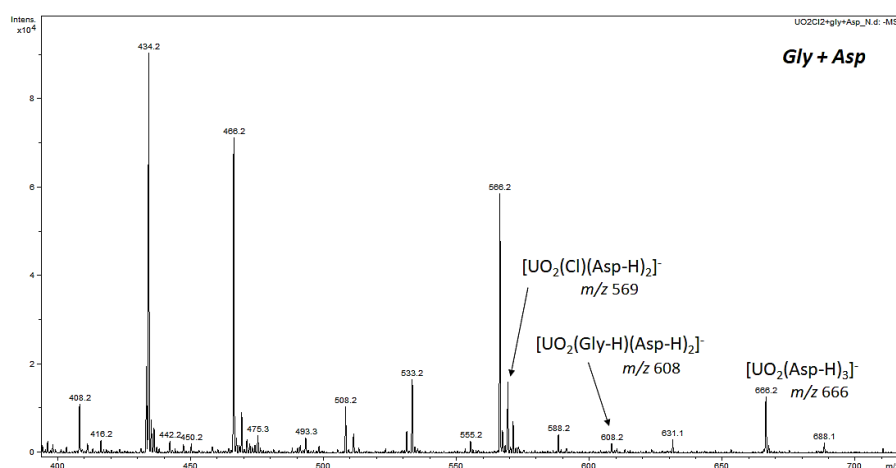


Figure S32. ESI-MS of a uranyl chloride + glycine + aspartic acid solution (1:2:2) in negative ion mode.

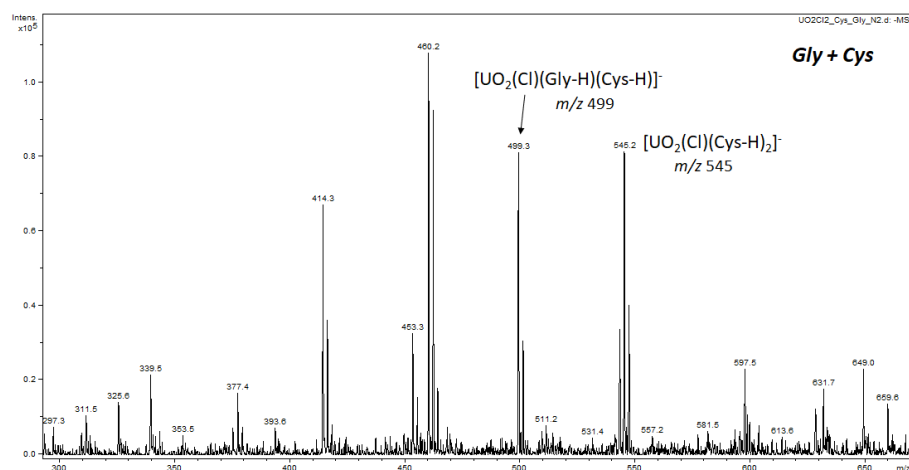


Figure S33. ESI-MS of a uranyl chloride + glycine + cysteine solution (1:2:2) in negative ion mode.

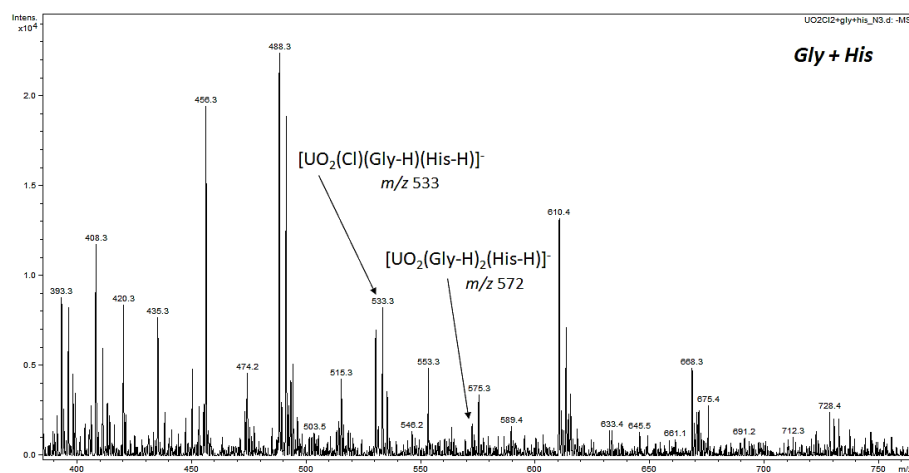


Figure S34. ESI-MS of a uranyl chloride + glycine + histidine solution (1:2:2) in negative ion mode.

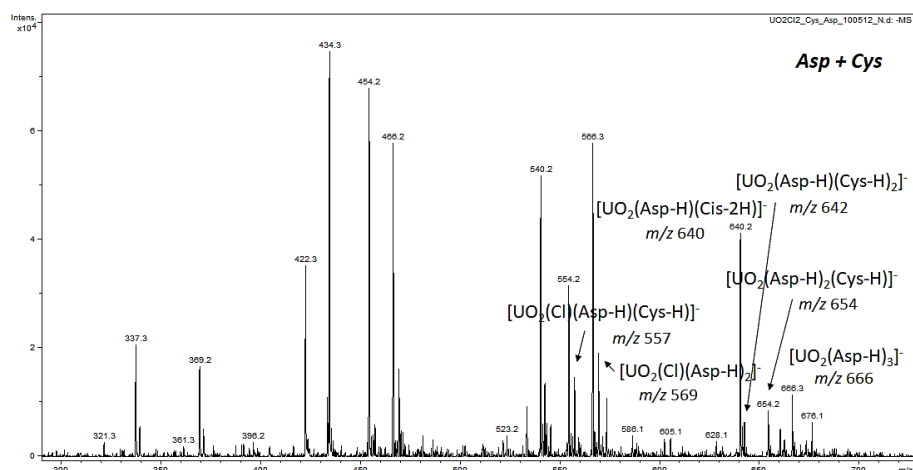


Figure S35. ESI-MS of a uranyl chloride + aspartic acid + cysteine solution (1:2:2) in negative ion mode.

