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Structural and electronic effects of cation binding (Li⁺, Na⁺, K⁺, Mg²⁺ and Ca²⁺) to the π system of the (η^6 -benzene)–Cr(CO)₃ complex: A theoretical study

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Abstract: Cation binding to the π -electrons of benzene is known to show a periodic trend in interaction energies. In the present work, the chemistry of cation– π interaction in a benzene ring bound with tripodal Cr(CO)₃ (BC) was considered. In contradiction to the anticipated destabilisation due to competition between two Lewis acids towards a common sandwiched base, cation binding with BC showed a similar trend as that to benzene. Furthermore, it was found to activate the benzene ring by reducing the frontier orbital energy gap substantially. The *NICS*_{zz} index adds sufficient evidence to the arguments. In addition, TDDFT studies indicate a bathochromic shift upon cation binding as an immediate consequence of the reduction in the energy of the Frontier orbital.

Keywords: Cation complexed (η^6 -benzene)–tricarbonylchromium system; cation– π -interaction energy; charge transfer; nucleus-independent chemical shifts (*NICS*); time-dependent density functional theory (TDDFT).

INTRODUCTION

The dominant supramolecular and biological macromolecular interactions involve non-covalent ones, such as dispersive forces, van der Waals interactions, hydrogen bonding, hydrophilic and hydrophobic forces, and ion– π interactions between aromatic rings and metal ions.^{1,2} In particular, intermolecular cation– π -interaction arising from the electrostatic interaction of a cation with the face of a π -system is widely recognized and studied in recent years since it offers great potential in drug design, structural biology, conformational analysis and asymmetric catalysis.³ Thus, cation– π interactions are ubiquitous and are of prime importance in several fields of contemporary interest, such as chemistry, material science, biology and allied areas.^{4–8} The interaction of a metal cation with the π -system of aromatic residues is arguably the strongest non-covalent interaction

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with high complexation energies and is comparable with some covalent bonds.^{9–11} First evidence of cation– π -interaction in the gas phase resulted from the work by Kebarle and co-workers in 1981.¹² A pioneering work on the fundamental nature of cation– π interactions and the factors that modulate their strength was reported by Dougherty and co-workers.^{9,10} A survey of the literature revealed that several theoretical studies have been performed on cation– π interactions with focus on understanding the strength of cation– π interactions.^{3,13–21} Furthermore, a series of experimental studies realized by Rodgers and Amunkgama²² and Dunbar *et al.*²³ supported the existence of cation– π systems. A recent review article³ demonstrates the ubiquity of cation– π interactions with special focus on extensive theoretical studies on ion– π interactions quantifying the preference of metal ion binding to π -systems, *viz.*, aromatic amino acids, substituted benzene, polyaromatic hydrocarbons and heteroaromatics. The nature of the cation, the presence of hetero atoms in the π -systems, the presence of solvent, the site of solvation are factors that were found to play a pivotal role determining the strength of cation– π interactions.³

In parallel, arene–chromium tricarbonyl compounds are highly versatile and the most widely explored organometallics,²⁴ with prospective applications ranging from organic synthesis, molecular switches, tunable molecular wires, optical information storage devices to non linear optical (NLO) materials.²⁵ Many earlier studies explored the conformational biasing in these complexes^{26,27} and recently, tuning the barrier to tripodal rotation of $\text{Cr}(\text{CO})_3$ with fluorine substitution and skeletally substituted phosphorus and boron atoms in (η^6 -benzene)tricarbonylchromium complexes were reported.²⁸ The structure, reactivity, and aromaticity of the arene ring are altered significantly upon complexation of the arene ring with the $\text{Cr}(\text{CO})_3$ fragment. Aromaticity and anti-aromaticity in transition metal systems were explored by Boldyrev *et al.*²⁹ In depth diagnosis of the σ -, π - and ($\sigma+\pi$)-aromaticity of organic and inorganic molecules were reported by Tsipis *et al.*³⁰ Although many indices *viz.*, nucleus independent chemical shift (*NICS*), magnetic susceptibility exaltation, chemical shift data, coupling constants, *etc.*, are available for quantifying aromaticity, it was demonstrated that almost none of the indices uncompromisingly explain the real electronic manipulation that is created in the aromatic ring on $\text{Cr}(\text{CO})_3$ complexation.^{31–33} The failure of many aromaticity indices could be attributed to steric, and Sola *et al.*³⁴ ended the controversial debate about the aromaticity of the benzene ring in the (η^6 - C_6H_6) $\text{Cr}(\text{CO})_3$ complex by suggesting *NICS*_{zz} as a more reliable index of aromaticity for this particular system.

