

Mass Spectrum Report from Lionel Hill, John Innes Centre

Compounds **P2**, **P3** and [NBu₄]₂[**1**] to [NBu₄]₂[**4**] published in *Inorg. Chem.* **2025**, *64*, 8408

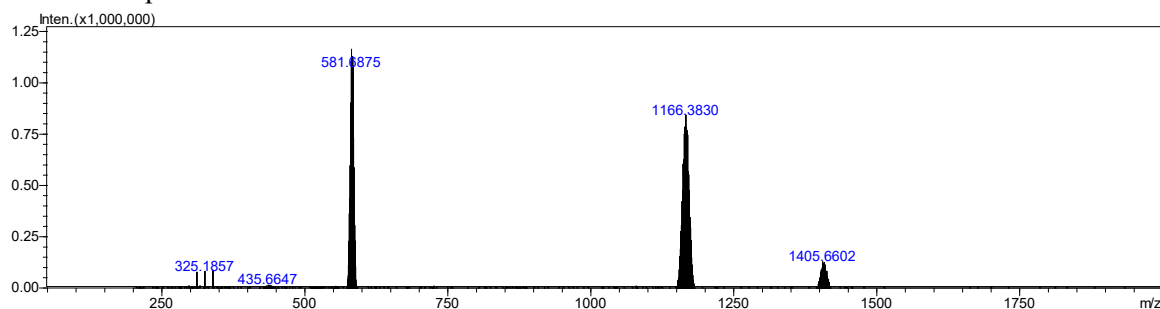
Method

I ran the samples on a Shimadzu IT-ToF mass spectrometer equipped with a Prominence/Surveyor UHPLC which I used to deliver the samples. I diluted the samples serially 2-fold in acetonitrile three times, finding that the second dilution (1:400) gave the best results.

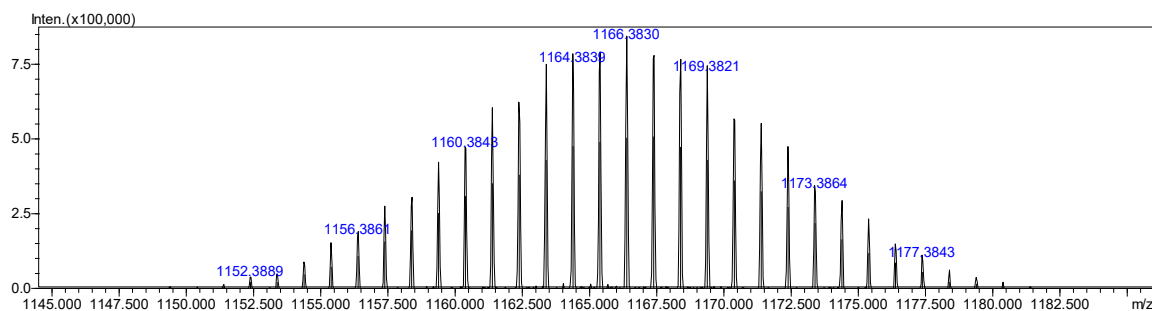
The autosampler was set up to inject 20 µL sample into a flow of 300 µL.min⁻¹ acetonitrile (two minute total method time), with a piece of tubing replacing the column. Detection was by UV/visible absorbance and electrospray MS. Since your compounds were anions I set up the MS to collect negative spectra only, from *m/z* 200–2000. The MS also collected data-dependent MS2 (50–2000 *m/z*) of the most abundant peaks with an isolation width of *m/z* 3.0, 50% collision energy and 50% collision gas. Spray chamber conditions were 1.5 L/min⁻¹ nebulizer gas, 250 °C curved desorption line, 300 °C heat block, and drying gas “on”. The instrument was calibrated immediately before use, according to the manufacturer’s instructions, using sodium TFA cluster ions.

Compound P2 ([NBu₄]₂[Mo₆O₁₈NC₁₂H₁₆I], BRH1-73)

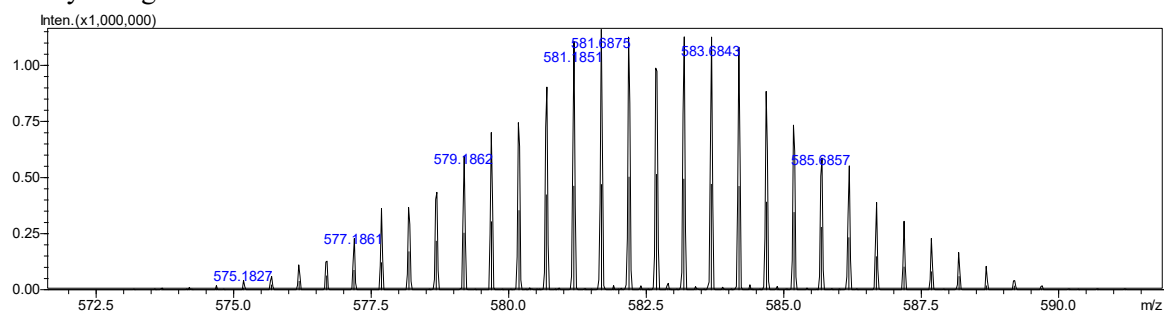
The overall spectrum was



Zoomed view of singly-charged cluster at 1166:

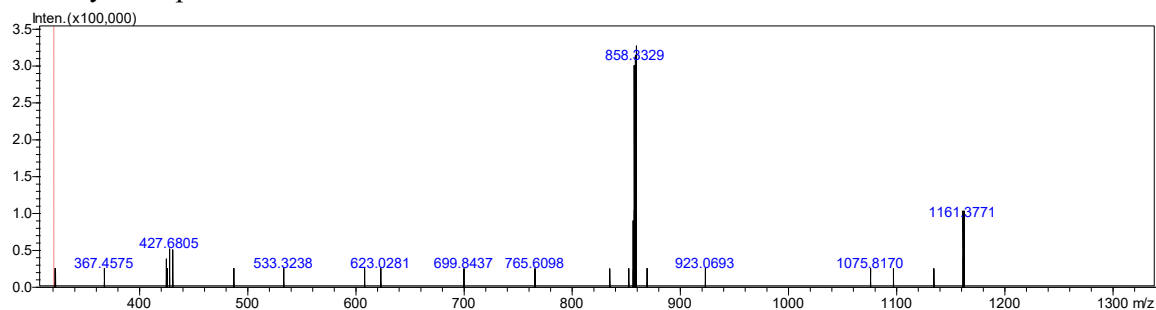


Doubly-charged at 581:

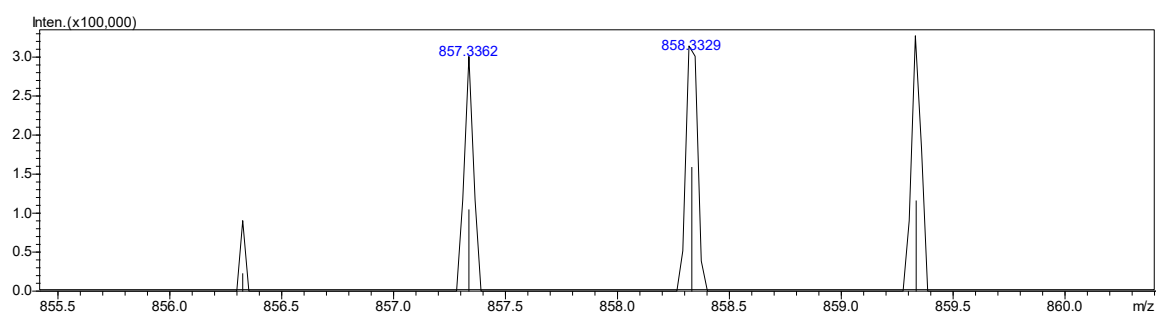


Note the increase of mass of 56 relative to BRH1-76, consistent with addition of C_4H_8 .

I have not attempted to check the accurate mass of the cluster peaks above to the expected accurate mass, but have attempted to check the accurate loss in MS2. The following is the MS2 spectrum nominally from precursor ion 1160.38:



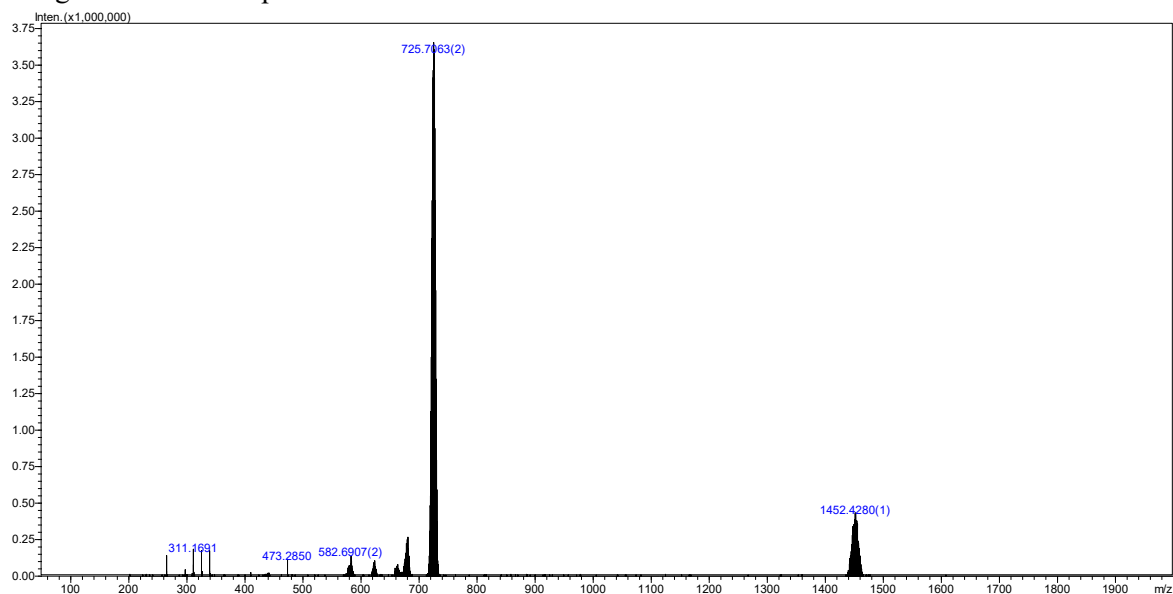
Zoomed view:



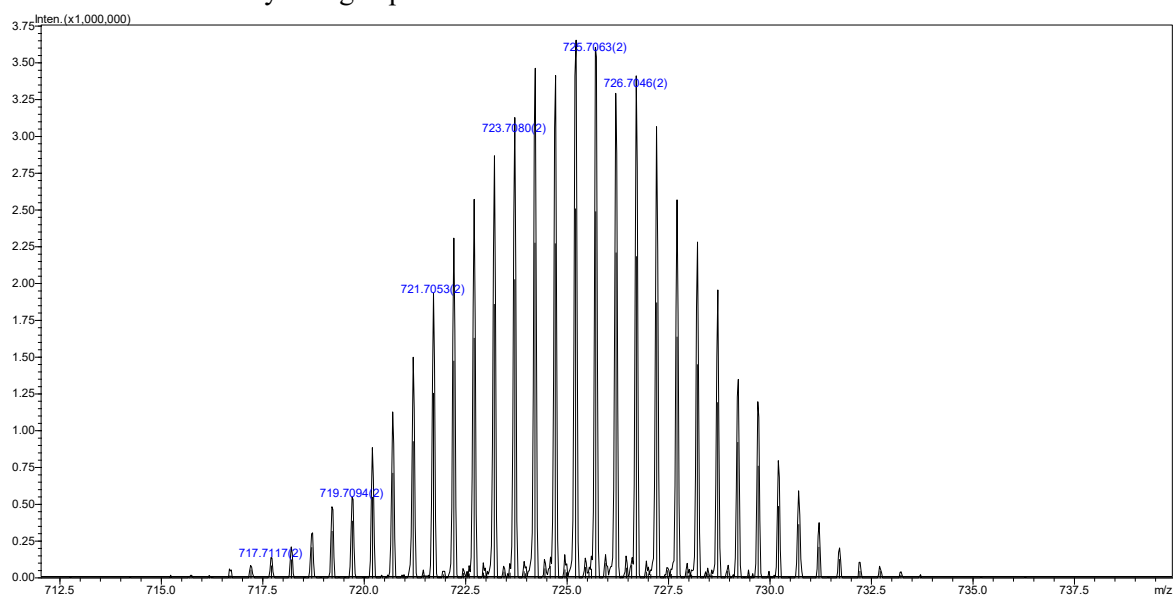
If we assume the precursor is 1160.3848, then loss of $C_{12}H_{18}IN$ (exact monoisotopic mass 303.0484) should result in a fragment of m/z 857.3359. This is very good agreement to one of the three isotope peaks found in the zoomed view.