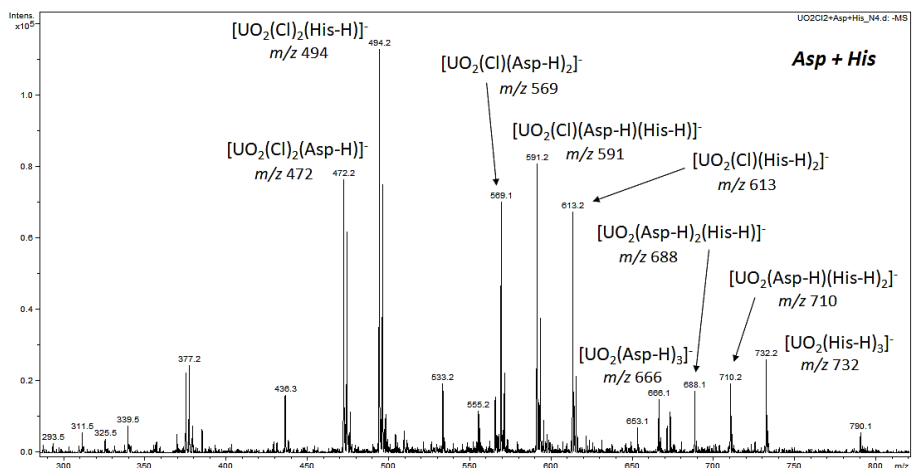


Figure S36. ESI-MS of a uranyl chloride + aspartic acid + histidine solution (1:2:2) in negative ion mode.

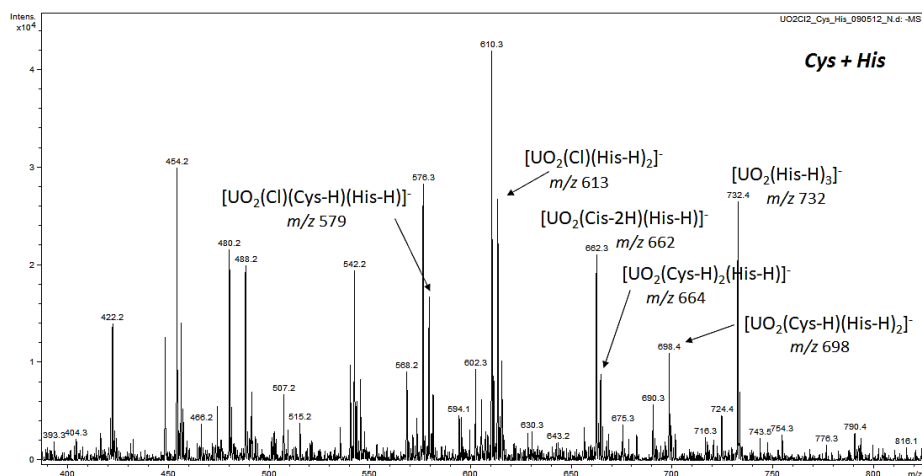


Figure S37. ESI-MS of a uranyl chloride + cysteine + histidine solution (1:2:2) in negative ion mode.

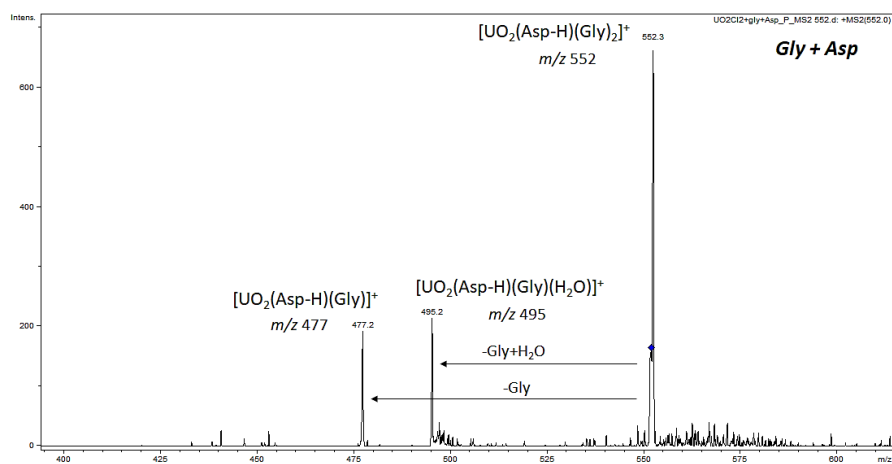


Figure S38. CID mass spectrum of $[\text{UO}_2(\text{Asp-H})(\text{Gly})_2]^+$.

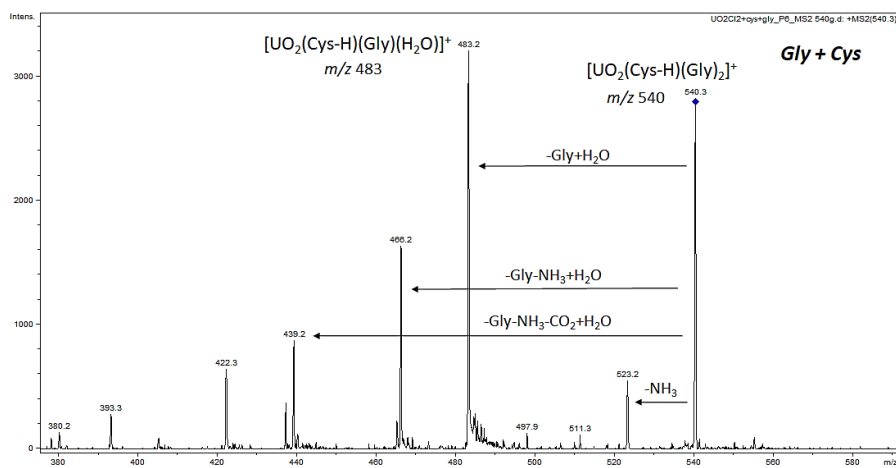


Figure S39. CID mass spectrum of $[\text{UO}_2(\text{Cys-H})(\text{Gly})_2]^+$.

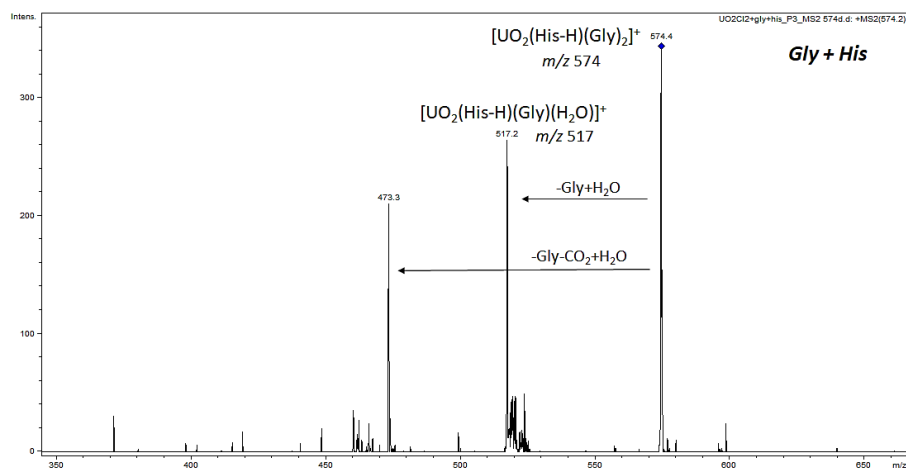


Figure S40. CID mass spectrum of $[\text{UO}_2(\text{His-H})(\text{Gly})_2]^+$.

