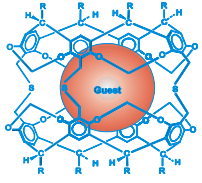
Characterization of Carceplexes Using APCI, ESI and MALDI Mass Spectrometry

Cindy Chiao-Yuan Lee, Pamela Miller, Lufiani Madilao, Marshall Lapawa, Yun Ling

Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC V6T 1Z1, Canada

Objectives

- Carceplexes are carcerands that contain permanently entrapped guest molecules or ions within their confines.
- Investigate comparatively APCI, ESI and MALDI mass spectrometry for the characterization of host-guest complexes, carceplexes, (M+G) in which M is an enforced closed-shell molecule (carcerand).



Compounds Tested in This Study

Molecular Formula	MW[a]	Guest(G)	Guest Mass[b]
$C_{120}H_{152}O_{16}S_4@C_5H_6O$	2036.9	Acetone	58
$C_{120}H_{152}O_{16}S_4@C_4H_7N$	2047.8	Butyronitrile	69
$C_{120}H_{152}O_{16}S_4@C_3H_5NO$	2049.9	Methoxy Acetonitrile	71
$C_{120}H_{152}O_{16}S_4@CH_2Cl_2$	2063.7	Dichloromethane	84
$C_{120}H_{152}O_{16}S_4@C_4H_8O_2$	2066.9	1,4-Dioxane	88

a. Average mass, b. Norminal mass

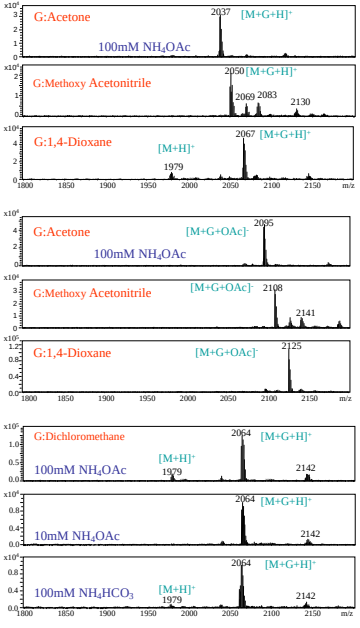
Methods

- The APCI and ESI-MS experiments were carried out on Bruker Esquire~LC and Micromass LCT. The MALDI-MS was performed on Bruker Biflex IV.
- Stock solutions of the carceplex samples were normally prepared in $CHCl_3$. The working solutions were made by the dilution of stock solutions with different solvents or buffers.
- For ESI-MS or APCI-MS, tested solvents and buffers include $CHCl_3$, CH_3OH, NH_4OAc, NaOAc, KOAc, NH_4HCO_3 and triethylammonium bicarbonate (TEAB).
- MS/MS spectra of the carceplexes were measured on Bruker Esquire~LC.
- Several different matrices including dithranol and 2-amino-5-nitropyridine (ANP) as well as different cationization reagents were tested for MALDI-MS.

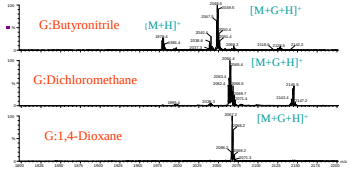
Results and Discussion

ESI-MS

- For ESI-MS of carceplexs, solution conditions were found to be critical. It was found that 100 mM NH_4OAc solutions gave good results for most of carceplexes.
- ✓In positive mode, protonated carceplex, $(M+G+H)^+$, was appeared as the dominant peak.
- ✓In negative mode, the base peak was the acetate adduct, $(M+G+OAc)^-$, which is generally stronger than $(M+G+H)^+$ in the positive mode .

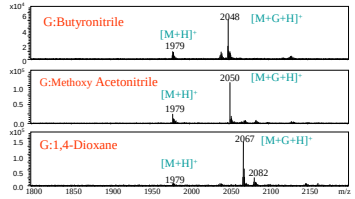


- Stronger $(M+G+H)^+$ peak was observed with NH_4OAc solutions than with NH_4HCO_3. No $(M+G+Cat)^+$ peaks were observed with KOAc and NaOAc as well as TEAB.
- Similar results were observed on LCT.



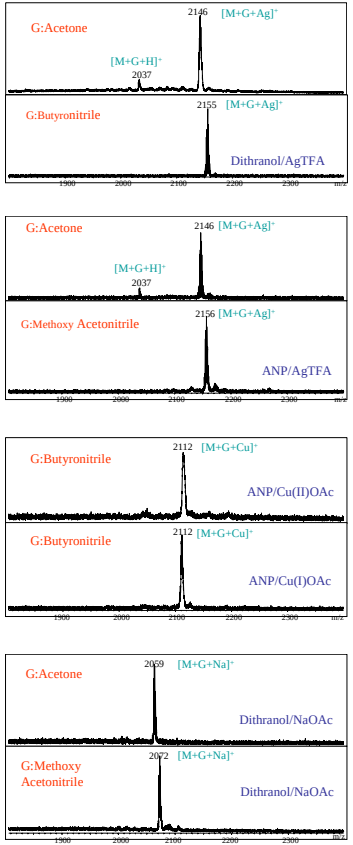
APCI-MS

- For APCI-MS of carceplexes, the protonated ion of carceplexs, $(M+G+H)^+$, was shown as the dominant peak.



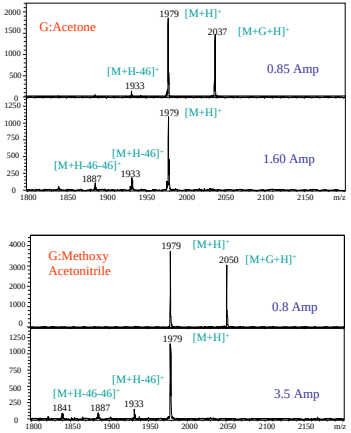
MALDI-MS

- The best matrices were 2-amino-5-nitropyridine (ANP), dithranol as well as DHB.
- The best cationazation reagents were AgTFA and NaOAc.
- Argetinated carceplexes, $(M+G+Ag)^+$, were observed as the dominate peaks with AgTFA as cationization reagent. No negative ions related to carceplexes were observed.
- Cuparated carceplexes, $(M+G+Cu)^+$, were observed as the dominate peaks with Cu(I)Oac and Cu(II)OAc as cationization reagents.
- Sodiated carceplexes, $(M+G+Na)^+$, were observed as the dominate peaks with NaOAc as cationization reagent.
- Only week peaks for protonated carceplexes, $(M+G+H)^+$, were observed with 100 mM NH_4OAC as cationization reagent.



Structure Information from MS/MS

- MS/MS spectra of $(M+G+H)^+$ gave mainly $(M+H)^+$ for most of carceplexes and no fragmentation was observed for the MS/MS of $(M+G+OAc)^-$.
- Fragmentation of $(M+H)^+$, the protonated carcerand, was also observed and loss of 46 was the major channel. Neutral loss of 46 is likely SCH_2 and suggests the breakage of the bridges.



Conclusions

- MS Conditions for characterization of carceplexes were proposed.
- All ESI, APCI, MALDI can be used to characterize carceplexes.

Acknowledgements

Prof. John Sherman, Ayub Jasat for providing the carceplex samples.