Dalton Transactions

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2025, **54**, 7700

Cation recognition by benzene sandwich compounds – a DFT perspective†

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Cation–π interactions between alkali, alkaline earth and ammonium cations and sandwich compounds of benzene and the cyclopentadienyl (Cp) anion were studied using quantum chemical CCSD(T)/CBS and DFT (B3LYP/def2-TZVP) calculations. The results show significantly stronger interactions of sandwich compounds with respect to (uncoordinated) benzene. Moreover, very strong cation–π interactions of Cp sandwich compounds are furthermore surpassed by cation–π interactions of benzene sandwich compounds, which are capable of reaching a remarkable interaction energy value of –196.8 kcal mol^{-1} (Mg^{2+}/W(benzene)$_2$). While there are only small variations of interaction energy values for sandwich compounds of different transition metals (3d metals < 4d < 5d), cation–π interactions progressively become stronger in the following order: (uncoordinated) benzene < Cp sandwich < benzene sandwich. Aside from interaction energies, the cation–π interactions can be assessed by means of their influence on the geometries of sandwich compounds, which are found to strongly correlate with the strength of cation–π interactions. These results emphasize sandwich compounds, particularly those containing C_6 aromatic rings, as promising candidates for new receptors for common metal cations.

Received 18th February 2025,
Accepted 2nd April 2025

DOI: 10.1039/d5dt00395d

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1 Introduction

Cation–π interactions are noncovalent interactions between cations and electron clouds of π-systems.[1–4] The first report on cation–π interaction was by Kebarle *et al.* for that between the K^+ cation and benzene. The study showed that the potassium cation has a slight preference for bonding with benzene over water.[4,5] Cation–π interactions can be found in chemical systems, biological systems and in materials science.[4,6–10] Interactions involving aromatic rings are key to processes in both chemical and biological recognition and in catalysis.[2,3,11–14] These interactions, depending on the nature of the cation and the π systems, can be among the strongest noncovalent interactions.[1–4] Cation–π interactions are dominated by electrostatic and ion-induced polarization terms.[11,15–17] SAPT (symmetry adapted perturbation theory) analysis showed that the largest contribution to the interaction energy is induction.[18] There have been a number of theoretical and experimental studies done to determine the strength of cation–π interactions.[12–14,19–21] The binding energy of Li^+ to benzene is −38 kcal mol^{-1} while that of NH_4^+ to benzene is −19 kcal mol^{-1}.[12–14] The trend of weakening binding energies in the gas phase with increasing size of cation ($Li^+ > Na^+ > K^+ > Rb^+$) has been observed. When the ion is larger the charge is dispersed over a larger sphere and binding interactions weaken, since the electrostatic component of the interaction is important.[14,17] While most of the studies on cation–π interactions have dealt with alkali metal cations, a few studies have shown that alkaline earth cations form even stronger cation–π interactions.[1,22] The cation–π interaction between Ca^{2+} and benzene has an energy value of −70 kcal mol^{-1}, while the Mg^{2+}/benzene interaction is calculated to be −120 kcal mol^{-1}.[1] Vijay and Sastry have investigated cooperativity of cation–π and π–π interactions between Li^+, Na^+, K^+, NH_4^+, PH_4^+, OH_3^+ and SH_3^+ and benzene in sandwich, parallel-displaced and T-shaped configurations. They have concluded that cation–π interactions are enhanced to a small extent in the presence of π–π interactions,[23] which is particularly important for biologically relevant systems.