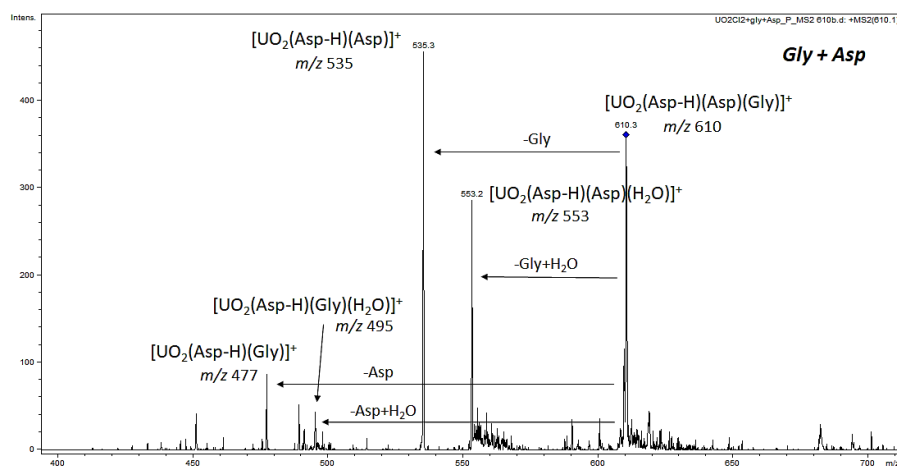


Figure S41. CID mass spectrum of $[\text{UO}_2(\text{Asp-H})(\text{Asp})(\text{Gly})]^+$.

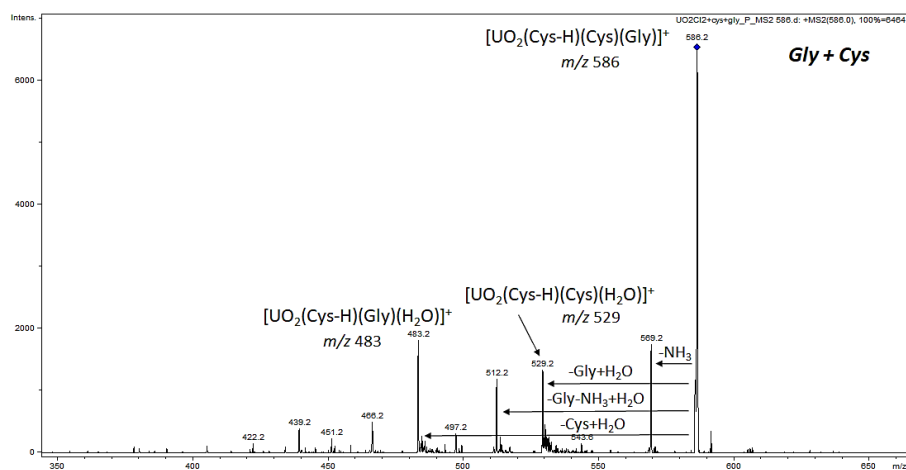


Figure S42. CID mass spectrum of $[\text{UO}_2(\text{Cys-H})(\text{Cys})(\text{Gly})]^+$.

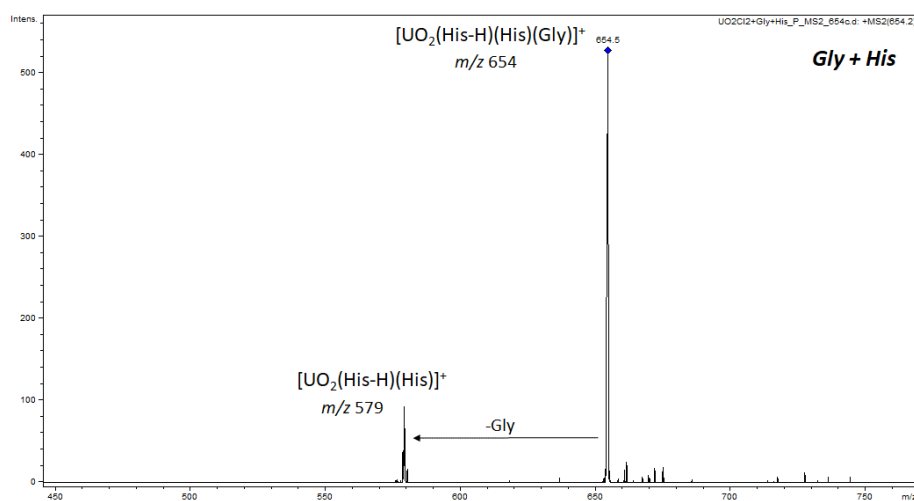


Figure S43. CID mass spectrum of $[\text{UO}_2(\text{His-H})(\text{His})(\text{Gly})]^+$.

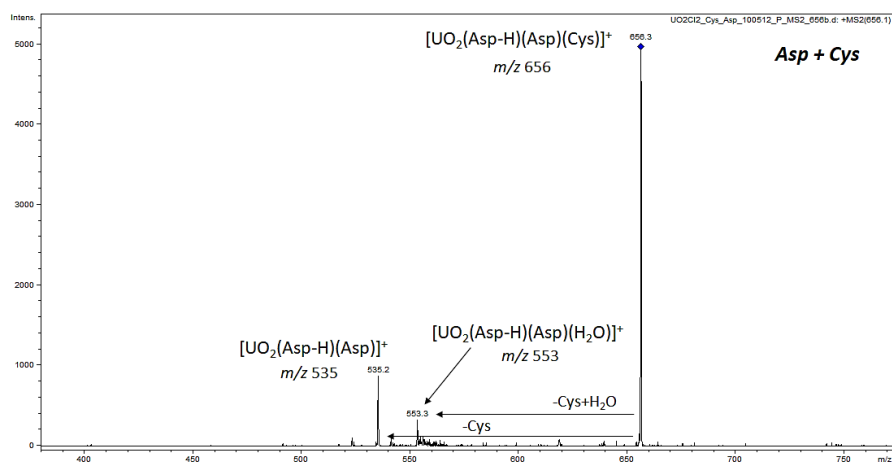


Figure S44. CID mass spectrum of $[\text{UO}_2(\text{Asp-H})(\text{Asp})(\text{Cys})]^+$.

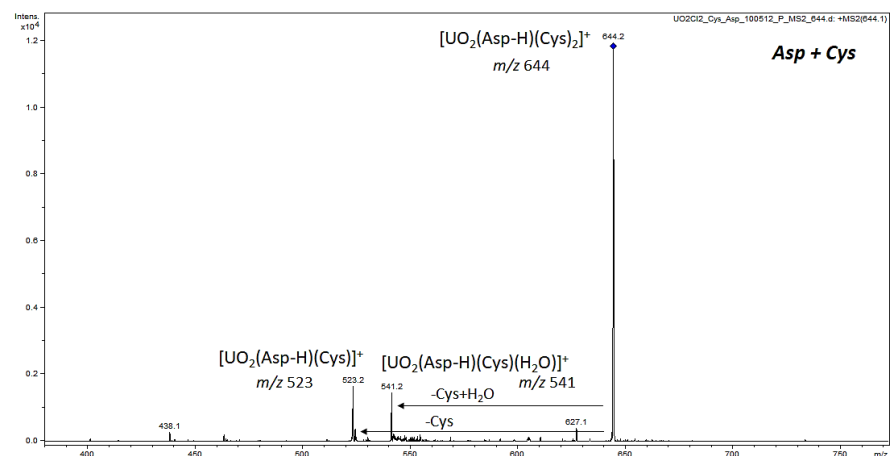


Figure S45. CID mass spectrum of $[\text{UO}_2(\text{Asp-H})(\text{Cys})_2]^+$.

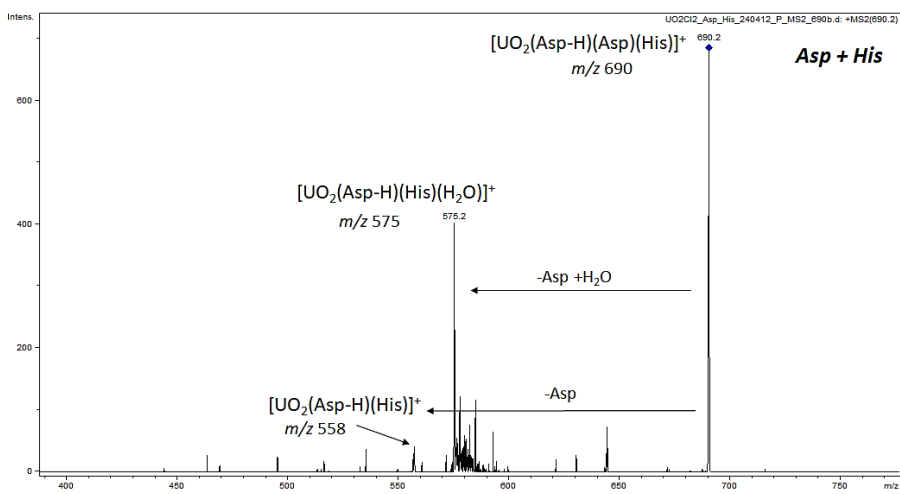


Figure S46. CID mass spectrum of $[\text{UO}_2(\text{Asp-H})(\text{Asp})(\text{His})]^+$.

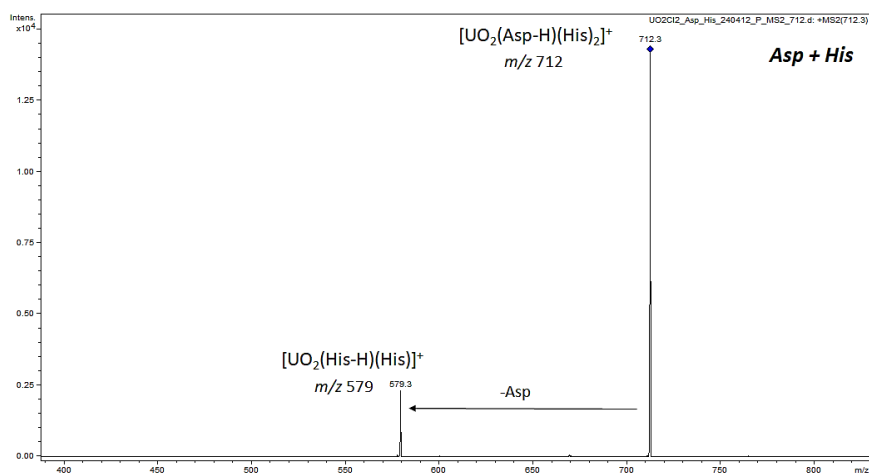


Figure S47. CID mass spectrum of $[\text{UO}_2(\text{Asp-H})(\text{His})_2]^+$.

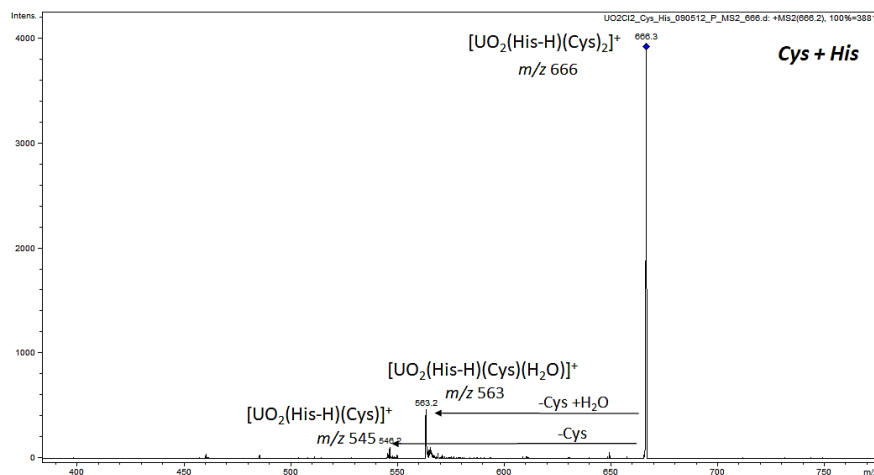


Figure S48. CID mass spectrum of $[\text{UO}_2(\text{His-H})(\text{Cys})_2]^+$.

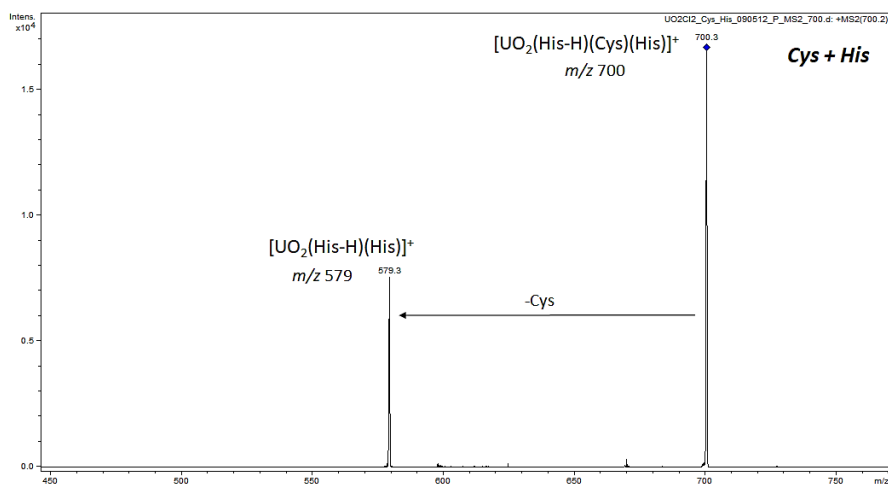


Figure S49. CID mass spectrum of $[\text{UO}_2(\text{His-H})(\text{Cys})(\text{His})]^+$.

