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.

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 CHCl₃ or CH₃CN. 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).

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 Zn²⁺ (Fig. 6).

The binding of Zn²⁺ to the N₃O₂ pocket by displacement of protons competes with the coordination to the central phenolic oxygen pocket in the macrocycle.

The structures of (3MC₆+nZn-zH)²⁺ and (4MC₆+nZn-zH)²⁺ are proposed as supramolecular triangle and squares, respectively.

Fig. 1: ESI-MS spectra of MC₆ macrocycle with CsOAc at different cone voltages: formation of (m:n) macrocycle:metal complexes, (mMC₆+nCat)n⁺ (m=2, 3, 4, 5; n=1, 2, 3, 4) (Figs. 1 & 3).

Fig. 2: Breakdown graphs (BDGs) for adducts of MC₆ macrocycles with CsOAc, (m:n) macrocycle:metal complexes, (mMC₆+nCat)n⁺.

Fig. 3: ESI-MS spectra of MC₆ macrocycle with KOAc at different cone voltages: formation of (m:n) macrocycle:metal complexes, (mMC₆+nK)⁺ (m=2, 3, 4; n=1, 2, 3, 4) (data not shown here).

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

Fig. 5: Ion-induced tubular assembly of macrocycles

Fig. 6: ESI-MS spectra of MC₆ macrocycle with ZnOAc₂ at different cone voltages: formation of (mMC₆+Zn) macrocycle:metal complexes, (mMC₆+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⁺ bind differently to the macrocycles, forming different structures.

Acknowledgement

Amanda Gallant, Carmen Yeung, Marshall Lapawa