Metal complexes and organometallic compounds can also form cation–π interactions. In these interactions, a metal complex can be the cation, where the ligands of the complex interact with aromatic or other π-systems (metal ligand aromatic cation–π (MLAC–π) interactions).[24–28] These interactions were first studied by using quantum chemical calculations[29,30] and later recognized in crystal structures.[31–33] The MLAC–π interactions have also been recognized and described in numerous proteins.[34] In our recent paper, the interactions of coordinated ammonia in metal ammine complexes with C_6-

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†Electronic supplementary information (ESI) available: Interaction energies and geometrical parameters of cation–π interactions, Cartesian coordinates of optimized structures. See DOI: https://doi.org/10.1039/d5dt00395d

aromatic rings were recognized in crystal structures and by quantum chemical calculations.[35] The strongest NH–π interaction with energy of −34.16 kcal mol^{-1} was obtained for the interactions of the $[Co(NH_3)_6]^{3+}$ complex with benzene, where three ammine ligands were involved in the interaction.[35]

Organometallic sandwich compounds can also form cation–π interactions *via* their aromatic ligands. Ferrocene has been recognized as an organometallic system capable of forming interactions with alkali metal cations *via* its cyclopentadienyl rings.[36–39] These interactions have found application in assembling organometallic polymers,[40] and have recently been shown to play important roles in electrochemical processes, most notably the ones relevant to lithium-ion batteries.[41–44] According to calculated binding enthalpies, Li^+ forms a stronger cation–π interaction with ferrocene (−44.0 kcal mol^{-1}) than with benzene (−36.1 kcal mol^{-1}).[36] Another example of a sandwich compound forming cation–π interactions was (benzene)(hexafluorobenzene)chromium reported by Frontera *et al.*, who calculated somewhat weaker cation–π interactions of −31.7 kcal mol^{-1} with Li^+ and −10.5 kcal mol^{-1} with K^+.[11]

Organometallic half-sandwich compounds containing benzene or Cp-type ligands with additional electron-withdrawing ligands were recently shown to be capable of forming anion–π interactions.[45] In this way, transition metal coordination can be used as a way to make aromatic rings without electron-withdrawing substituents or heteroatoms suitable for anion–π interactions. The strongest anion–π interaction that has been calculated is that between fluoride and the Cp ligand in $[FeCp^*(CN)(CO)_2]$, with an interaction energy of −25.0 kcal mol^{-1}, making these types of interactions stronger than anion–π interactions of almost all organic molecules.[45]

In the present study we re-examined ferrocene as an organometallic system suitable for recognition of alkali metal cations *via* cation–π interactions, and extended our study to its analogues – ruthenocene and osmocene. In addition, we propose benzene sandwich compounds – bis(benzene)chromium and its molybdenum and tungsten analogues – as more efficient systems for cation recognition, particularly for alkaline earth metal cations, which form remarkably strong cation–π interactions.

2 Methodology

The effect of transition metal coordination onto cation–π interactions of aromatic rings was analyzed by performing calculations on sandwich compounds. We studied interactions of six cations, Mg^{2+}, Ca^{2+}, Li^+, Na^+, K^+ and NH_4^+, with sandwich compounds of benzene and cyclopentadienyl (Cp) coordinated to different metals. For benzene sandwich compounds we studied bis(benzene)chromium, bis(benzene)molybdenum and bis(benzene)tungsten, while for Cp sandwich compounds we studied ferrocene, ruthenocene and osmocene. In this way we were able to analyze the influence of 3d, 4d, and 5d metals in sandwich compounds on cation–π interactions. The singlet state of all sandwich compounds was considered in all calculations. Influence of cation–π interactions on the geometries of sandwich compounds was evaluated by observing several geometrical parameters (Fig. 1).

DFT calculations were done by employing the Gaussian09 (v. D.01) software.[46] The B3LYP method[47–50] with the def2-TZVP basis set[51] was chosen for optimization of the cation–π complexes, with def2-TZVP effective core potentials used for heavier 4d and 5d metals (Mo, W, Ru, Os), and with an ultrafine integration grid. This level of theory gives interaction energy values in good agreement with those at the CCSD(T)/CBS level (Table 1). All optimized structures were verified as true minima by performing the calculations of vibrational frequencies (no imaginary frequencies found). Interaction energies at the CCSD(T)/CBS level,[52] considered to be the gold standard in quantum chemistry,[53] were calculated using the two-point extrapolation method of Helgaker.[54] Interaction and binding energies calculated at B3LYP/def2-TZVP level were corrected for basis set superposition error using the counterpoise method of Boys and Bernardi.[55]

