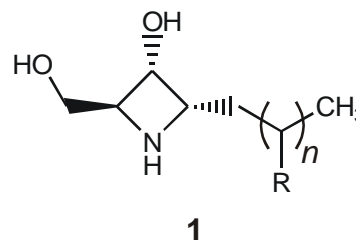
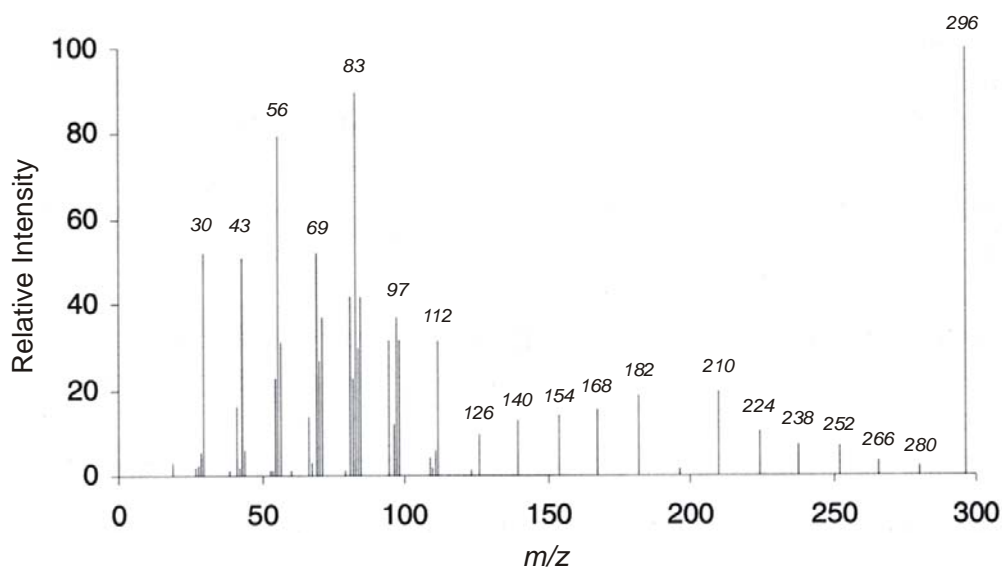


Workshop 6
MS Analysis with Even-Electron Ions

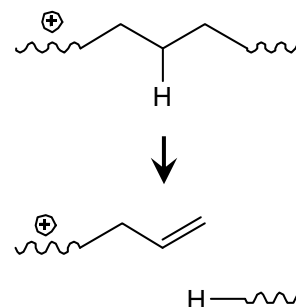
1. Penazetidine (**1**) was isolated from a marine sponge from an extract which showed activity against protein kinase C. NMR analysis showed the compound to contain an azetidine ring and an attached alkyl chain with only two $-\text{CH}_3$ groups; thus, in the structure below, $\text{R} = \text{H}$ for all chain carbons except one, where $\text{R} = \text{CH}_3$.



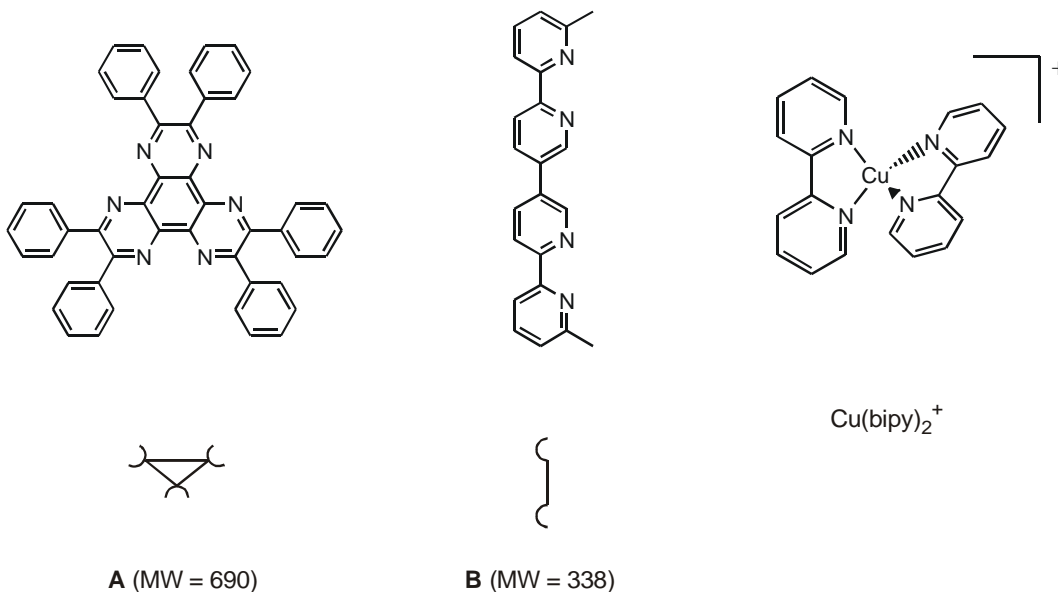
- a) Initial mass spectrometric analysis showed by FAB-MS in a protonating matrix gave $[\text{M}\cdot\text{H}]^+ = 370$, with major fragment peaks at $m/z = 296$ and 60 . What is the molecular weight of the alkyl side chain in the structure above? What fragmentation processes yield the two primary fragments?
- b) Tandem mass analysis (FAB-MS/MS) was performed on the $m/z = 296$ peak, to give the spectrum shown below.