Although studies related to cation binding to aromatic moieties are enormous, there are limited or almost no studies (especially computational) related to cationic interactions with aromatic systems that are haptotropically coordinated to transition metals, *viz.* $\text{Cr}(\text{CO})_3$. Therefore, in the present work, an investi-

gation of the aforementioned type of cationic interactions was undertaken with the (η^6 -C₆H₆)-Cr(CO)₃ system. In such systems, there are two types of interactions, *viz.* simple electrostatic interactions between simple cations and the π cloud of benzene and the synergistic interaction of haptotropically bound tripodal Cr(CO)₃ with the arene π -cloud. The study will highlight the elusive competition for two acids towards a common aromatic base. The following are the intriguing questions that the present work intends to address whether the sandwiched benzene would cater for the electronic requirements of both the Mⁿ⁺/Cr(CO)₃ and whether or not there would be a cooperative approach between the metal towards the sandwiched aromatic ring. Furthermore, whether the metals would de-aromatize or in other words reduce the diamagnetic ring current due to electron partitioning due to the competing π -acid interactions. Hence, it was hoped that the present study, being the first to give theoretical insights on cation- π -interactions in haptotropically complexed benzene-Cr(CO)₃, would pave the way for exploring the broader concept of cation- π -base interactions.

COMPUTATIONAL DETAILS

All calculations were performed with the Gaussian-09 program.³⁵ Geometry optimizations were performed at the B3LYP³⁶ level. Additionally, as non-covalent interactions are known to be dependent on dispersion corrections, the computations were performed by incorporating dispersion functions. Recently reported benchmark studies document the DFT-D3³⁷ (Grimme's dispersion function) and D3(BJ)³⁸ (Grimme's dispersion with Becke-Johnson damping) methods to be relatively reliable to introduce dispersion corrections into B3LYP, and hence, the B3LYP-D3³⁷ and B3LYP-D3(BJ)³⁸ methods were also adopted in the present study. The 6-31G(d) basis set³⁹ was used for carbon, oxygen, hydrogen atoms and metal ions (Li⁺, Na⁺, K⁺, Mg²⁺ and Ca²⁺). The LANL2DZ basis set, in conjunction with the LANL2DZ pseudo-potential⁴⁰, was used for the chromium atom in Cr(CO)₃. All the optimized structures were characterized by frequency analysis. The interaction energies obtained were corrected for the basis set superposition error (BSSE) using the counterpoise method described by Boys and Bernardi.⁴¹ Natural bond orbital analysis (NBO)⁴² and nucleus-independent chemical shifts (NICS_{zz})⁴³ (calculated at the geometrical centres of the ring atoms NICS_{zz}(0), and also 1 Å above the ring NICS_{zz}(1) using the gauge invariant atomic orbital (GIAO)⁴⁴ method) calculations were realized employing the B3LYP method using the 6-31G(d) basis set³⁹ for carbon, oxygen, hydrogen atoms and metal ions (Li⁺, Na⁺, K⁺, Mg²⁺ and Ca²⁺) and the LANL2DZ basis set, in conjunction with the LANL2DZ pseudo-potential,⁴⁰ for the chromium atom in Cr(CO)₃. Time dependent density functional theory (TDDFT) calculations were performed for 10 singlet excited states and the percentage contribution of the molecular orbitals (MOs) for different transitions and natural transition orbitals (NTO) pictures were collected using Chemissian software.⁴⁵

RESULTS AND DISCUSSION

A series of Mⁿ⁺-(η^6 -benzene)tricarbonylchromium complexes, labelled as MBC ((Li⁺-BC), (Na⁺-BC), (K⁺-BC), (Mg²⁺-BC) and (Ca²⁺-BC, Fig. 1) were chosen for the study. To understand the effect of the Cr(CO)₃ fragment, Mⁿ⁺-benzene complexes labelled as MB ((Li⁺-B), (Na⁺-B), (K⁺-B), (Mg²⁺-B), and

(Ca²⁺-B)) were also analysed. For comparison, benzene (B) and (η^6 -benzene)-tricarbonylchromium complex (BC) are presented along with the other results.