We calculated values of the interaction energy, E_{int}, between cations and sandwich compounds using the equation:

$$E_{int} = E^{opt}_{sandwich–cation} - (E^{frozen}_{sandwich} + E^{frozen}_{cation}) + E_{BSSE}$$

as well as values of binding energy, E_{bind}, using the equation:

$$E_{bind} = E^{opt}_{sandwich–cation} - (E^{opt}_{sandwich} + E^{opt}_{cation}) + E_{BSSE}$$

$E^{opt}_{sandwich–cation}$ represents the energy of the optimized sandwich–cation complex; $E^{frozen}_{sandwich}$ and E^{frozen}_{cation} represent the energy of the sandwich compound and cation as they are within the geometries of sandwich–cation complexes, respectively; $E^{opt}_{sandwich}$ and E^{opt}_{cation} represent the energy of the optimized structures of the isolated sandwich compounds and cations,

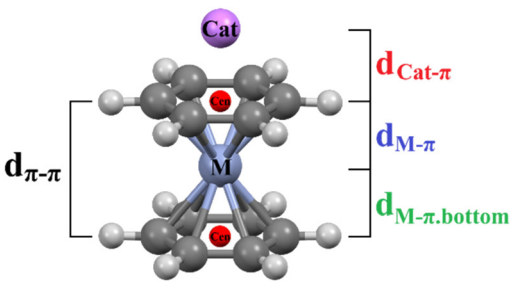

Fig. 1 Geometrical parameters used to describe cation–π interactions between sandwich compounds and various cations (Cat). M is the metal atom in a sandwich compound, which can be Fe, Ru, or Os for Cp sandwich compounds, or Cr, Mo, or W for benzene sandwich compounds. The label Cen denotes the centroid of the aromatic ring (benzene or Cp) forming the cation–π interaction. Cat is the cation and it can be Mg^{2+}, Ca^{2+}, Li^+, Na^+, K^+, or NH_4^+ ion, while $d_{Cat-\pi}$ is the distance from the cation (Cat) to the center of the aromatic ring (Cen), $d_{M-\pi}$ is the distance from the metal of a sandwich compound (M) to the center of the aromatic ring forming the cation–π interaction (Cen). $d_{M-\pi,bottom}$ is the distance from the metal M to the center of the aromatic ring not involved in cation–π interactions.

Table 1 Interaction energy (E_{int}) values calculated at the B3LYP/def2-TZVP and the CCSD(T)/CBS levels for cation–π interactions of benzene, bis(benzene)chromium and ferrocene. The $d_{cat-\pi}$ value indicates the distance from the cation to the aromatic ring center (see Fig. 1); for NH_4^+ the N-centroid distance was considered

System	Cation	$d_{cat-\pi}$ [Å]	E_{int} B3LYP/def2-TZVP [kcal mol^{-1}]	E_{int} CCSD(T)/CBS [kcal mol^{-1}]
Benzene	Mg^{2+}	1.924	−121.78	−115.50
	Ca^{2+}	2.357	−81.88	−70.95
	Li^+	1.840	−38.37	−36.83
	Na^+	2.395	−23.87	−22.12
	K^+	2.907	−15.88	−13.13
	NH_4^+	3.018	−16.22	−19.09
Bis(benzene) chromium	Mg^{2+}	1.864	−183.71	−178.87
	Ca^{2+}	2.170	−131.25	−117.28
	Li^+	1.773	−52.52	−50.47
	Na^+	2.277	−35.92	−33.37
	K^+	2.767	−24.60	−19.64
	NH_4^+	2.837	−25.67	−29.75
Ferrocene	Mg^{2+}	1.900	−152.98	−147.26
	Ca^{2+}	2.271	−108.77	−95.15
	Li^+	1.837	−47.44	−44.50
	Na^+	2.346	−30.21	−27.40
	K^+	2.821	−20.46	−23.52
	NH_4^+	2.947	−21.17	−23.58

respectively. E_{BSSE} is the energy attributed to the basis set superposition error.

3 Results and discussion

We performed B3LYP/def2-TZVP calculations on cation–π interactions of metal cations (Mg^{2+}, Ca^{2+}, Li^+, Na^+, K^+ and NH_4^+) with sandwich organometallic compounds containing benzene and a Cp ring (Tables S1–S7†). The calculated data enable the evaluation of influence of a metal atom (Fe, Ru, Os, Cr, Mo and W) and type of aromatic ring (Cp or benzene) within the sandwich compound on the strength of cation–π interactions.

The obtained interaction energies show that the cyclopentadienyl sandwich compounds form stronger cation–π interactions than (uncoordinated) benzene (Table 1 and Fig. 2). However, the sandwich compounds of benzene are capable of forming even stronger cation–π interactions (Table 1 and Fig. 2). The strongest interaction energies are calculated for complexes with Mg^{2+} cations, with −121.78 kcal mol^{-1} for interaction with benzene, −155.62 kcal mol^{-1} for interaction with osmocene, and the remarkable interaction energy of −196.77 kcal mol^{-1} for interaction with bis(benzene)tungsten (Fig. 2).

The cation–π interactions of benzene sandwich compounds are significantly stronger than those previously reported for the sandwich compound $Cr(C_6H_6)(C_6F_6)$, whose benzene ligand forms cation–π interactions with B3LYP/6-31++G** energies of −31.7 kcal mol^{-1}, −19.2 kcal mol^{-1} and −10.5 kcal mol^{-1} with Li^+, Na^+ and K^+, respectively.[11] Our calculations

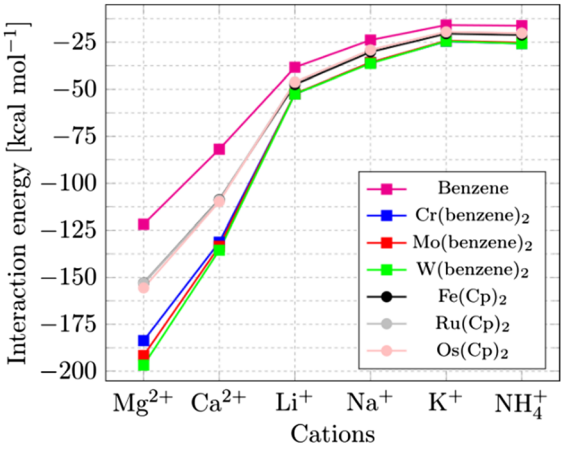

Fig. 2 Interaction energies (in kcal mol^{-1}) between benzene and Cp sandwich compounds and various cations, calculated at the B3LYP/def2-TZVP level of theory.

show that bis(benzene)chromium forms significantly stronger interactions with these cations: −52.52 kcal mol^{-1}, −35.92 kcal mol^{-1} and −24.60 kcal mol^{-1} with Li^+, Na^+ and K^+, respectively (Table 1 and Fig. 2). These results imply that substituents on the lower (non-interacting) aromatic ring can affect interaction energies through long-range electronic effects, a point which deserves more attention in our future research.

In accordance with interaction energies, the $d_{cat-\pi}$ distances for Cp sandwich compounds are shorter than those of uncoordinated benzene, and even shorter for benzene sandwich compounds (Table 1 and Fig. S3, S4†). As one can anticipate, the interaction energies and $d_{cat-\pi}$ distances for sandwich compounds are most significantly influenced by the charge and size of cations, whose influences are similar to those observed for the interactions with uncoordinated benzene (Table 1 and Fig. 2), and in agreement with the literature data.[1]

Our calculations show that coordinated aromatic rings in sandwich compounds form stronger cation–π interactions than uncoordinated benzene (Fig. 2 and Table 1). The type of the aromatic ring in the sandwich compound has an important influence, since the benzene ring has approximately 20% stronger interactions than the Cp ring. However, even though it is evident that transition metal coordination itself strengthens cation–π interactions, the particular metals within the sandwich compounds have surprisingly little influence on interaction energies. Interaction energies for Cp sandwich compounds with Fe, Ru and Os in the sandwich are very similar for all the studied cations (Fig. 2). The interaction energies of benzene sandwich compounds with Cr, Mo and W in the sandwich are also very similar, with notable differences observed only in the case of very strong interactions with Ca^{2+} and Mg^{2+} ions (Fig. 2).