Compound P3 ([NBu₄]₂[Mo₆O₁₇(NC₁₂H₁₆I)₂], BRH2-212)

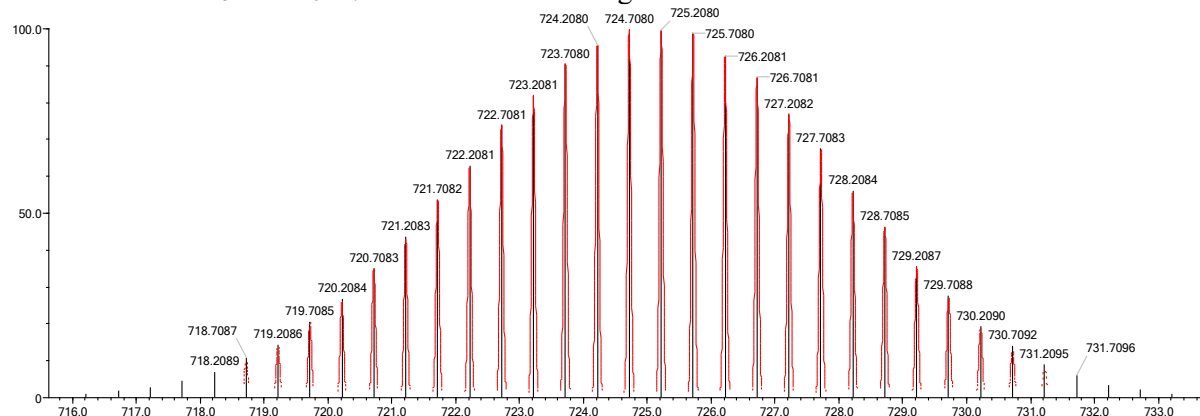
In negative mode the spectrum was:



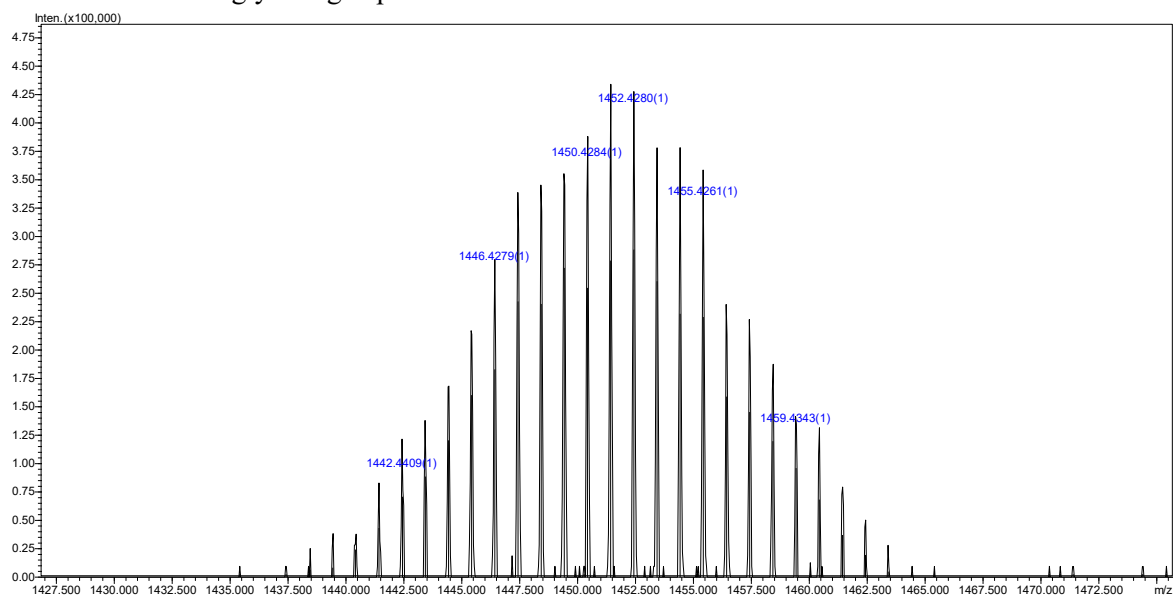
Zoomed view of doubly-charged peak



The anion is C₂₄H₃₂N₂Mo₆O₁₇I₂⁽²⁻⁾ with the following simulation

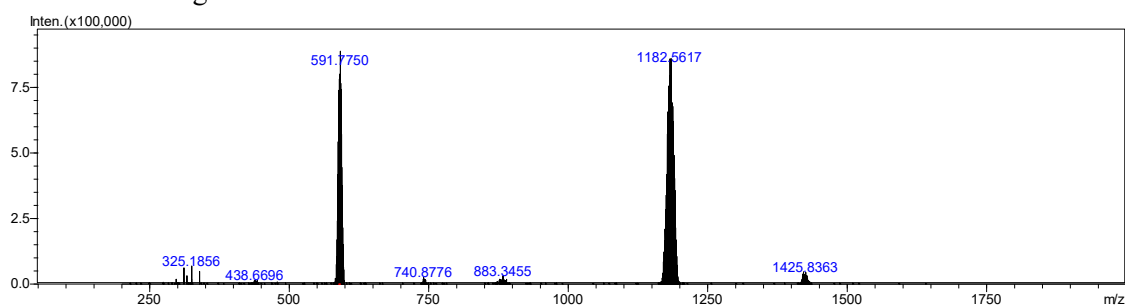


Zoomed view of singly charged peak

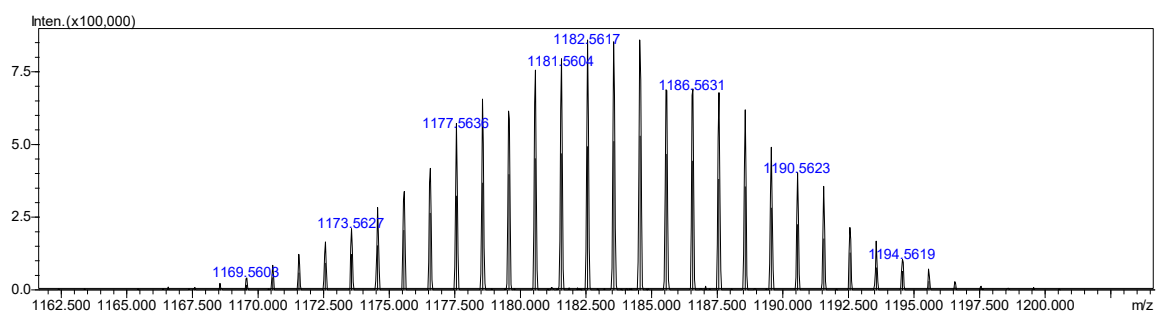


Compound [NBu₄]₂[1] ([NBu₄]₂[Mo₆O₁₈N₂C₃₄H₃₄], BRH2-116)

