**Abstract**

The interaction of monovalent metal ions with cyclo[(1R,3S)-γ-Acc-Gly]3 hexapeptide ((TAG)3) is studied using density functional theory calculations. The (TAG)3 and its Li+, Na+ and K+ metal ionic complexes are optimized at B3LYP/6-311+G∗ level of theory. The optimized structure of (TAG)3 ionic complexes agrees well with the various cyclic peptide cationic complexes that are obtained experimentally. The valence, peptide deformation and Ramachandran angles clearly explain the structural effects in (TAG)3 upon ionic interaction. The dependability of cavity size towards the size of ions is noted. The molecular electrostatic potential (MEP) map effectively illustrates the weak interaction between metal ion and (TAG)3, and further confirms carbonyl oxygens to be the active sites. The binding energy of (TAG)3 towards metal ion increases as Li+ > Na+ > K+, which is consistent with the electron density at bond critical points. The significant binding energies and the symmetric nature of (TAG)3 upon Na+ and K+ enclosures in turn shows that its nanotubular structures might act as the ion channels of biological interest.