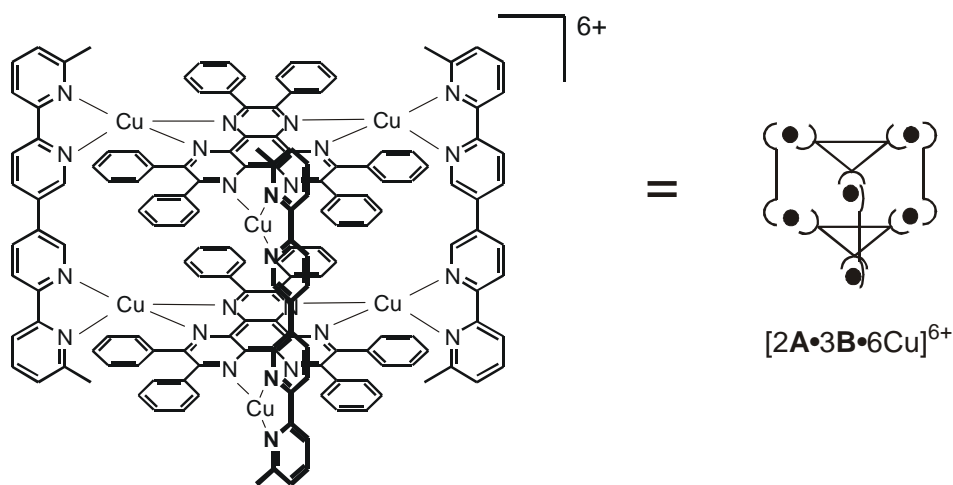
Even-electron cations (like the $m/z = 296$ species) can lose neutral alkane fragments by ion-assisted elimination. (Unusual, but it happens.) The way that I have drawn the structure of **1**, the alkyl side chain could be linear or branched. What is the precise structure of **1**?