Overall MS averaged 0.317-0.458min:

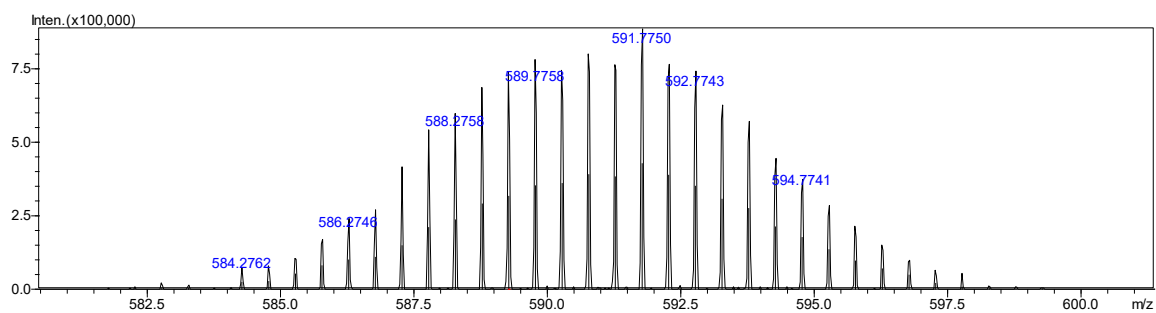


Zoomed view of 1182 cluster:

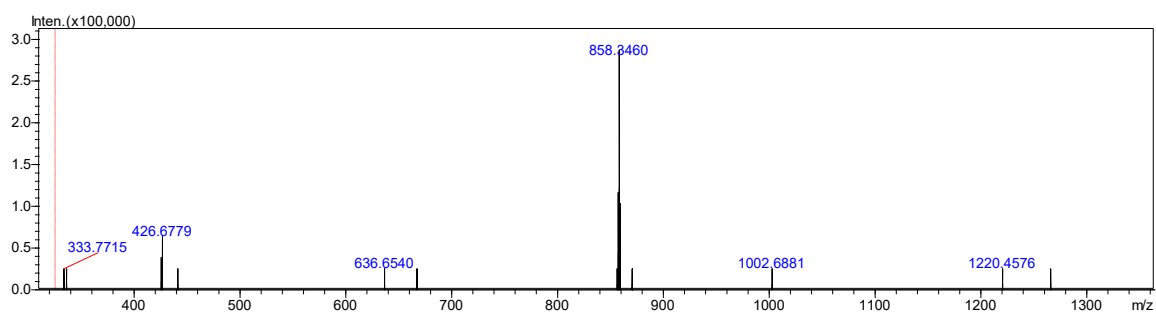


I believe the mass difference between this and the previous sample to be consistent with the expected change of mass given your structures.

Zoomed view of 591 cluster:

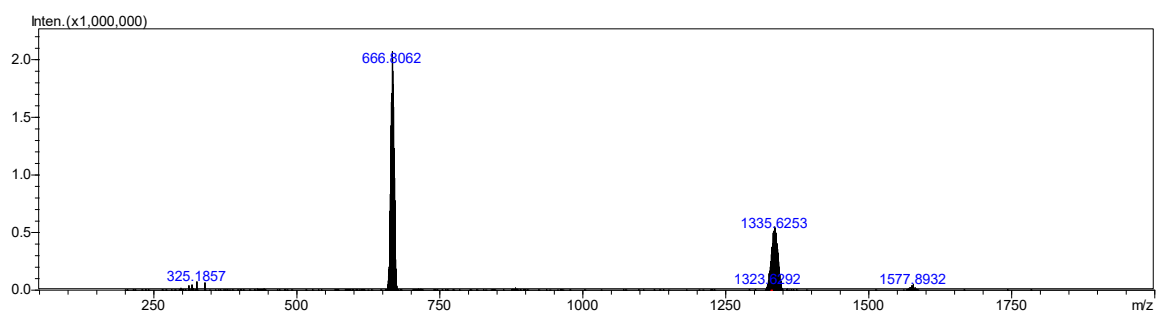


MS2 1177.6→

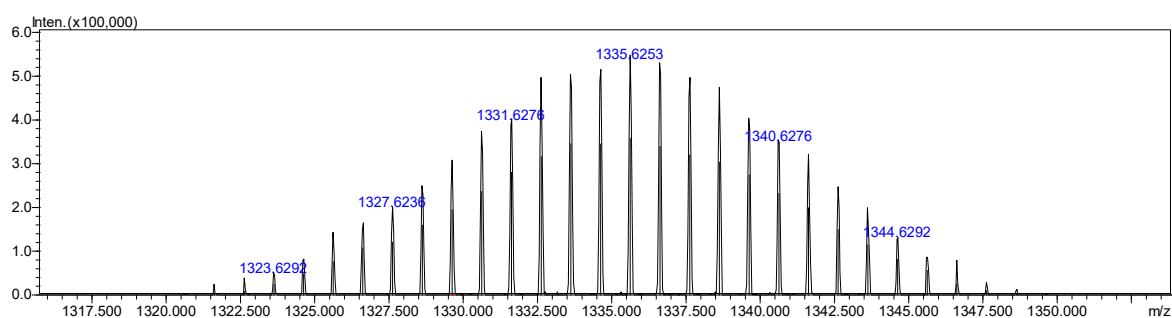


Compound [NBu₄]₂[2] ([NBu₄]₂[Mo₆O₁₈N₂C₂₂H₂₆], BRH2-128)

