Mass Spectrometric Detection of Metal-Directed Self-Assembly of Conjugated Schiff-Base Macrocycles

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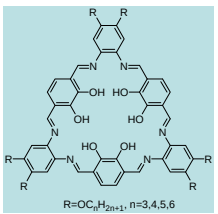
Objectives

➢Probe the formation and stability of supramolecular structures from metal-directed self-assembly of novel conjugated Schiff-base macrocycles in the gas phase using ESI-MS and ESI-MS/MS.



Scheme 1: Structure of conjugated Schiff-base macrocycles

Methods

➢ESI-MS experiments were carried out on Bruker Esquire Ion Trap and Micromass LCT TOF.

➢Stock solutions of the synthesized macrocycle samples were prepared in CH_2Cl_2 or $CHCl_3$. The working solutions were made by dilution of stock solutions with methanol and mixed with different alkali, alkaline earth or transition metal salt solutions.

➢MS/MS spectra of the metallated supramolecular complexes of macrocycles were measured on Bruker Esquire. In-source CID on Micromass LCT was used to build breakdown graphs (BDG).

Results and Discussion

Alkali and alkaline earth metal ions

➢ESI-MS of the macrocycles mixed with alkali metal ions indicate the formation of various supramolecular complexes, $(mMC+nCat)^{n+}$ (m=2, 3, 4, 5, ; n=1, 2, 3, 4) (Figs. 1 & 3).

➢Higher charged adducts such as 5:4 and 4:3 macrocycle:metal complexes were observed at low cone voltages. With increasing cone voltage, 3:2 macrocycle:metal complexes were formed. The dominant adducts are 2:1 and 1:1 macrocycle:metal complexes at higher cone voltages (Fig. 2).

➢Similar patterns were also observed for alkaline earth metals (data not shown here).

➢MS/MS of multiply charged adducts show mainly charge separation reactions. No neutral loss was observed (Fig. 4).

➢Small alkali cations are coordinated to the central phenolic oxygen atoms of macrocycles, forming sandwich type supramolecular complexes (Fig. 5).

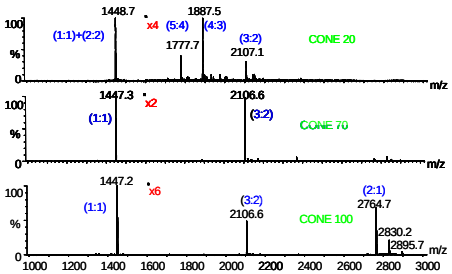


Fig. 1: ESI-MS spectra of MC6 macrocycle with CsOAc at different cone voltages: formation of (m:n) macrocycle:metal complexes, $(mMC+nCs)^{n+}$

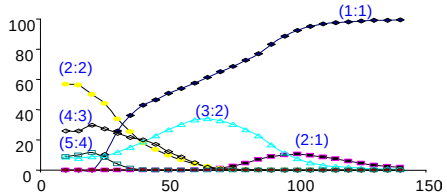


Fig. 2: Breakdown graphs (BDGs) for adducts of MC6 macrocycles with CsOAc, (m:n) macrocycle:metal complexes, $(mMC+nCs)^{n+}$.

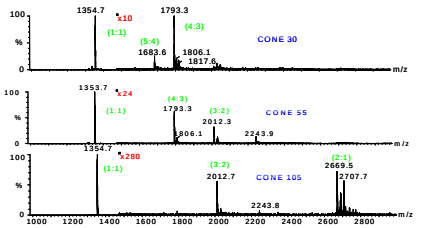


Fig. 3: ESI-MS spectra of MC6 macrocycle with KOAc at different cone voltages: formation of (m:n) macrocycle:metal complexes, $(mMC+nK)^{n+}$.

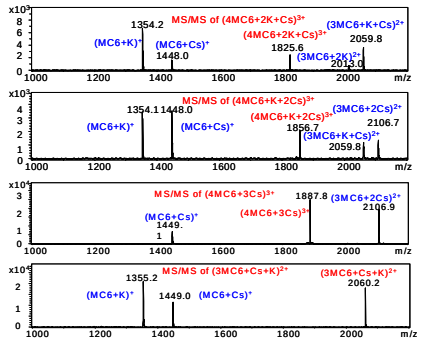


Fig. 4: MS/MS spectra of multiply charged adducts of MC6 macrocycle with CsOAc and KOAc.

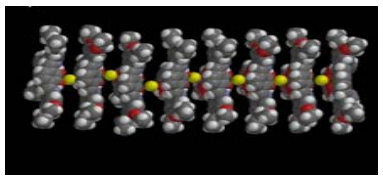


Fig. 5: Ion-induced tubular assembly of macrocycles

Transition metal ions

➢ESI-MS of macrocycle with Ag^+ shows the formation of singly and doubly charged adducts, $(mMC+nAg-zH)^{2+}$ (m=2, 3, 4; n= 2, 3, 4, 5) (data not shown here).

➢Only doubly charged adducts, $(mMC+nZn-zH)^{2+}$ (m=2, 3, 4; n=1, 2, 3, 4, 5, 6) were observed with Zn^{2+} (Fig. 6).

➢The binding of Zn^{2+} to the N_2O_2 pocket by displacement of protons competes with the coordination to the central phenolic oxygen pocket in the macrocycle.

➢The structures of $(3MC+nZn-zH)^{2+}$ and $(4MC+nZn-zH)^{2+}$ are proposed as supramolecular triangle and squares, respectively.

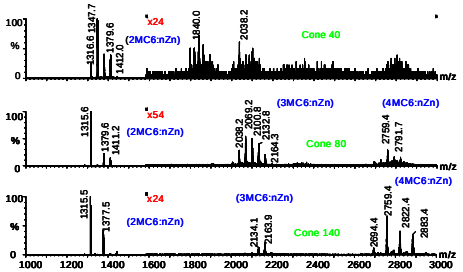


Fig. 6: ESI-MS spectra of MC6 macrocycle with $Zn(OAc)_2$ at different cone voltages: formation of (mMC:nZn) macrocycle: metal complexes, $(mMC+nZn-zH)^{2+}$.

Conclusions

➢Supramolecular complexes of tubular structure were formed with macrocycles and alkali metal ions. Alkali cations are coordinated to the central phenolic oxygen atoms in the macrocycles.

➢Transition metals such as Zn^{2+} bind differently to the macrocycles, forming different structures.

Acknowledgement

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