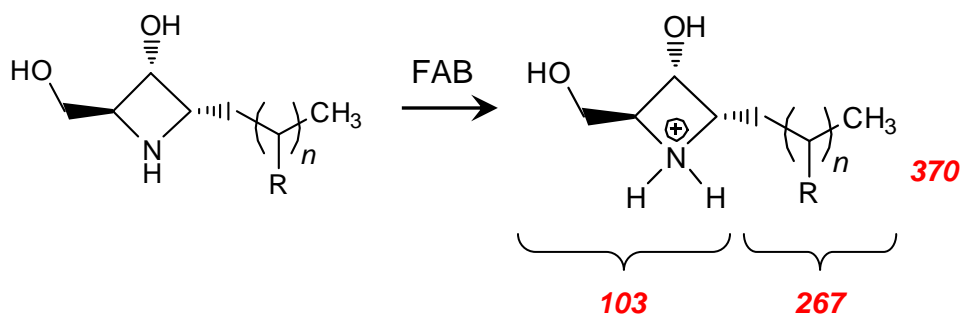## Workshop 6 Solutions
MS Analysis with Even-Electron Ions

1. a. FAB-MS is a (relatively) soft ionization technique that generates even-electron ions—no radical cations, just protonated cations.


A mass of 267 means the alkyl portion of the molecule has molecular formula -$C_{19}H_{39}$. The only way that we could get a m/z = 60 cation fragment from this molecule is either if the right-hand alkyl fragment broke into ionic pieces—highly unlikely—or if the left-hand four-membered ring broke into pieces. So let's break the ring into pieces.
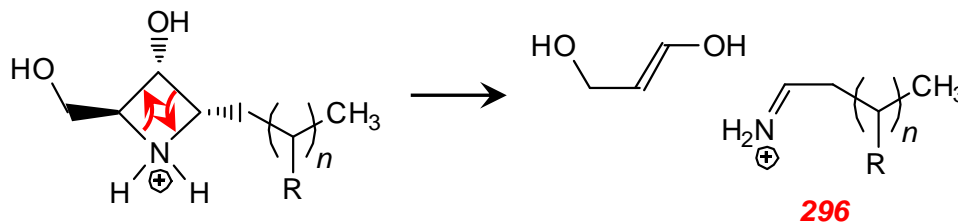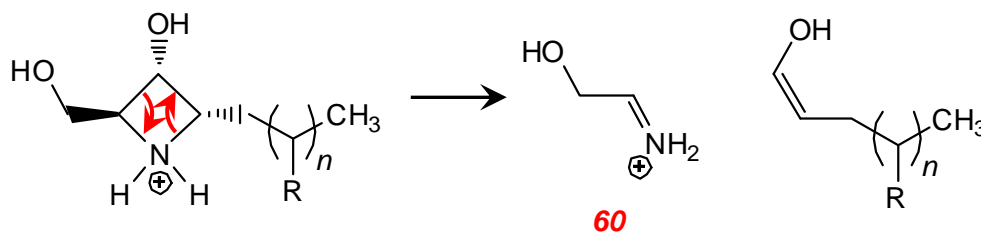

(I've drawn these fragmentations as concerted retro-[2+2] cycloreversions, but the Woodward-Hoffmann rules for these kinds of reactions says that kind of reaction is thermally forbidden; it probably happens stepwise, with the C-N bond breaking first.)

b) The mechanism drawn in the question would be a way of getting rid of alkane pieces from the $m/z = 296$ cation. For example, to eliminate a methane molecule,