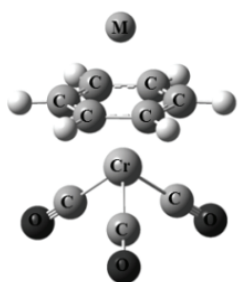


Fig. 1. M^{n+} -(η^6 -benzene)tricarbonylchromium complexes, MBC, $M = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Mg}^{2+}$ or Ca^{2+} ; $B = \text{C}_6\text{H}_6$; $C = \text{Cr}(\text{CO})_3$.

Interaction energy

Interaction energies (BSSE corrected) of alkali and alkaline earth metal ions, *viz.*, $\text{Li}^+, \text{Na}^+, \text{K}^+, \text{Mg}^{2+}$ and Ca^{2+} , with the π -cloud of BC and B are presented in Table I.

TABLE I. Interaction energy, $IE / \text{kcal}^* \text{mol}^{-1}$, frontier orbital energy gap, $\Delta\varepsilon / \text{eV}$, hardness, η / eV , distance from the metal cation to the centroid of benzene, $d_{M-\Omega} / \text{\AA}$, and from the chromium to the centroid of benzene, $d_{Cr-\Omega} / \text{\AA}$, computed for the minimum energy structures for both the studied systems; calculated parameters represented in regular (B3LYP), italic (B3LYP-D3) and bold-italic (B3LYP-D3(BJ)); $IE = \text{BSSE corrected interaction energy}$; $\Delta\varepsilon = 27.2116(\varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}}) \text{ eV}$; $\eta = 27.2116 \text{ eV}(\varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}})/2^{46}$

System	MB				MBC				
	<i>IE</i>	$\Delta\varepsilon$	η	$d_{M-\Omega}$	<i>IE</i>	$\Delta\varepsilon$	η	$d_{M-\Omega}$	$d_{Cr-\Omega}$
B	–	6.78	3.39	–	–43.98	4.65	2.33	–	1.81
	–	6.78	3.39	–	–44.00	4.68	2.34	–	1.81
	–	6.78	3.39	–	–43.74	4.71	2.35	–	1.81
Li^+	–40.17	6.97	3.48	1.87	–73.77	4.35	2.18	1.85	1.72
	–40.18	6.97	3.48	1.88	–73.70	4.38	2.19	1.85	1.72
	–40.13	6.97	3.48	1.87	–73.08	4.44	2.22	1.83	1.71
Na^+	–26.66	6.23	3.12	2.34	–62.28	3.78	1.89	2.28	1.78
	–26.68	6.18	3.09	2.36	–62.27	3.78	1.89	2.30	1.75
	–26.68	6.10	3.05	2.40	–61.66	3.86	1.93	2.27	1.73
K^+	–16.62	6.18	3.09	2.82	–51.36	3.86	1.93	2.82	1.77
	–16.55	6.01	3.01	2.92	–51.26	3.78	1.89	2.86	1.78
	–16.61	6.12	3.06	2.85	–50.71	3.95	1.97	2.76	1.77
Mg^{2+}	–124.28	4.71	2.35	1.92	–185.54	1.99	0.99	1.81	1.67
	–124.22	4.71	2.35	1.92	–185.35	2.07	1.03	1.79	1.66
	–124.18	4.65	2.33	1.92	–184.25	2.07	1.03	1.79	1.67
Ca^{2+}	–72.12	5.06	2.53	2.39	–122.74	2.34	1.17	2.21	1.77
	–72.12	5.03	2.52	2.39	–122.67	2.45	1.22	2.19	1.76
	–72.12	5.03	2.52	2.39	–121.74	2.42	1.21	2.19	1.77

