

Role of the cation formal charge in cation- π interaction. A survey involving the [2.2.2]paracyclophane host from relativistic DFT calculations

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The role of the metal formal charge in the cation- π interactions has been evaluated with relativistic DFT methods involving a versatile π -cryptating structure, namely [2.2.2]paracyclophane. Our study focuses on experimentally characterized $[(2.2.2)pCp]M^{n+}$ systems with $M = Ag^+$ and Sn^{2+} and their Cd^{2+} and In^+ counterparts, which exhibit $5s^05p^0$ and $5s^25p^0$ electron configurations. The acceptor capabilities increase when the metal charges go from 1^+ to 2^+ , resulting in a large stabilization of the interaction. For the studied $5s^05p^0$ cations Ag^+ and Cd^{2+} , the most stable conformation namely $[(2.2.2)pCp]M^{n+}$, the electrostatic contribution is more favorable by $-9.3 \text{ kcal mol}^{-1}$, whereas the πE_{Orb} contribution increases by $-151.6 \text{ kcal mol}^{-1}$ towards a more favourable situation in the 2^+ counterpart. Similarly in the $5s^25p^0$ cationic group, the isoelectronic Sn^{2+} and In^+ systems depict variation of the electrostatic and orbital terms, with a considerable decrease of the stabilizing πE_{Orb} contribution, and in a lesser amount the πE_{Elstat} term. Thus, the variation of the interaction energy between the M^+ and M^{2+} isoelectronic counterparts can be ascribed mainly to the variation of the πE_{Orb} term, leading to a more covalent character of the interaction retaining a similar bonding scheme. © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique.