

## Stacking interactions of chelate rings of transition metal complexes

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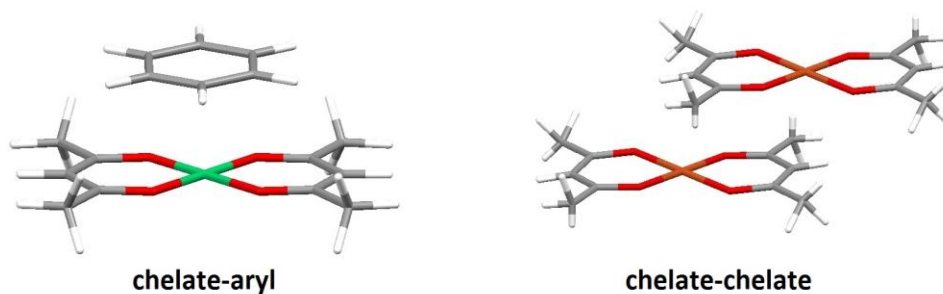
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Stacking interactions of aromatic fragments are ubiquitous in many chemical and biological systems [1]. Benzene dimer, as a prototype, has stacking energy of -2.73 kcal/mol, in the most stable parallel-displaced geometry [2]. However, stacking interactions can also be formed by non-aromatic fragments, most notably by metal-chelate rings [3].

Stacking interactions between chelate and aromatic rings were described in crystal structures deposited in the Cambridge Structural Database [3], and were shown to have parallel-displaced geometries (Fig. 1), similar to stacking of aromatic molecules. The study of crystal structures with stacking interactions between aromatic rings and systems that have chelate ring fused with aromatic ring showed that aromatic ring is dominantly closer to chelate than to aromatic ring of the fused system, indicating that chelate-aryl stacking is stronger than aryl-aryl stacking [3]. Calculated CCSD(T)/CBS and DFT interaction energies confirmed this; stacking of benzene with nickel chelate of *acac* type has the energy of -5.52 kcal/mol, while stacking of benzene with zinc chelate of *acac* type is even stronger, -7.56 kcal/mol [4].

Stacking interactions can be formed between two chelate rings as well. This type of stacking was also described by studying the CSD crystal structures [3]. Geometries of chelate-chelate stacking interactions are mostly parallel-displaced, but there are examples of *face-to-face* geometries (Fig. 1). Chelate-chelate stacking is even stronger than aryl-aryl and chelate-aryl stacking. Stacking energy between two *acac* type chelates of nickel is -9.47 kcal/mol [4], while stacking between two dithiolene chelates of nickel is -10.34 kcal/mol [5].

Chelate-aryl and chelate-chelate stacking interactions are much stronger than aryl-aryl stacking due to much stronger electrostatic interactions caused by the presence of metals [4]. Stacking geometries and relative strengths of interactions can be rationalized by observing electrostatic potentials of the complexes that contain metal-chelate rings.



**Figure 1.** Stacking of  $[\text{Ni}(\text{acac})_2]$  complex with benzene (*chelate-aryl stacking*) and stacking of two  $[\text{Cu}(\text{acac})_2]$  complexes (*chelate-chelate stacking*).

[1] Salonen, L. M., Ellermann, M., Diederich, F. (2011). *Angew. Chem. Int. Ed.* **50**, 4808.

[2] Lee, E. C., Kim, D., Jurečka, P., Tarakeshwar, P., Hobza, P., Kim, K. S. (2007). *J. Phys. Chem. A* **111**, 3446.

[3] Malenov, D. P., Janjić, G. V., Medaković, V. B., Hall, M. B., Zarić, S. D. (2017). *Coord. Chem. Rev.* **345**, 318.

[4] Malenov, D. P., Zarić, S. D. (2019). *Dalton. Trans.* **48**, 6328.

[5] Malenov, D. P., Veljković, D. Ž., Hall, M. B., Brothers, E. N., Zarić, S. D. (2019). *Phys. Chem. Chem. Phys.* **21**, 1198.

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