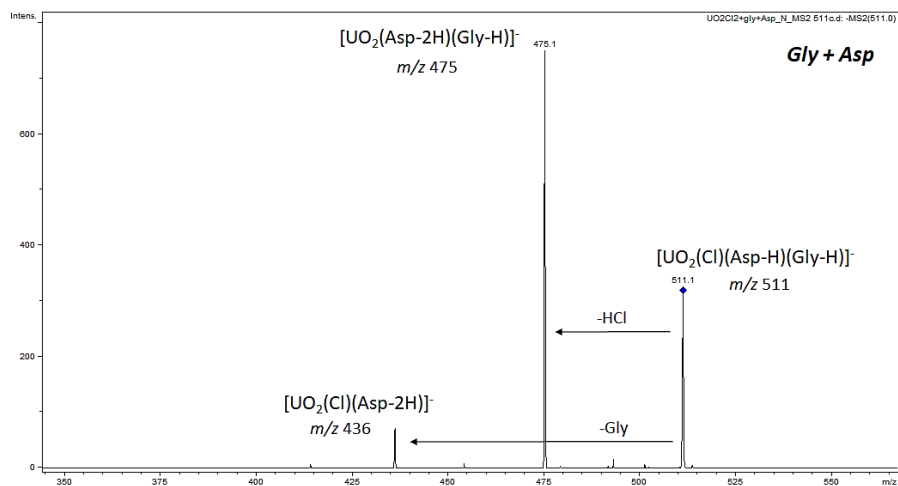


Figure S50. CID mass spectrum of $[\text{UO}_2(\text{Cl})(\text{Asp-H})(\text{Gly-H})]^-$.

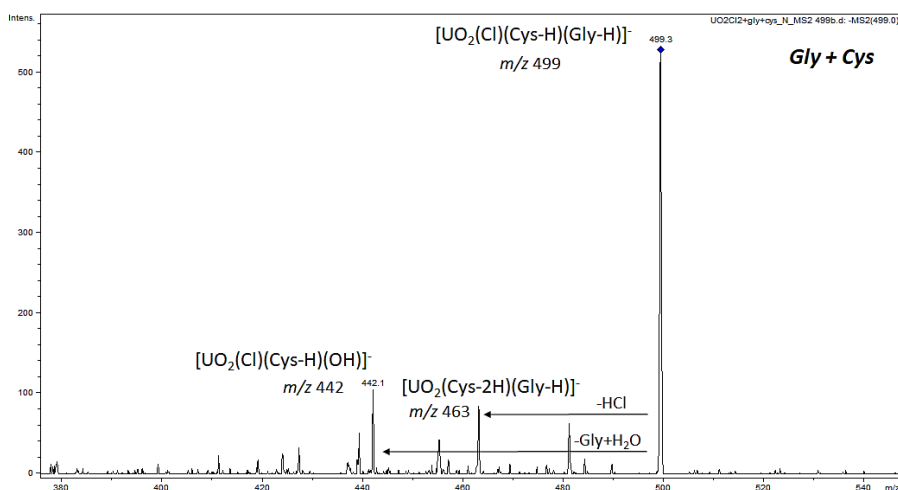


Figure S51. CID mass spectrum of $[\text{UO}_2(\text{Cl})(\text{Cys-H})(\text{Gly-H})]^-$.

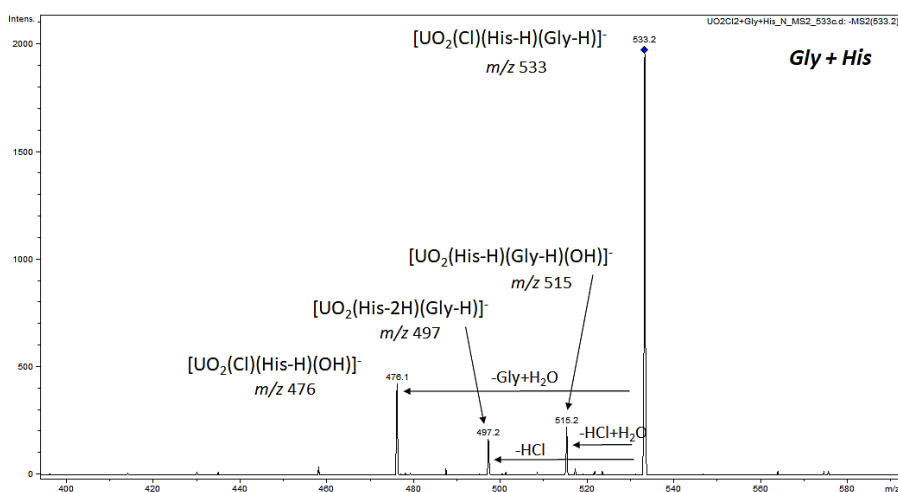


Figure S52. CID mass spectrum of $[\text{UO}_2(\text{Cl})(\text{His-H})(\text{Gly-H})]^-$.

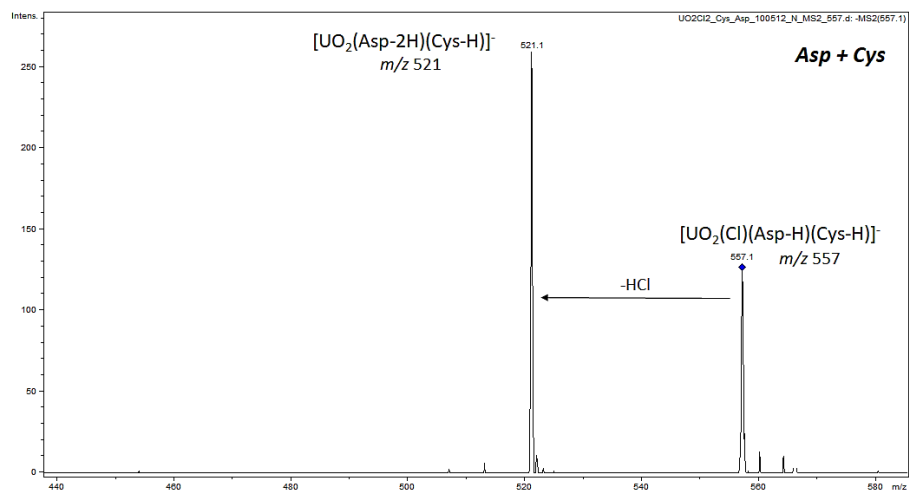


Figure S53. CID mass spectrum of $[\text{UO}_2(\text{Cl})(\text{Asp-H})(\text{Cys-H})]^-$.

