

Helicenes as Molecular Tweezers in the Formation of Cation-π Complexes. Bonding and Circular Dichroism Properties from Relativistic DFT Calculations

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Helicene ligands possess a unique helicoidal π -conjugated framework providing high optical rotation values. This has stimulated a growing interest in helicene derivatives as building blocks, which has triggered the development of simple strategies to tune their properties. In this context, we evaluated the formation of cation- π complexes derived from [6]- and [7]helicene, involving Sn^{2+} , Cd^{2+} , and In^{+} in addition of Ag^{+} , which appears as a plausible modification of such helicoidal structure. The nature of the cation- π interaction in the studied helicene complexes exhibits a covalent character, accounting for ligand π -donation to 5 s and 5p empty orbitals of the involved cations. Furthermore, the evaluation of their optical activity exhibits notorious modification patterns in the circular dichroism spectrum, suggesting that the modifications of the optical activity are dependent on the nature of the cation and its related charge state. Thus, the plausible formation of new cation- π complexes derived from helicene ligands, as discussed here, may lead to the characterization of novel species expanding the chemistry of helicene metal complexes to even to larger helicene units. We believe that the present study may open new avenues in the formation of cation- π helicene complexes. ©

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cation- π complexes

chirality

circular dichroism

helicenes

silver