Anion Recognition by Organometallic Calixarenes: Analysis from Relativistic DFT Calculations

Ortolan A.O.

Øestrøm I.

Caramori G.F.

Parreira R.L.T.

Muñoz-Castro A.

Bickelhaupt F.M.

The physical nature of the noncovalent interactions involved in anion recognition was investigated in the context of metalated calix[4]arene hosts, employing Kohn-Sham molecular orbital (KS-MO) theory, in conjunction with a canonical energy decomposition analysis, at the dispersion-corrected DFT level of theory. Computed data evidence that the most stable host-guest bonding occurs in ruthenium complexed hosts, followed by technetium and molybdenum metalated macrocyclic receptors. Furthermore, the guest's steric fit in the host scaffold is a selective and crucial criterion to the anion recognition. Our analyses reveal that coordinated charged metals provide a larger electrostatic stabilization to anion recognition, shifting the calixarenes cavity toward an electron deficient acidic character. This study contributes to the design and development of new organometallic macrocyclic hosts with increased anion recognition specificity. Copyright © 2018 American Chemical Society.