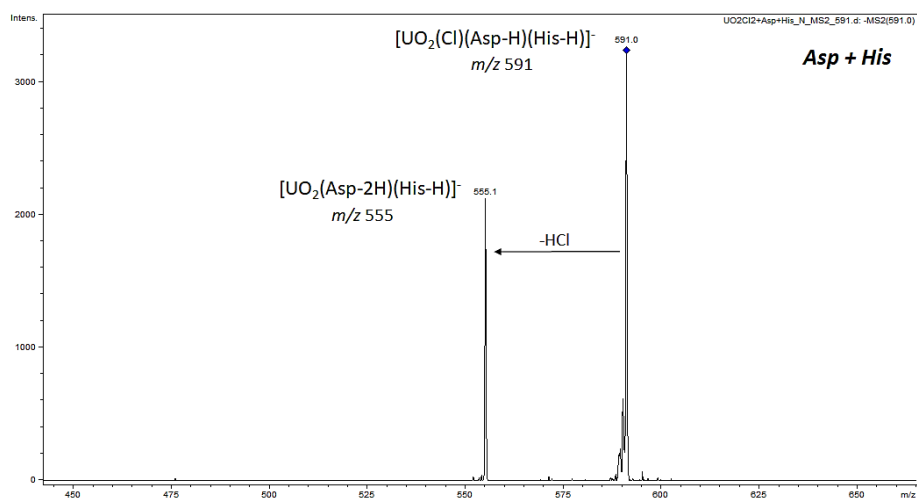


Figure S54. CID mass spectrum of $[\text{UO}_2(\text{Cl})(\text{Asp-H})(\text{His-H})]^-$.

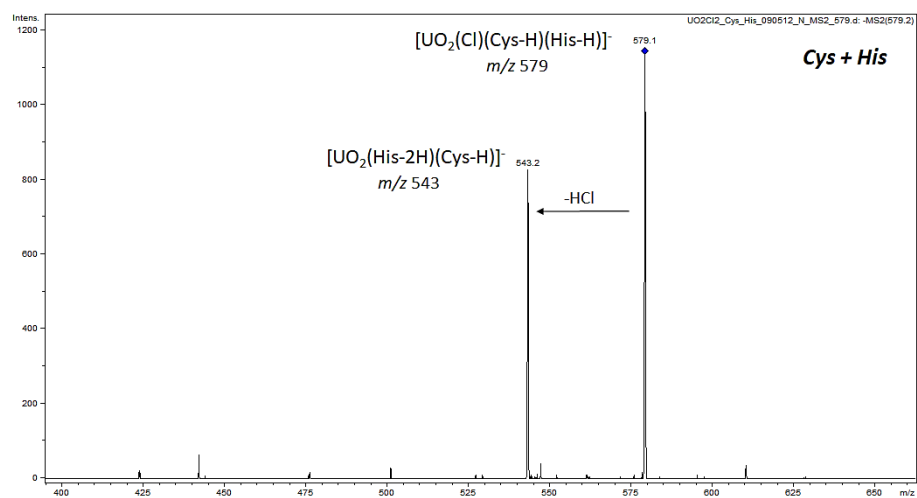


Figure S55. CID mass spectrum of $[\text{UO}_2(\text{Cl})(\text{Cys-H})(\text{His-H})]^-$.

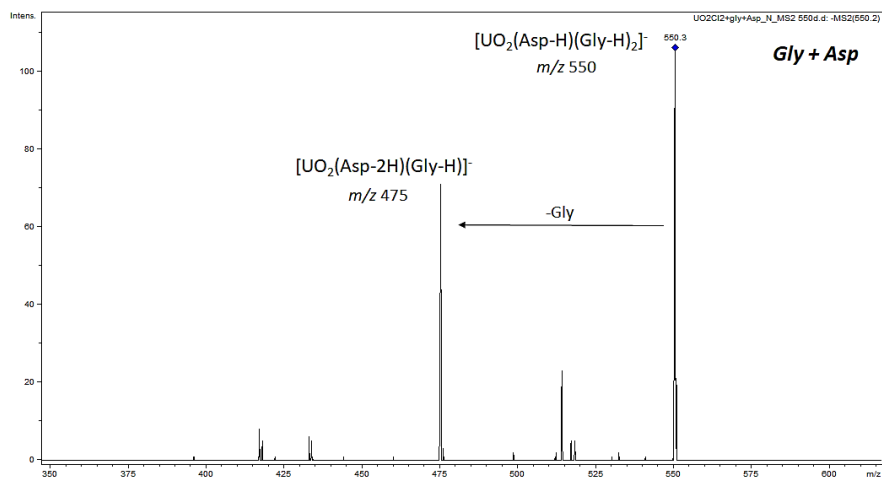


Figure S56. CID mass spectrum of $[\text{UO}_2(\text{Asp-H})(\text{Gly-H})_2]^-$.

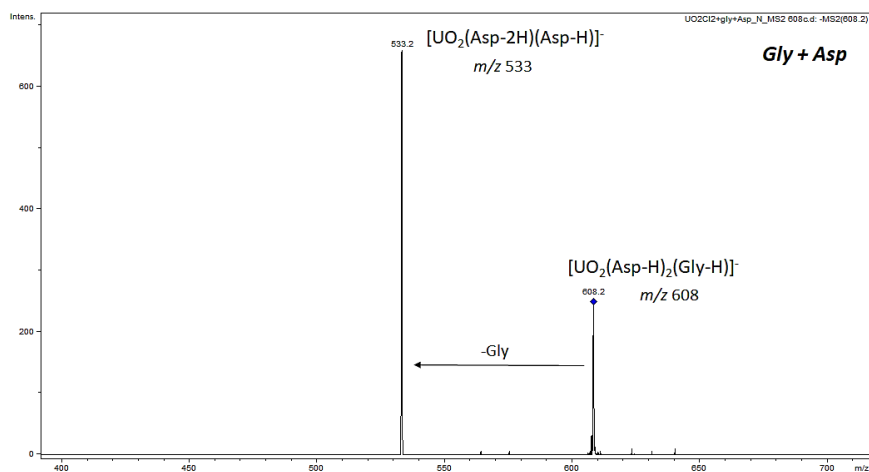


Figure S57. CID mass spectrum of $[\text{UO}_2(\text{Asp-H})_2(\text{Gly-H})]^-$.

