Modeling ion-π interactions of transition metal complexes

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Abstract: Interactions of π-systems with ions are very important for many chemical and biological systems. In this work we show how transition metal coordination strengthens cation-π interactions, and how it makes anion-π interactions of some systems possible. The calculations showed that cation-π interactions between ferrocene and alkali metal ions are stronger than cation-π interactions of benzene. The strongest cation-π interaction is between ferrocene and Li^+, with interaction energy of -44.0 kcal/mol, while benzene-Li^+ interaction has the energy of -36.1 kcal/mol. Cation-π interactions can also involve transition metal complexes as cations, with $[Co(NH_3)_6]^{3+}$/benzene interaction being very strong (-31.4 kcal/mol), while $[Zn(H_2O)_6]^{2+}$/benzene interaction somewhat weaker (-14.0 kcal/mol). Anion-π interactions of unsubstituted aromatic rings without heteroatoms are possible if they are ligands in organometallic half-sandwich complexes with electron-withdrawing ligands. The anion-π interactions of such transition metal complexes with halides can reach the energy of -25.0 kcal/mol, and they are stronger than anion-π interactions of organic aromatic molecules.

Keywords: anion-π interactions, cation-π interactions, half-sandwich compounds, transition metal complexes, density functional theory

1. Introduction

Interactions of ions with π-systems are of great importance in many areas of science. Cation-π interactions have primarily found their importance in many biological systems [1], while anion-π interactions have found their application in many areas, most notably the design of receptors and materials chemistry [2].

Computational studies have shown that transition metal coordination can lead to strengthening of noncovalent interactions. Coordination of water to transition metals increases the strength of hydrogen bonds [3], while stacking interactions of metal-chelate rings are stronger than stacking interactions of organic aromatic rings [4]. Moreover, stacking interactions of aromatic ligands of sandwich and half-sandwich compounds are stronger than stacking interactions of uncoordinated aromatic rings [5].

In this proceeding, we present computational studies on cation-π and anion-π interactions involving transition metal complexes. We show that cation-π interactions

can be strengthened by transition metal coordination. Moreover, we show an interesting case of anion-π interactions that exist due to transition metal coordination and are comparable in strength with anion-π interactions of organic aromatic molecules.

2. Methodology

The energies of anion-π and cation-π interactions were calculated by keeping the monomer geometries rigid and by changing their mutual orientation to obtain the dimer geometries with the strongest interactions. The choice of methods and basis sets was based on the agreement of the applied level of theory with the gold standard CCSD(T)/CBS for the studied systems. The B97-D3/6-31++G** level was used for anion-π calculations, B3LYP/6-31++G**(C,H,M),DZVP(Fe) for cation-π interactions of ferrocene, while cation-π interactions of benzene with ammine and aqua metal complexes were calculated at B3LYP/631G*(C,H,N),LANL2DZ(Co) and MP2/def2-QZVP levels, respectively.

3. Results and discussion

Benzene cannot form anion-π interactions due to negative electrostatic potentials above its aromatic ring. Introducing heteroatoms and electron-withdrawing substituents produces areas of positive electrostatic potentials above the aromatic ring, which makes anion-π interactions possible [5]. Unsubstituted aromatic moieties without heteroatoms can also form anionπ interactions, provided that they are coordinated to transition metals in half-sandwich compounds with electron-withdrawing ligands. The electron withdrawal makes electrostatic potentials above aromatic ligands positive (Figure 1), and they are available for anion-π interactions (Figure 2) [6].

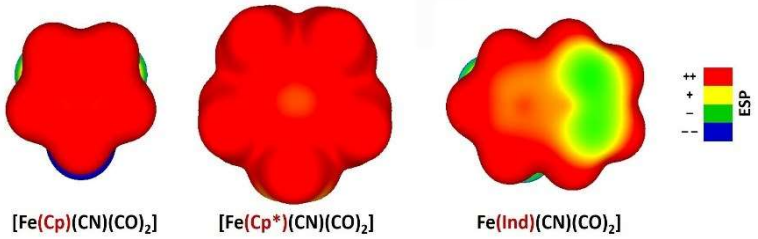

Figure 1. Electrostatic potentials of aromatic ligands in half-sandwich compounds of iron mapped on the isosurfaces defined by electron density 0.001 a.u.

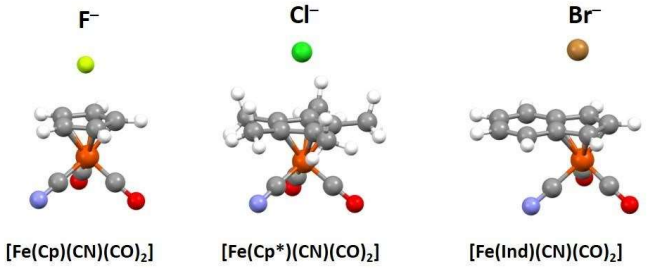

Figure 2. Anion-π interactions of halides and aromatic ligands in half-sandwich compounds.

The calculations show that anion-π interactions between iron half-sandwich compounds and halide anions (Figure 2) are stronger than anion-π interactions of organic aromatic molecules, such as hexafluorobenzene (Table 1) [6]. The anion-π interactions are particularly strong with Cp* ligand – the strongest calculated interaction is for fluoride-Cp* system, with the interaction energy of -25.0 kcal/mol (Table 1).

Table 1. Energies (in kcal/mol) of anion-π interactions of half-sandwich compounds. Interaction energies for hexafluorobenzene are given for comparison.

π-system	F^-	Cl^-	Br^-	Methodology
C_6F_6	-20.2	-14.8	-13.6	CCSD(T)/CBS
$Fe(Cp)(CN)(CO)_2$	-21.6	-17.0	-16.0	
$Fe(Cp^*)(CN)(CO)_2$	-25.0	-21.2	-20.5	B97-D3/6-31++G**
$Fe(Ind)(CN)(CO)_2$	-21.2	-15.6	-14.8	

Due to negative electrostatic potentials above its aromatic ring, benzene forms strong cation-π interactions with alkali metal ions. This interaction is the strongest with Li^+ (36.1 kcal/mol), and weaker, but still substantial with K^+ (20.0 kcal/mol) [7]. Transition metal coordination increases the strength of cation-π interactions, since cation-π interactions of Li^+ and Na^+ with ferrocene (Figure 3) are stronger than interactions with benzene, with particularly strong ferrocene-Li^+ interaction (-44.0 kcal/mol, Table 2) [7].

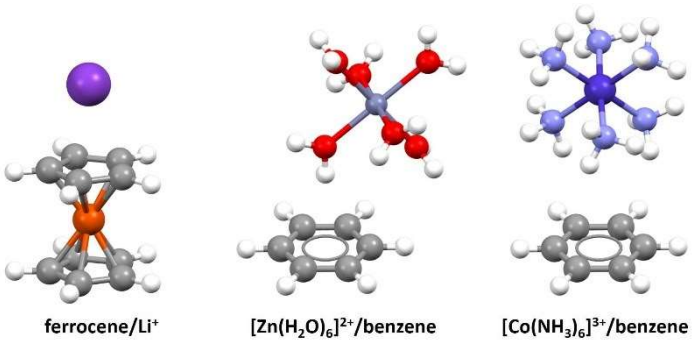

Figure 3. Cation-π interactions of some transition metal complexes.

Table 2. Energies (in kcal/mol) of cation-π interactions of selected transition metal complexes and corresponding systems that do not contain transition metal complexes.

cation	benzene	ferrocene	cation	benzene
Li^+	-36.1	-44.0	$[Zn(H_2O)_6]^{2+}$	-14.0
Na^+	-24.2	-30.0	$[Co(NH_3)_6]^{3+}$	-31.3
K^+	-20.0	-20.1		

The role of cation in cation-π interactions can be played by the transition metal complex as well. These interactions are called metal-ligand NH-π (MLNH-π) and metal-ligand OH-π interactions (MLOH-π) if N-H or O-H bond is directed toward the π-system. The first calculations were performed on MLNH-π interactions between $[Co(NH_3)_6]^{3+}$ and benzene (Figure 3) and showed quite attractive interaction (-31.3 kcal/mol, Table 2) [8]. Also, substantially strong MLOH-π interaction was calculated between $[Zn(H_2O)_6]^{2+}$ and benzene (Figure 3), with an interaction energy of -14.0 kcal/mol (Table 2) [9].

4. Conclusions

In this proceeding, we showed how transition metal coordination can lead to the formation of strong cation-π interactions, whether the transition metal compound is a cation or contains a π-system. More interestingly, we showed that the anion-π interactions of unsubstituted aromatic species can exist if they are coordinated to transition metal in half-sandwich compounds with electron-withdrawing ligands. Both cation-π and anion-π interactions involving transition metal complexes can be stronger than corresponding ion-π interactions of organic aromatic species.

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