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Conformational effect on the preferential binding of alkali metal cation with crown ether: A molecular level investigation

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ABSTRACT

We report density functional theory (DFT) based study to predict various conformation of free 12-crown-4 ether and its complexes with alkali metal cations. The optimized geometries, binding energies, and binding enthalpies of crown ether–cation complexes have been determined with a correlated hybrid density functional, namely Becke's three-parameter functional, B3LYP using split valence basis function, 6-311++G(d, p). Geometry optimizations for all the conformers of free 12-crown-4 ether and its metal cation complexes are carried out with several initial guess structures based on semi-empirical PM3 optimized results. The optimized structure for free 12-crown-4 ether and its metal cation complexes obtained from the present DFT calculation confirmed the experimentally reported structures. The calculated values of the gas phase binding energy for lithium ion is always found to be higher than that of the sodium ion for all the conformers of macrocyclic 12-crown-4 ethers reported in the present study. Expected preferential binding of Li^+ ion over Na^+ ion in case of a particular conformer of 12-crown-4 ligand is reversed due to micro-solvation effects reflecting its significant influence towards metal ion selectivity. The density functional theoretical calculated values of binding enthalpy are in fair agreement with the available reported experimental values.

Keywords: Crown ether; Alkali metal ion; Conformation; Extraction; Density functional theory; Molecular modeling

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