Deciphering the Strength of Cation-π Interactions of Benzene Sandwich Compounds with the Help of AIM, XEDA and NOCV

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Cation-π interactions are significantly stronger with benzene sandwich compounds than with (uncoordinated) benzene [1]. In this work we analyzed and compared the nature of cation-π interactions of benzene and benzene sandwich compounds ($Cr(benzene)_2$, $Mo(benzene)_2$ and $W(benzene)_2$) with six cations (Be^{2+}, Mg^{2+}, Ca^{2+}, Li^+, Na^+, K^+) using three different methods: AIM, XEDA and NOCV. All cation-π complexes were optimized at the B3LYP-D3/def2TZVP level of theory, which was also used for interaction energy calculations.

Topological analysis using Atoms in Molecules (AIM) helped to explain that cation-π interactions involving the Be^{2+} cation have a covalent character ($\nabla^2\rho(r) > 0$, $H(r) < 0$ and the ratio $-G(r)/V(r) < 1$) for all systems, while the interactions with other cations are classical non-covalent interactions ($\nabla^2\rho(r) > 0$, $H(r) > 0$ and the ratio $-G(r)/V(r) > 1$). The Xiamen Energy Decomposition Analysis (XEDA) revealed that the electrostatic component is very important for the interaction, but the polarization component is the key component that is responsible for the remarkable strength of these interactions. The Natural Orbitals for Chemical Valence (NOCV) analysis determined that, in addition to π orbitals of aromatic ring, d orbitals of the metal in the sandwich compounds are also involved in the interaction with orbitals of the cation, providing additional stabilization for cation-π interactions of sandwich compounds.

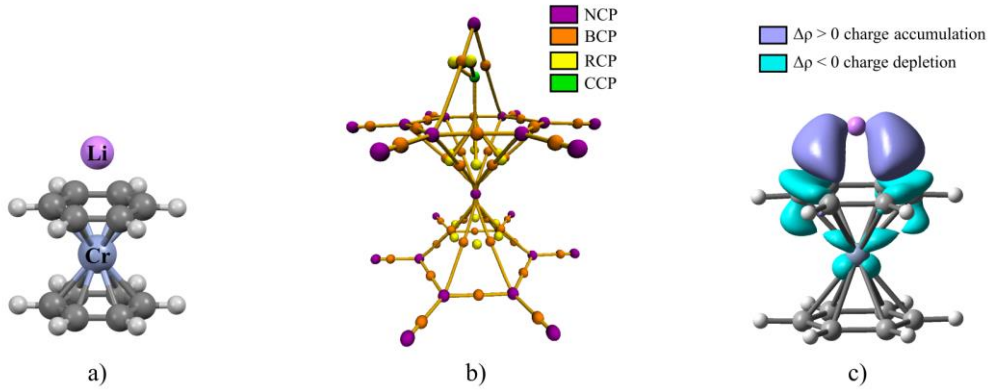

Figure 1. Cation-π interaction between Li^+ and $Cr(benzene)_2$: a) side-view, b) AIM critical points (Nuclear, Bond, Ring and Cage Critical Points) and c) NOCV pair depicting the strongest orbital interaction.

References:

[1] K. Ćeranić, S. Zarić, D. Malenov, *Dalton Trans.* **54** (2025) 7700-7706.