By analyzing the geometries of sandwich–cation complexes, it was observed that the binding of cations causes the deformation of the sandwich compound geometry. This deformation is most notable in the changes in d_{C-C} bond lengths

and $d_{M-\pi}$ distances (Fig. 1). Namely, cation–π interactions lead to lengthening of C–C bonds of interacting aromatic rings in all of the studied systems (Tables S3 and S5†), with linear correlation between C–C bond lengths and the binding energies (Fig. S16†). In addition to the changes within the aromatic ring forming the interaction, the formation of cation–π interactions causes shortening of the $d_{M-\pi}$ distances in all studied systems (Fig. 3). As the $d_{M-\pi}$ distance decreases, the $d_{M-\pi,bottom}$ distance increases (Fig. 3a), resulting in very similar $d_{\pi-\pi}$ distances compared to the sandwich compound without cation–π interactions (Fig. 3a and Fig. S15†). Therefore, it can be observed that the overall size of the sandwich compound remains similar upon the formation of cation–π interactions, but the sandwiched transition metal is affected by the presence of cation and shifts towards it, becoming closer to the aromatic ring forming cation–π interaction. This implies that the transition metal is most likely involved in the formation of the cation–π interaction, which deserves further analysis in our upcoming studies. In addition, the changes in $d_{M-\pi}$ are in good linear correlation with binding energies for both benzene and Cp sandwich compounds (Fig. 3b and Fig. S17†), indicating that $d_{M-\pi}$ is another geometrical parameter, together with C–C bond lengths, that can be used for assessment of the strength of cation–π interactions.

Experimental support for our results was found within the crystal structure of organometallic compounds containing both C_6 and C_5 aromatic rings coordinated to transition metals,[56] where K^+ prefers the C_6 ring to form the cation–π interaction (Fig. 4). In this example, K^+ is situated almost exactly above the C_6 aromatic ring, being horizontally displaced only 0.18 Å relative to the ring center, with the cation–center distance of 2.83 Å, which is similar to the distances we have obtained for benzene sandwich compounds (Table 1).

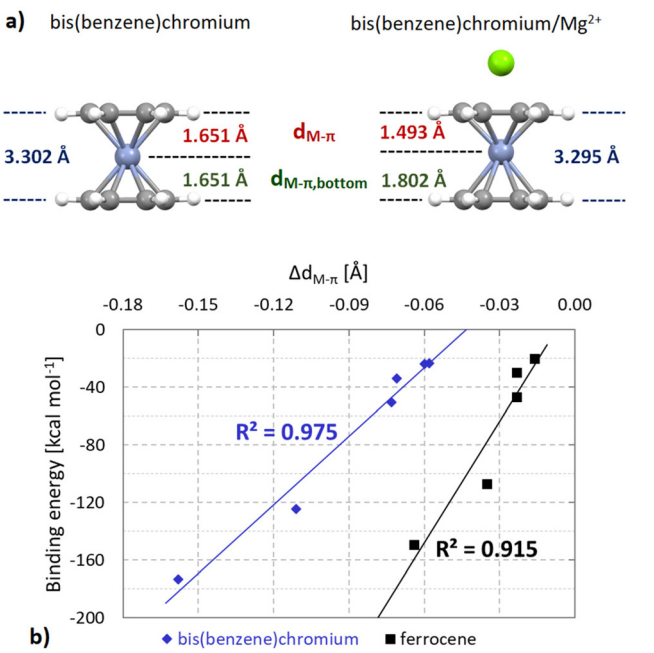

Fig. 3 (a) M–π and M–π,bottom distances for bis(benzene)chromium with and without cation–π interaction with Mg^{2+}. (b) The correlation between the change in M–π distances and B3LYP/def2-TZVP binding energies for cation–π complexes of bis(benzene)chromium and ferrocene.