296   **280**
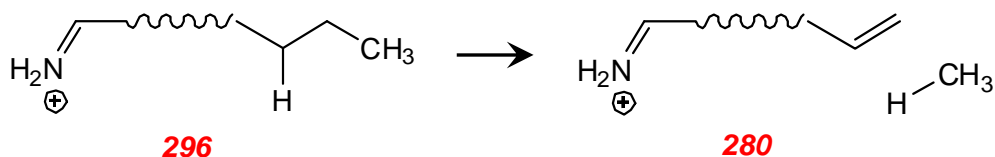
The CID-MS shows that the 296 fragment can lose methane, ethane, propane, butane, pentane, and hexane, but not heptane. Why not heptane? It must be because the positioning of the R group won't let a C_7 alkane be ejected:
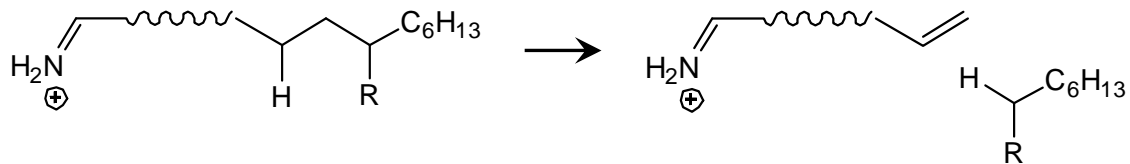
If R were equal to H, the neutral fragment on the right would be heptane. So R must not be H; it must be whatever is needed for the next highest mass. That's octane, so R must be a methyl group. That means the structure of penazetidine is
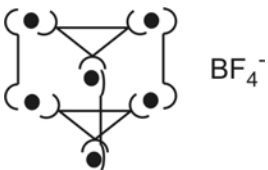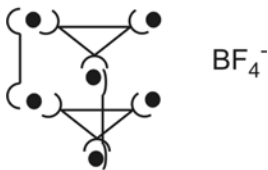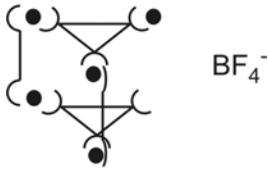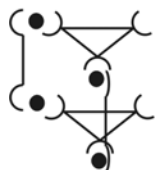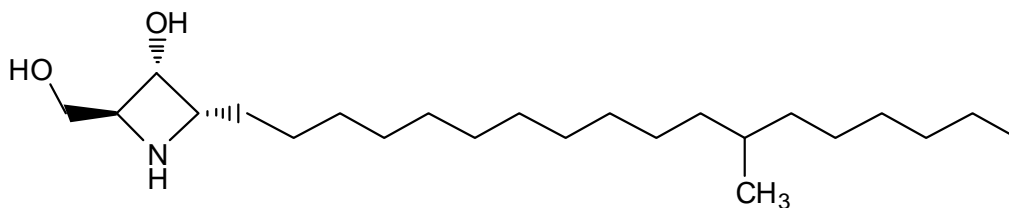
2. a. We can think of the target complex, $[2\mathbf{A}\cdot3\mathbf{B}\cdot6(Cu^+)]^{6+}\cdot6(BF_4^-)$, as having one big hexacation and six individual counteranions. The hexacation has mass $2(690) + 3(338) + 6(63.5) = 2775$, and $m/z = 462.5$. This is clearly not represented in our mass spectra. However, if we imagine that BF_4^- anions (with mass 87 each) are associated with the hexacation,

formula	total mass	z	m/z
$[2\mathbf{A}\cdot3\mathbf{B}\cdot6(Cu^+)](BF_4^-)$	2862	5+	572.4
$[2\mathbf{A}\cdot3\mathbf{B}\cdot6(Cu^+)]\bullet2(BF_4^-)$	2949	4+	737.3
$[2\mathbf{A}\cdot3\mathbf{B}\cdot6(Cu^+)]\bullet3(BF_4^-)$	3036	3+	1012.0
$[2\mathbf{A}\cdot3\mathbf{B}\cdot6(Cu^+)]\bullet4(BF_4^-)$	3123	2+	1561.5
$[2\mathbf{A}\cdot3\mathbf{B}\cdot6(Cu^+)]\bullet5(BF_4^-)$	3210	1+	3210

The first three ions in this list are present in spectrum (a).

b. For the ion at $m/z = 573.0$ to fragment to 799.3 (an *increase* in m/z), the parent ion needs to not only lose mass, but also lose positive charge. The only way this could happen is if the complex lost at least one copper ion.

cartoon	total mass	z	m/z
BF_4^- $[2\mathbf{A}\cdot3\mathbf{B}\cdot6Cu]^{6+}$	2862	5+	572.4
BF_4^- $[2\mathbf{A}\cdot2\mathbf{B}\cdot6Cu]^{6+}$	2524	5+	504.8
BF_4^- $[2\mathbf{A}\cdot2\mathbf{B}\cdot5Cu]^{5+}$	2460	4+	615

cartoon	total mass	z	m/z

BF_4^-

| | 2397 | 3+ | **799** |

$[2A \cdot 2B \cdot 4Cu]^{4+}$

And there it is, our $m/z = 799$ fragment.

c. Spectrum (b) contains too much **A**. To figure this out, I just started combining **A** and Cu ions to see what I could make, trying to make sure that Cu is coordinatively saturated (has two bidentate ligands) and that the ligand arrangement is tetrahedral:

cartoon	total mass	z	m/z

| | 1445 | 1+ | **1445** |

$[2A \cdot Cu]^+$

That's it actually. Then I started doing the same thing with **B** and Cu ions:

cartoon	total mass	z	m/z

| | 740 | 1+ | 740 |

$[2B \cdot Cu]^+$

| | 1141 | 2+ | 571 |

$[3B \cdot 2Cu]^{2+}$

| | 1606 | 4+ | **401.5** |

$[4B \cdot 4Cu]^{4+}$

This last cation could be it, although I think it's important to note that any cation with a 1:1 ratio of Cu^+ ions and ligands **B** would give the same m/z. However, a 1:1 complex of Cu:**B** wouldn't be coordinatively unsaturated, and I'm not sure that a 2:2 or 3:3 complex could be formed, given the geometric constraints of the ligand and complexes.