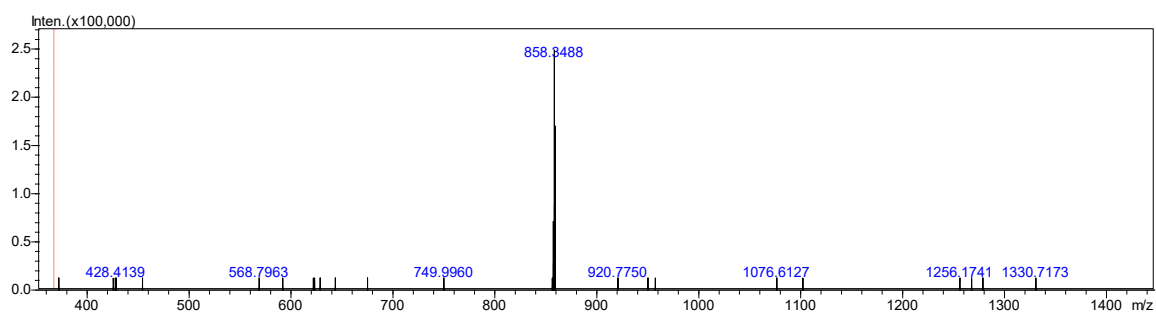
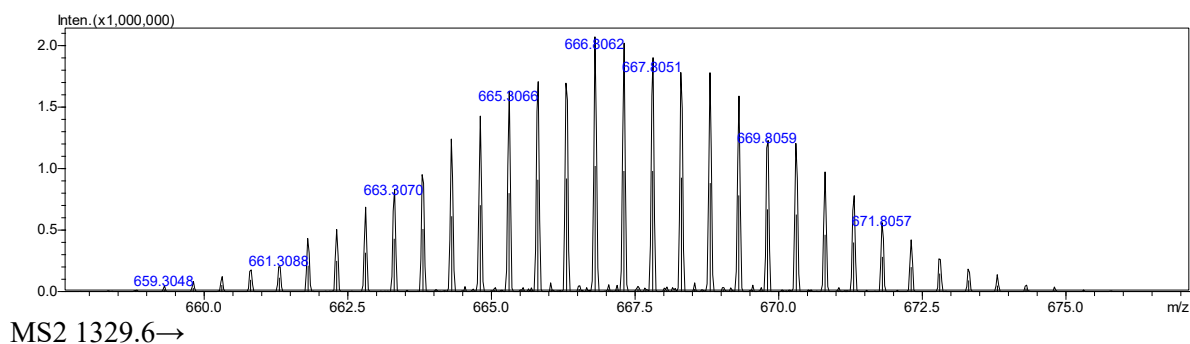
MS averaged 0.308-0.483min:



Zoom of cluster at 1335:



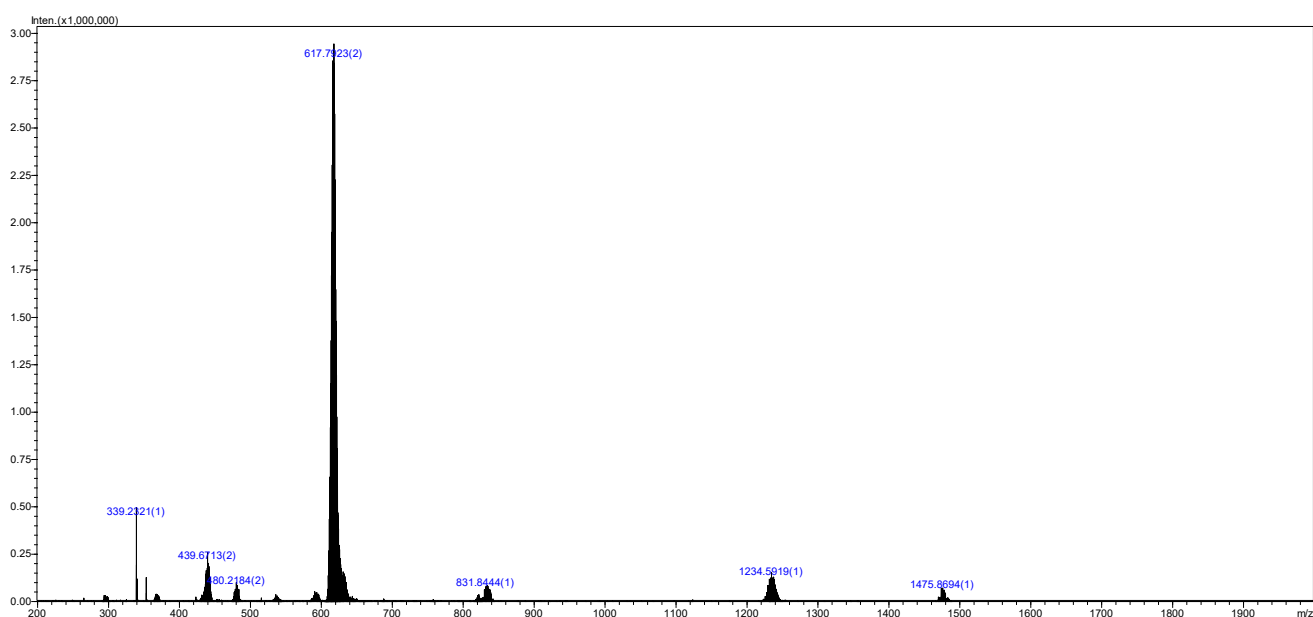
Zoom of cluster at 666 (doubly-charged):



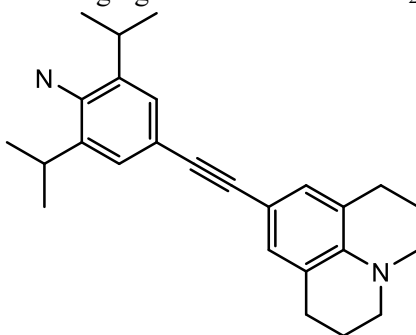
If the neutral leaving group is the entire functional group as an amine, $C_{34}H_{36}N_2$, with neutral mass 472.2878, then the expected parent of 858.3488 is 1,330.6366. The nearest measured mass in the first spectrum is 1330.6259, which was probably trapped within the m/z 3 window. To form this amine, we require a hydrogen to appear magically from somewhere; I have no experience of this sort of molecule so I cannot tell whether we are really losing an amine (requiring intermolecular reaction in the trap, since there is only one hydrogen, the adduct hydrogen, available) – or possibly whether we are losing a radical (unusual in low-energy collisions in traps), or $C_{34}H_{34}N_2$. Given that I do not know exactly which precursor was trapped, this is hard to tell. It would be possible to collect MS2 spectra with no collision energy to check the parent ions.