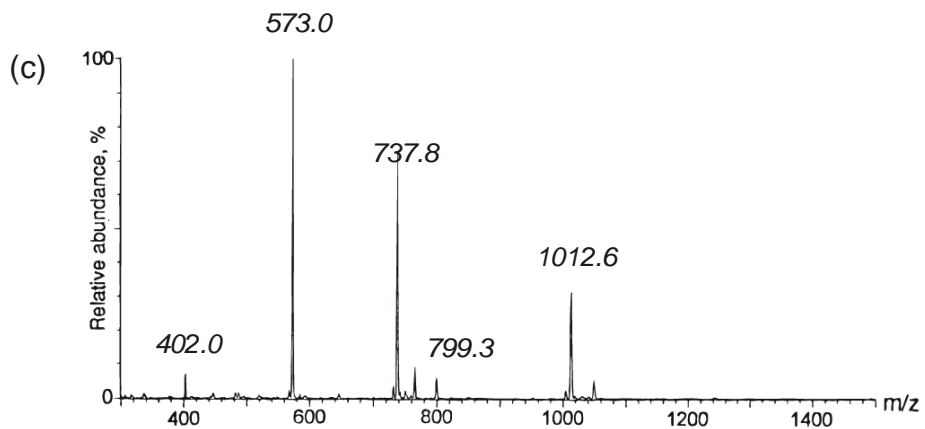
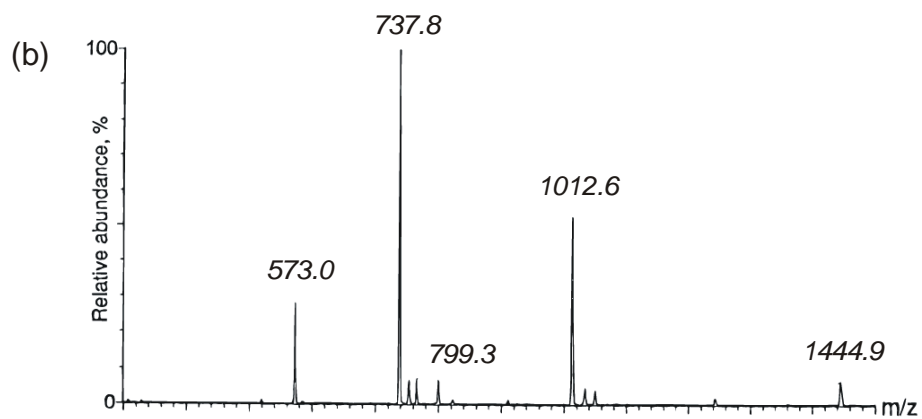
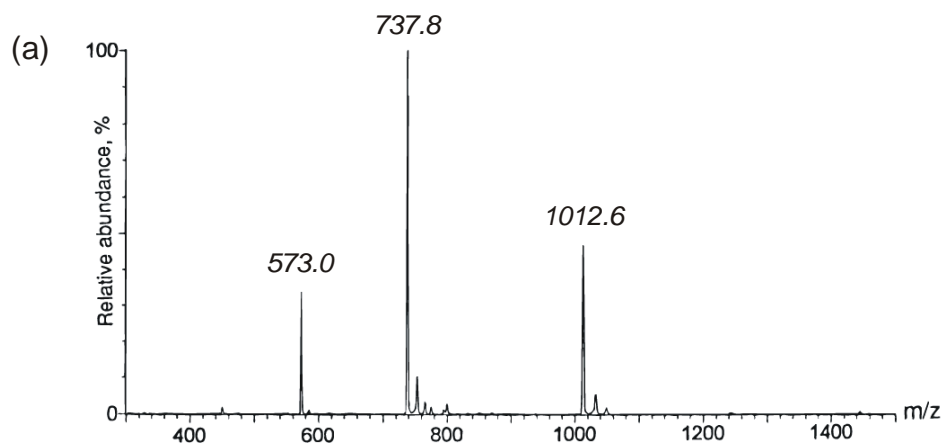
2. Ligands **A** and **B** both contain bipyridinyl (bipy) binding sites for metal ions. (These binding sites are represented as half-circles in the cartoon representations of the ligands below their structures.) Cu^+ ions, for example, will accept two bipyridinyl ligands in a tetrahedral arrangement, as shown below.



Jean-Marie Lehn and coworkers proposed that, when ligands **A** and **B** were mixed with CuBF_4 in a 2:3:6 ratio, the complex $[2\mathbf{A}\cdot 3\mathbf{B}\cdot 6(\text{Cu}^+)\cdot 6(\text{BF}_4^-)]$ was formed. (Ref.: Marquis-Rigault et al. *Inorg. Chem.* **1996**, 35, 2307.)



To study the process of this reaction, the Lehn group submitted the mixture to electrospray mass spectrometry with very low nozzle voltages, to avoid breaking up the formed complexes. The ESI-MS spectra shown below are for (a) stoichiometric amounts of the three components **A**, **B** and CuBF_4 ; (b) excess **A**; and (c) excess **B**.



All spectra were recorded in positive-ion mode. Although BF_4^- is ordinarily a non-complexing counterion, the cations observed did have multiple BF_4^- ions associated with them.

Other helpful data for this problem:

<i>element</i>	<i>atomic mass</i>	<i>common isotopes</i>
Cu	63.5	63 (69%), 65 (31%)
B	10.8	10 (20%), 11 (80%)
F	19.0	19

- All of the peaks in spectrum (a) correspond to the predicted hexakis(copper) complex. What are the charge states of these ions? How many BF_4^- counterions are associated with each?
- The peak at $m/z = 799.3$ in both spectra (b) and (c) is due to accidental fragmentation of the ion with $m/z = 573.0$. What was lost?
- The peaks at $m/z = 1444.9$ in spectrum (b) and $m/z = 402.0$ in spectrum (c) are unrelated to the predicted complex, and correspond to other complexes produced due to the excess reagents present. What structures do these ions have?