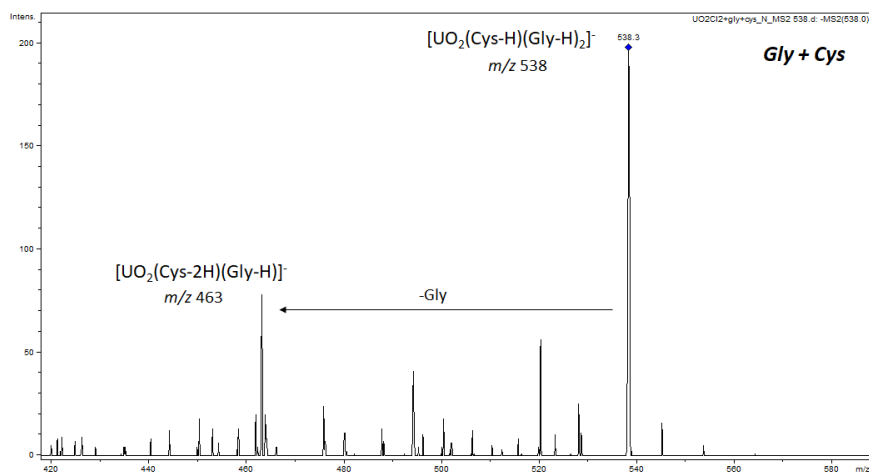


Figure S58. CID mass spectrum of $[\text{UO}_2(\text{Cys-H})(\text{Gly-H})_2]^-$.

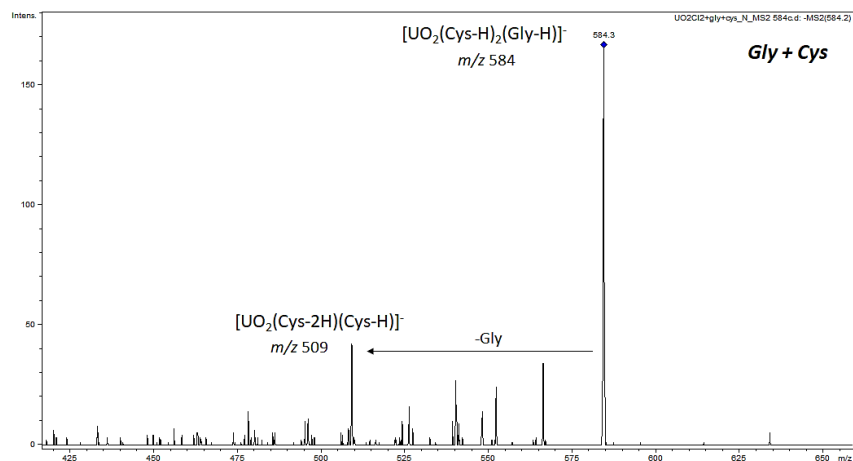


Figure S59. CID mass spectrum of $[\text{UO}_2(\text{Cys-H})_2(\text{Gly-H})]^-$.

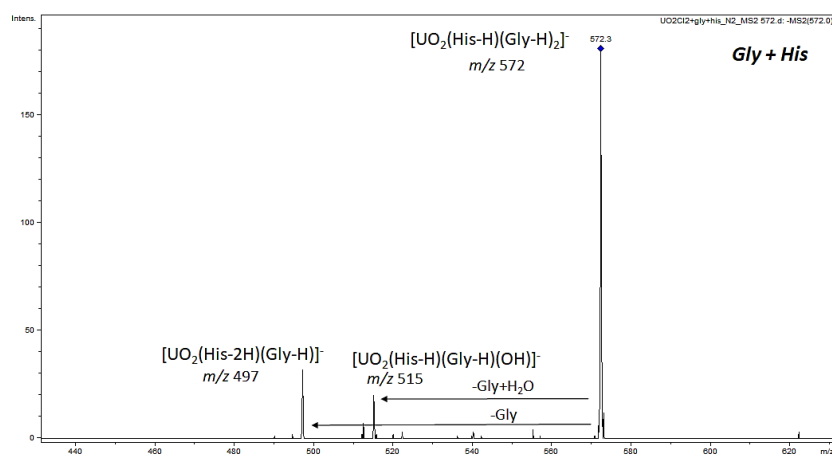


Figure S60. CID mass spectrum of $[\text{UO}_2(\text{His-H})(\text{Gly-H})_2]^-$.

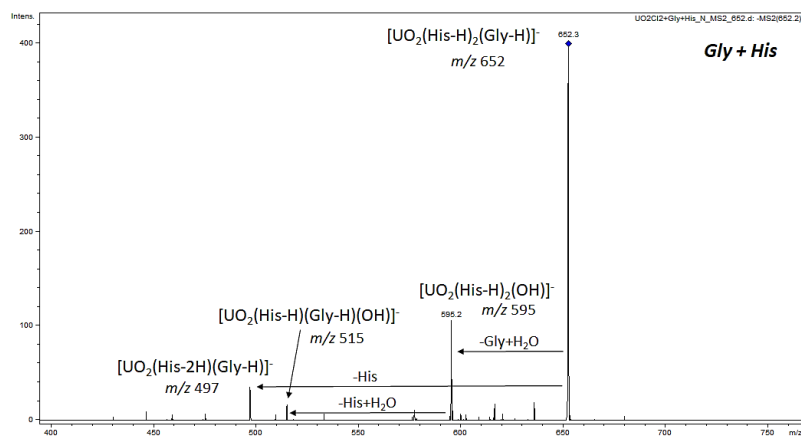


Figure S61. CID mass spectrum of $[\text{UO}_2(\text{His-H})_2(\text{Gly-H})]^-$.

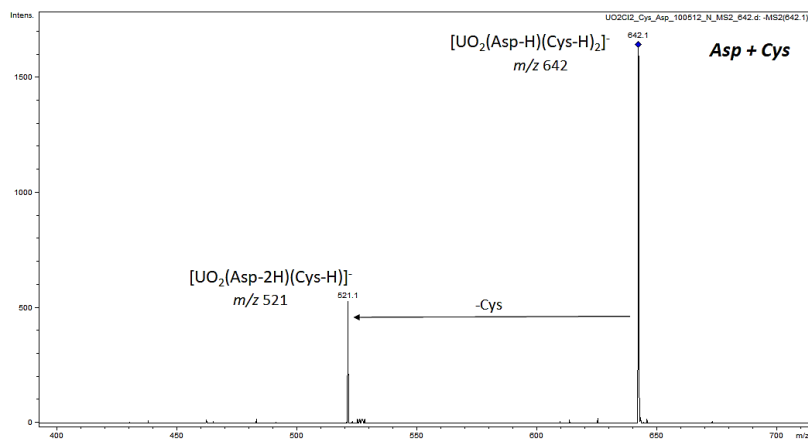


Figure S62. CID mass spectrum of $[\text{UO}_2(\text{Asp-H})(\text{Cys-H})_2]^-$.

