Gas-Phase Structures of Crown Ether Complexes with Divalent Metal Cations Studied by Cryogenic Ion Mobility–Mass Spectrometry

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Crown ethers are crucial in host-guest chemistry due to their remarkable ability to encapsulate guest ions efficiently and selectively. Previously, we studied the conformations of dibenzo-24-crown-8 (DB24C8) complexes with alkali metal ions using cryogenic ion mobility–mass spectrometry (IM-MS) and confirmed the coexistence of open and closed conformers with long and short distances between the two benzene rings.[1] In this study, we analyzed the conformations of DB24C8 complexes with alkaline earth metal ions (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) and transition metal ions (Fe^{2+}, Ni^{2+}, Zn^{2+}), focusing on how ionic radii and charges of the guest ions affect the conformations of the complexes.

For alkaline earth metal ion complexes, both closed and open conformers were observed at 86 K. Relative abundances of the conformers depended on the ionic radii of the guest ions, resembling the behavior observed with alkali metal ions. Among these, Ba^{2+}(DB24C8) exhibited a structure highly similar to K^{+}(DB24C8) because K^{+} and Ba^{2+} have close ionic radii (1.35 Å and 1.38 Å) (Fig. 1). In the closed conformers of these complexes, the distances between the centers of the two benzene rings were close (3.88 Å and 3.72 Å). These structural similarities suggest that the ionic radius of the guest ion predominantly governs the conformation of the DB24C8 complexes. In contrast, transition metal ion complexes exhibited diverse conformations, even among metals with similar ionic radii. The closed conformer was predominant in the Fe^{2+} complex, the open conformer was predominant in the Ni^{2+} complex, and both closed and open conformers were observed in the Zn^{2+} complex. Quantum chemical calculations suggested that the ions had different coordination numbers, which was responsible for the observed conformational differences.

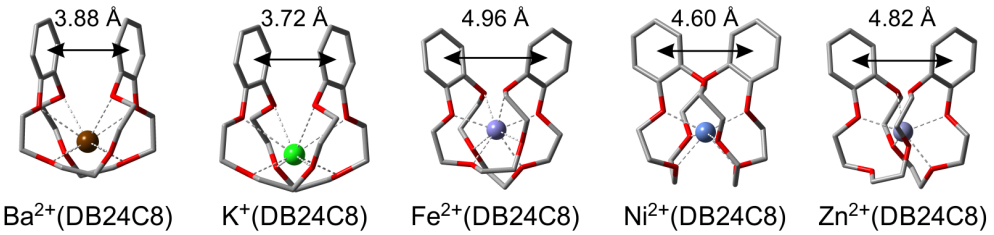

Fig. 1. The most stable closed conformers of DB24C8 complexes with Ba^{2+}, K^{+}, Fe^{2+}, Ni^{2+}, and Zn^{2+} obtained by B3LYP-D3(BJ)/def2-SVP level at 86 K. Hydrogen atoms are not shown for clarity.

1) K. Ohshimo, X. He, R. Ito, K. Tsunoda, S. Tainaka, F. Misaizu, *EPJ Techn. Instrum.* **2023**, *10*, 11.