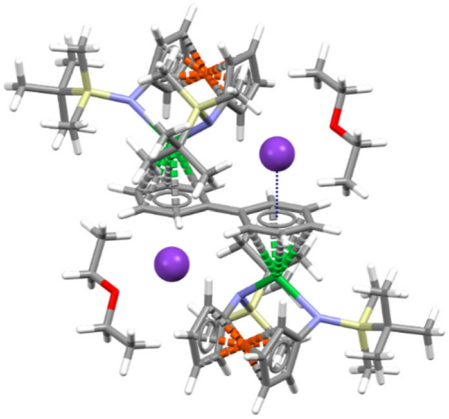

Fig. 4 Cation–π interaction between a coordinated C_6-aromatic ring and K^+ in the crystal structure of dipotassium (*m*-biphenyl)-bis(*N*,*N*′-bis(*t*-butyl(dimethyl)silyl)ferrocene-1,1′-diamide)-di-ytterbium diethylether solvate (CSD refcode XAJMOO).

4 Conclusions

To evaluate the effect of transition metal coordination on cation–π interactions, we have studied systems containing sandwich compounds of benzene and cyclopentadienyl (Cp) ligand and alkali, alkaline earth and ammonium cations. These cation–π interactions were studied by means of CCSD(T)/CBS and B3LYP/def2-TZVP calculations of binding and interaction energies, as well as the observation of geometrical parameters of cation–π dimers and the involved sandwich compounds.

The calculations have shown that coordinated cyclopentadienyl rings in ferrocene, ruthenocene and osmocene form stronger cation–π interactions than (uncoordinated) benzene. However, the strongest cation–π interactions were calculated for benzene sandwich compounds, namely bis(benzene)chromium, bis(benzene)molybdenum and bis(benzene)tungsten. The calculations performed for the small and highly charged Mg^{2+} cation reveal the strongest interactions, with interaction energy values of −121.78 kcal mol^{-1} with benzene, −152.98 kcal mol^{-1} with ferrocene and −183.71 kcal mol^{-1} with bis(benzene)chromium. Similarly to cation–π interactions of uncoordinated aromatic compounds, cation–π interactions of sandwich compounds are strongly influenced by charge and size of cations. Moreover, sandwich compounds containing larger transition metals form somewhat stronger cation–π interactions with 2+ cations. Therefore, the strongest calculated interaction is that between Mg^{2+} and bis(benzene)tungsten, with interaction energy of −196.77 kcal mol^{-1}.

The formation of cation–π interactions induces local changes in the structures of sandwich compounds, the most notable being the elongation of C–C bonds within aromatic rings and the shortening of distances between the transition metal and aromatic ring center, the latter implying additional interactions between the sandwiched transition metal and cation. Both of these parameters show linear correlation with the binding energies of cation–π interactions, which provides the assessment of the strength of cation–π interactions based on structural changes within the sandwich compounds.

In this work we demonstrate the ability of organometallic compounds to act as remarkable cation receptors. Very strong interactions obtained by quantum chemical calculations indicate the potential of sandwich compounds, especially those containing C_6 aromatic rings, to be used in cation recognition processes.

Author contributions

K. A. Ć. – data curation, formal analysis, investigation, software, visualization, writing – original draft; S. D. Z. – formal analysis, methodology, project administration, resources, supervision, validation, writing – original draft; D. P. M. – conceptualization, data curation, formal analysis, investigation, methodology, project administration, software, supervision, validation, writing – review & editing.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (contract numbers: 451-03-136/2025-03/200288 and 451-03-136/2025-03/200168). The high-performance computing resources used in this work were provided by the IT Research Computing Group at Texas A&M University in Qatar, which is funded by the Qatar Foundation for Education, Science and Community Development.

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