Compound [NBu₄]₂[3] ([NBu₄]₂[Mo₆O₁₈N₂C₂₆H₃₀], BRH3-299)

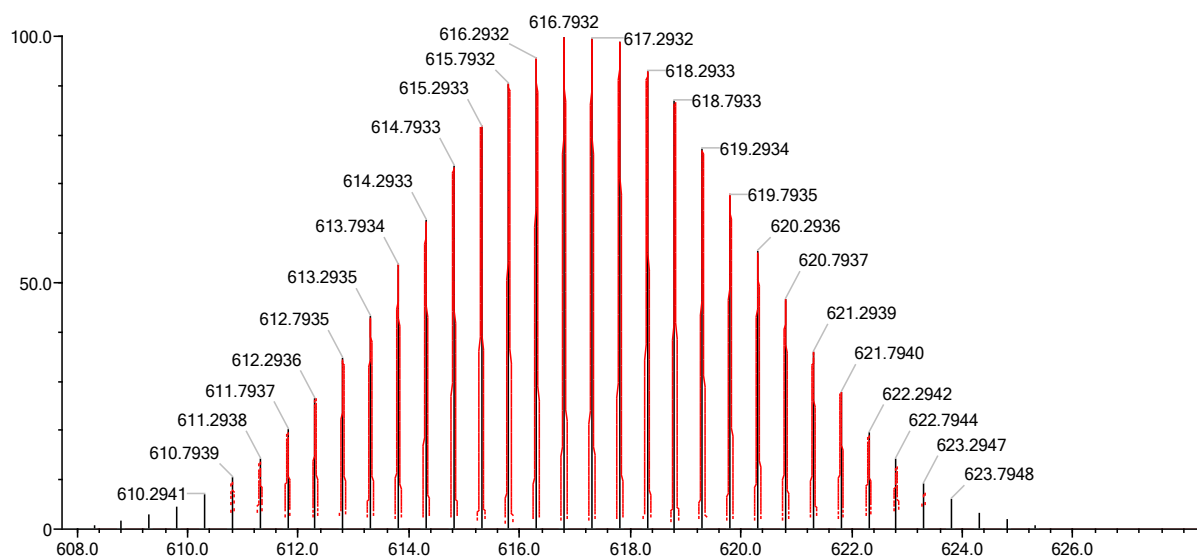
The spectrum averaged 0.308-0.458min was:



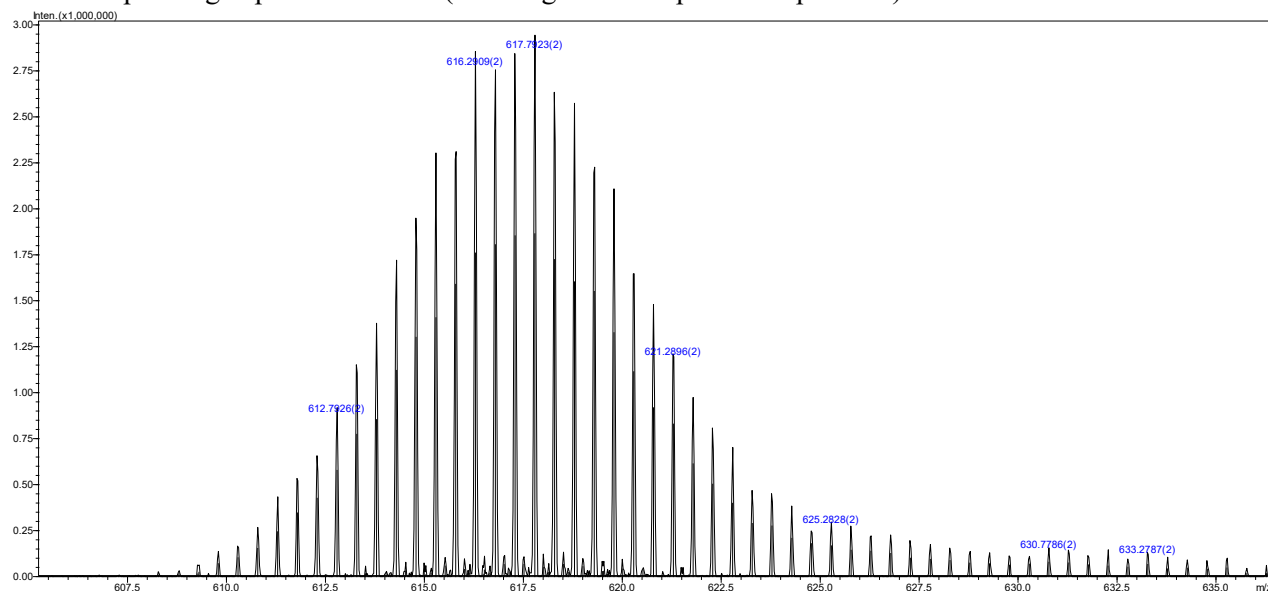
The formula you provided for the expected product was $C_{54}H_{100}N_4Mo_6O_{18}$, but this didn't seem to match the drawing. I believe the following ligand has the formula $C_{26}H_{30}N_2$:



A simulation of $C_{26}H_{30}N_2Mo_6O_{18}^{(2-)}$ is



The corresponding experimental data (zooming-in on the previous spectrum) are:

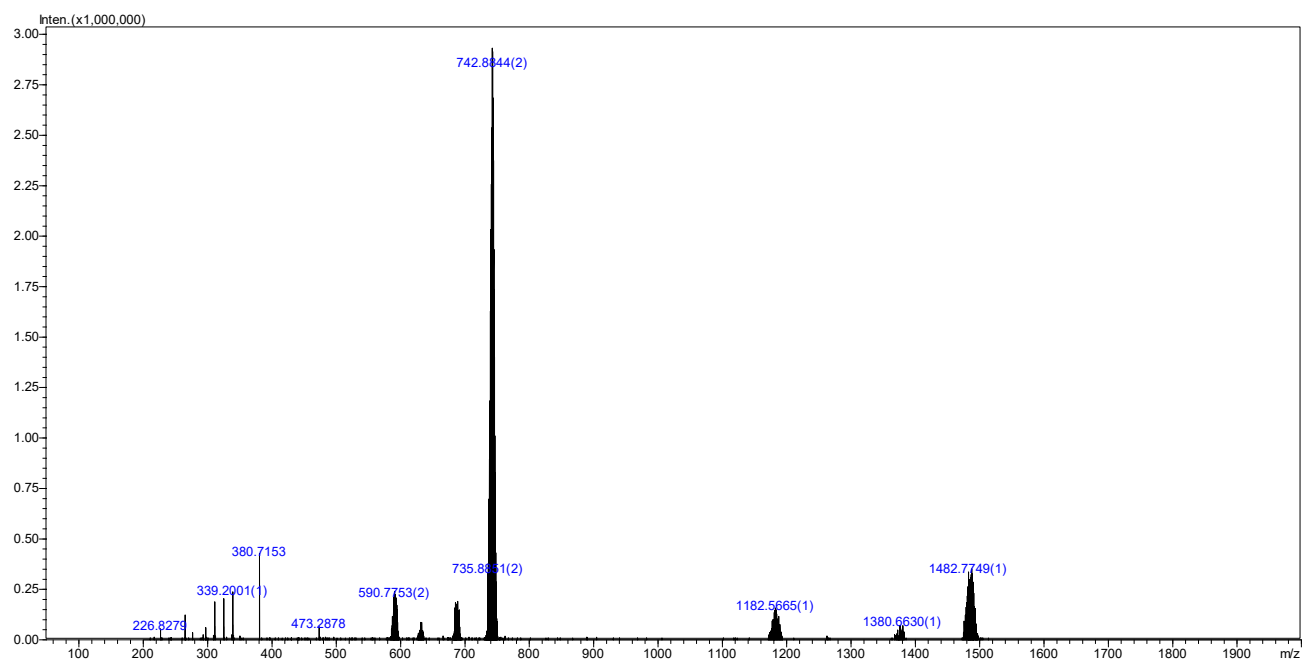


The match is good, both in the spread of the cluster and in the masses of the individual peaks (though note that there is a minor second product at higher mass, meaning that the cluster doesn't disappear right down to the base-line on that side of the overall envelope).

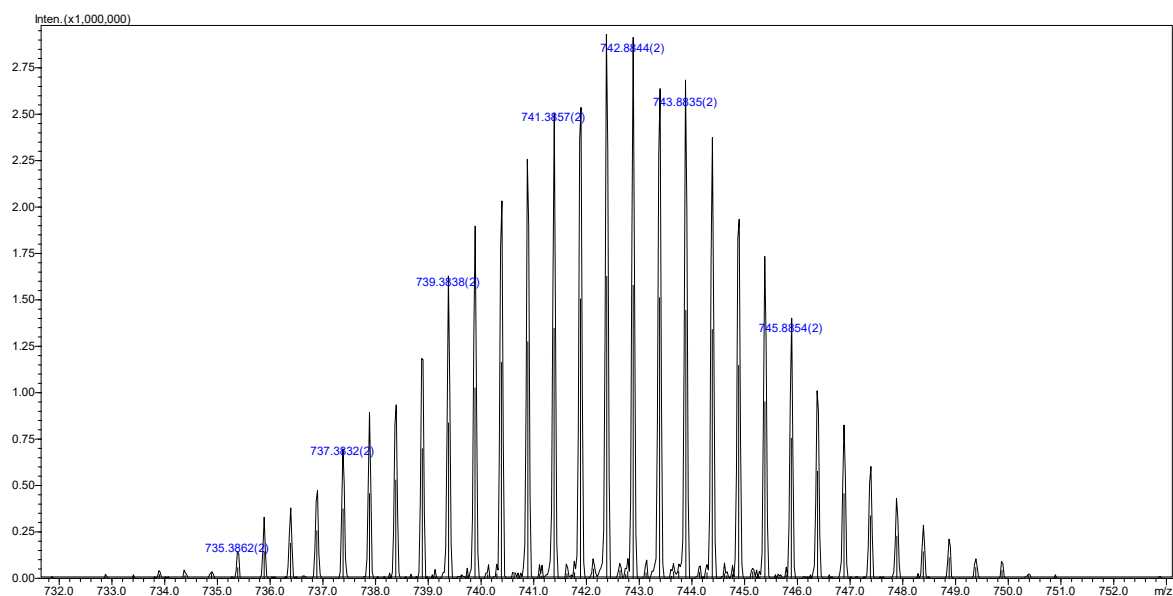
The minor clusters at m/z 1234 and 1475 are the singly-charged anion, and the singly-charged product produced by association with one tetrabutylammonium counter-ion. Let me know if you need zoom-scans of them.

Compound $[\text{NBu}_4]_2[4]$ ($[\text{NBu}_4]_2[\text{Mo}_6\text{O}_{17}(\text{N}_2\text{C}_{22}\text{H}_{16})_2]$, BRH3-221)

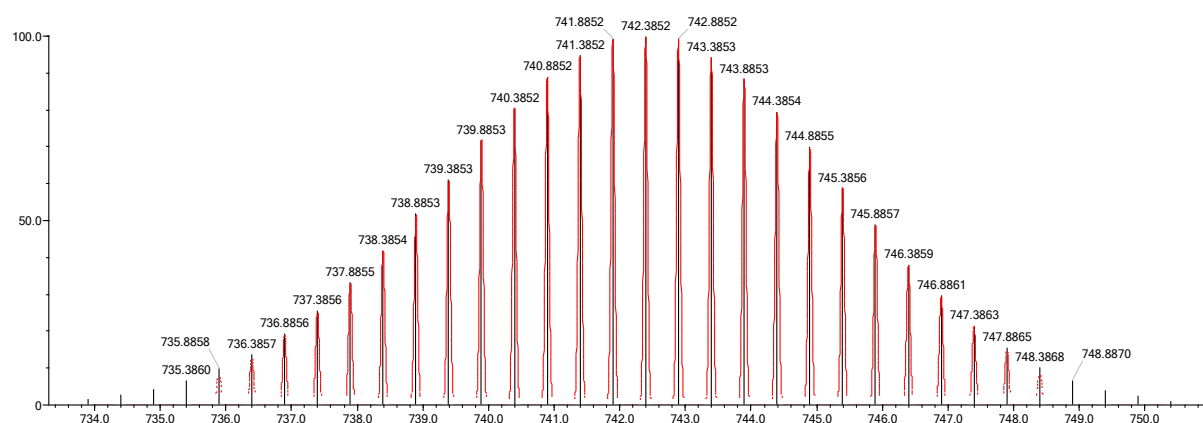
The full spectrum in negative mode was:



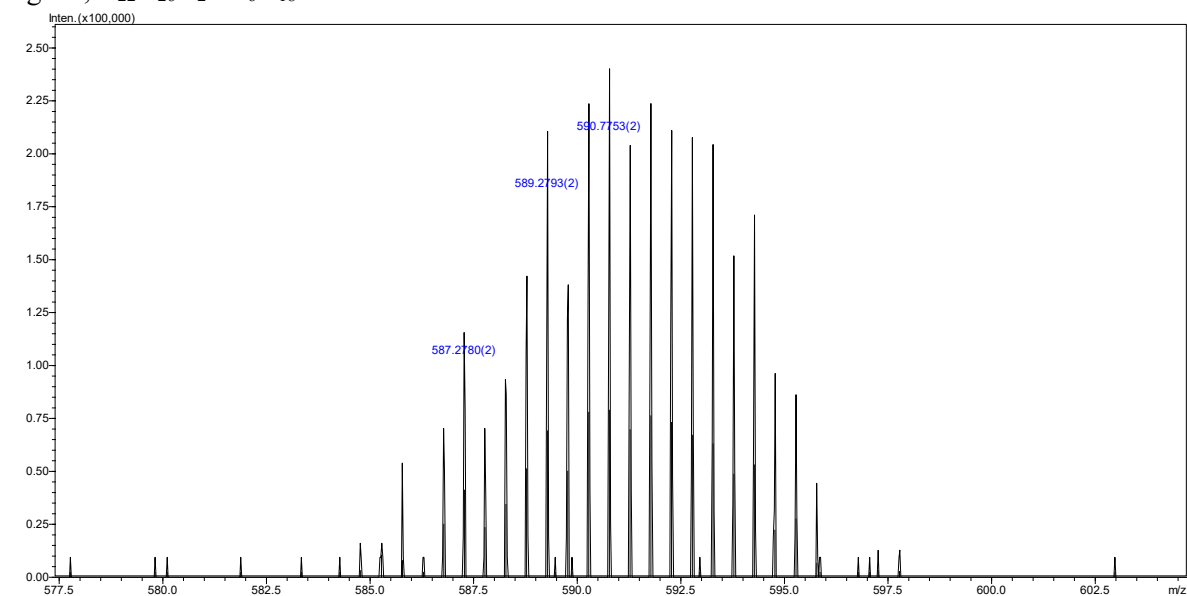
Zoomed view of the main doubly-charged peak:



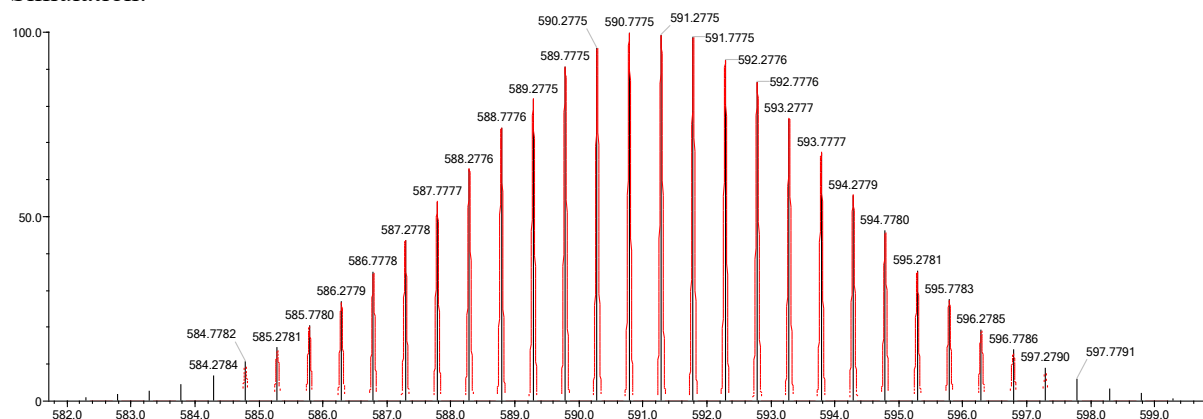
The expected anion is $\text{C}_{44}\text{H}_{52}\text{N}_4\text{Mo}_6\text{O}_{17}^{(2-)}$ with the following simulation



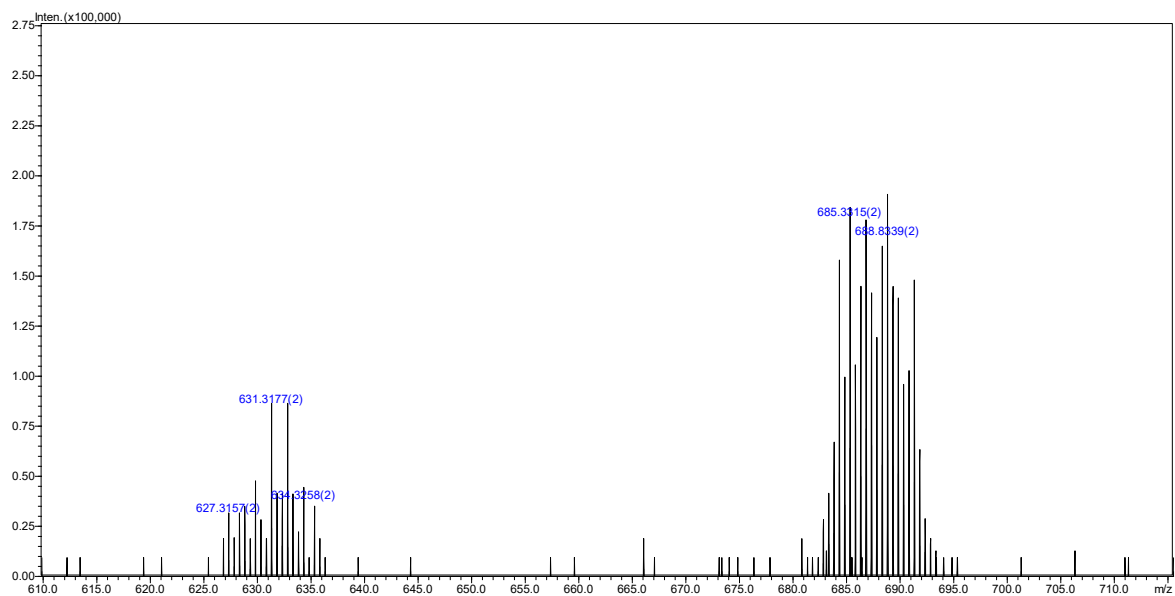
I believe one of the very minor doubly-charged clusters, around 590.7, is the product with only one ligand, $\text{C}_{22}\text{H}_{26}\text{N}_2\text{Mo}_6\text{O}_{18}^{(2-)}$



Simulation:



These are the other two minor doubly-charged clusters:



Singly-charged product