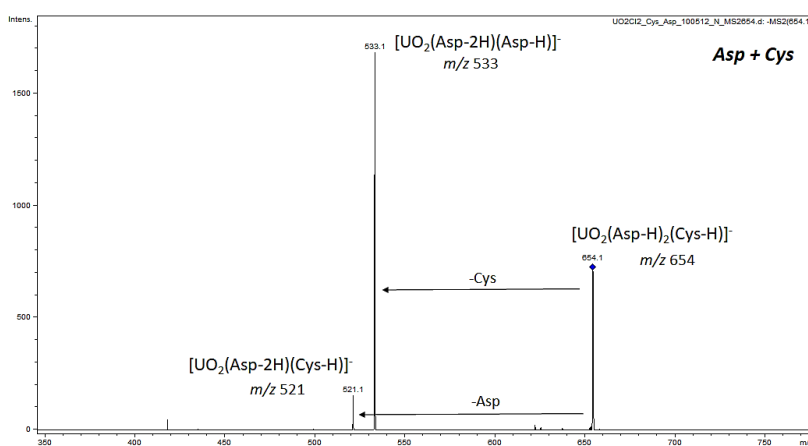


Figure S63. CID mass spectrum of $[\text{UO}_2(\text{Asp-H})_2(\text{Cys-H})]^-$.

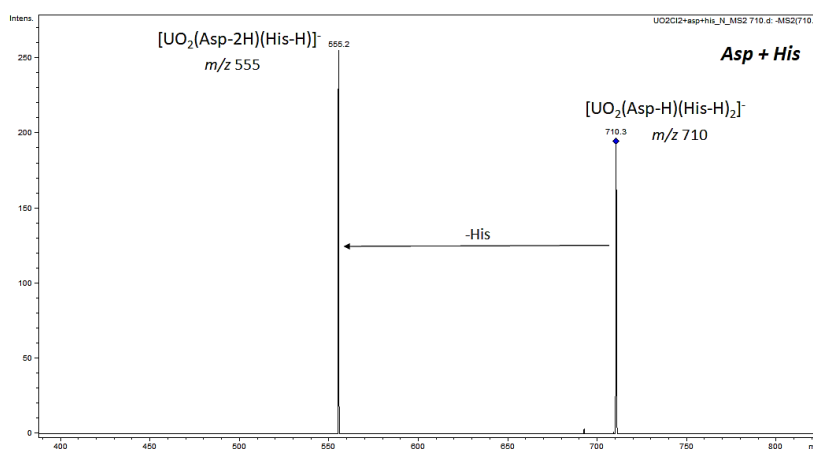


Figure S64. CID mass spectrum of $[\text{UO}_2(\text{Asp-H})(\text{His-H})_2]^-$.

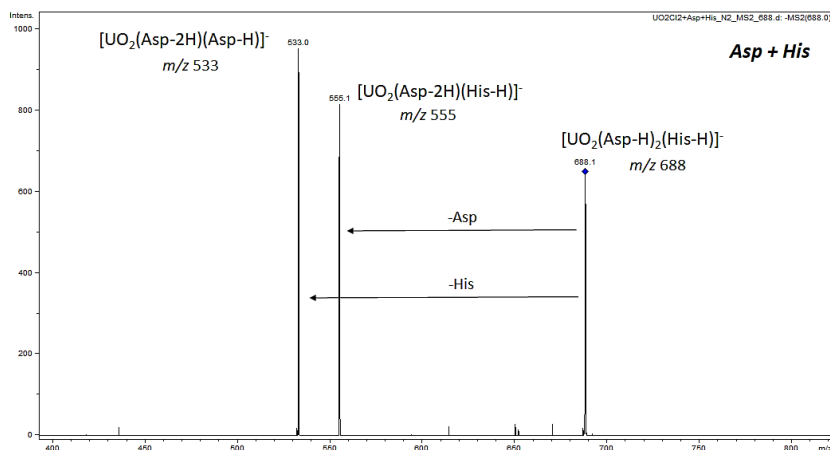


Figure S65. CID mass spectrum of $[\text{UO}_2(\text{Asp-H})_2(\text{His-H})]^-$.

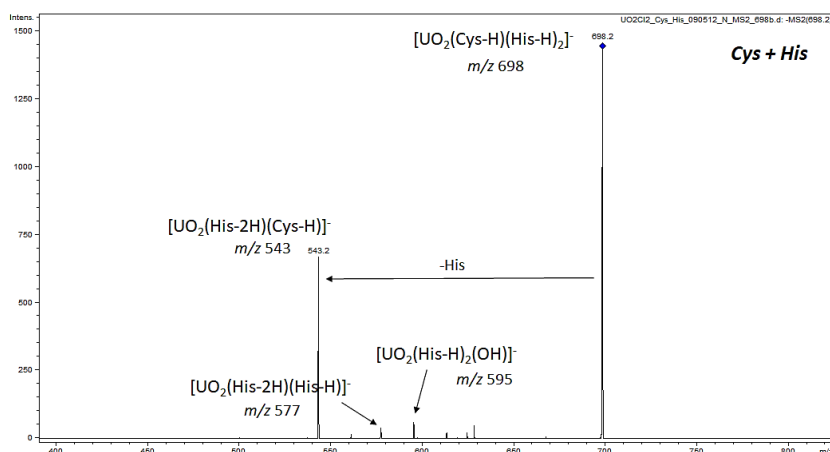


Figure S66. CID mass spectrum of $[\text{UO}_2(\text{Cys-H})(\text{His-H})_2]^-$.

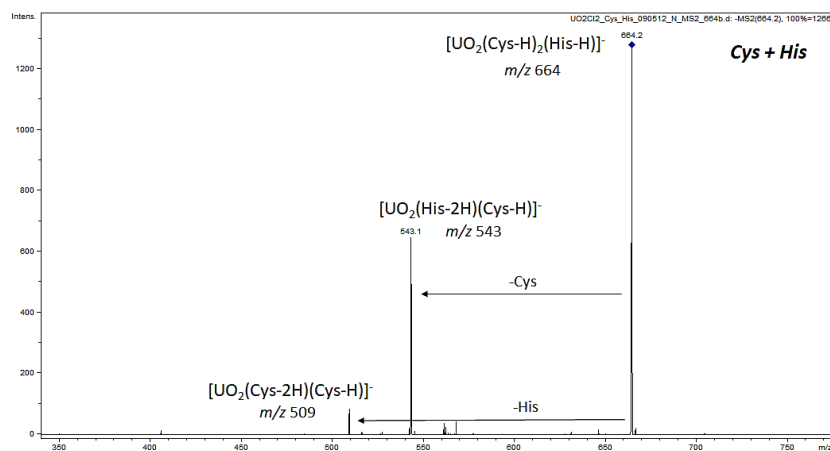


Figure S67. CID mass spectrum of $[\text{UO}_2(\text{Cys-H})_2(\text{His-H})]^-$.