* 1 kcal = 4184 J

The interaction energies for MB (Li^+ - Ca^{2+}) computed at the B3LYP/6-31g(d) level are in good agreement with reported values.⁴⁷ It is well known that in the case of BC, the tripodal $\text{Cr}(\text{CO})_3$ complexed to arene makes it electron deficient^{26,27} and hence in the present case, it was anticipated that the consequence of this interaction of $\text{Cr}(\text{CO})_3$ on benzene would be to reduce the interaction energy of BC with metal ions. However, in contrast, Table I lists reasonably large interaction energies for all the MBC complexes compared to their MB counterparts, which shows that a cooperative behaviour of the two acids (M^{n+} and $\text{Cr}(\text{CO})_3$) towards the common π -base exists. The interaction energies show the same trend for both MB (in agreement with Dougherty¹⁰) and MBC. The general trend shown by the MB system as reported in the present paper is Mg^{2+} -B > Ca^{2+} -B > Li^+ -B > Na^+ -B > K^+ -B (consistent with Sastry and coworkers⁴⁷). A similar trend is replicated in MBC but with a larger magnitude. It is understandable that due to the increase in the ionic radii, electrostatic interactions would be reduced between the cations and the benzene ring and this would be reflected in a reduction in the ionisation energy. The interaction energies obtained by the three methods, *i.e.*, B3LYP, B3LYP-D3 and B3LYP-D3(BJ), are quite comparable. Moreover, the trends in the interaction energies shown by both MB and MBC remained the same in all the three methods. The interaction energy profiles of various cation-aromatic complexes (MB and MBC) are shown in Fig. 2.

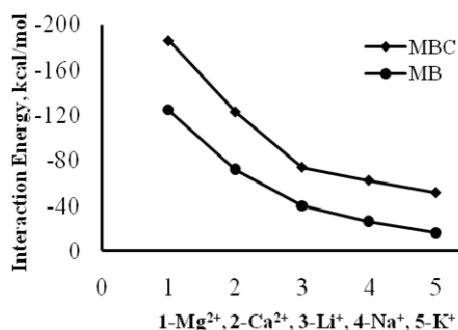


Fig. 2. Interaction energy profiles of the cation-aromatic complexes (MBC and MB).

The hardness, η ,⁴⁶ the reflector of reactivity, showed an enhanced reactivity of MBC over their MB counterparts (Table I) through their decreased frontier orbital energy gaps. This indicates that MBCs could be still better candidates for nucleophilic substitution reactions. It is worth mentioning that the magnitude of the reduction in hardness of MBC was higher for the alkaline earth metals than for the alkali metals.

Looking at the Cr- Ω and M- Ω distance in Table I, it is clear that the presence of metal ions (Li^+ , Na^+ , K^+ , Mg^{2+} or Ca^{2+}) was reflected in the Cr- Ω distance throughout the MBC system. The Cr- Ω distances were smaller and the smallest was found for Mg^{2+} -BC (1.67 Å). It is also interesting to observe the M- Ω

distance (Table I). Although there are very marginal changes in the bond distances, it is worth mentioning that in all the cases, the M– Ω in MBC is shorter than in MB (a larger magnitude of decrease was observed for Mg²⁺–BC). Shortening of the M– Ω and Cr– Ω distances occur on complexing the Cr(CO)₃ fragment in the MB system and a metal cation in the BC system, respectively. Both cases are accompanied by increases in the interaction energy. Thus, inter-dependant relationships between the magnitude of interaction, M– Ω and Cr– Ω distances are direct evidence for co-operative electrostatic and coordination type interaction of Mⁿ⁺ and Cr respectively towards a common π -base. From Table I, it is known that among MBC, the decrease in the interaction energy is in good agreement with the increase in the distance of metal cation to the centroid of benzene for the monovalent (M– Ω : Li⁺–BC < Na⁺–BC < K⁺–BC) and divalent (Mg²⁺–BC < Ca²⁺–BC) cations of the MBC systems and the trends are in concurrence with earlier reports for π -cationic systems of MB.⁴⁷

Charge transfer

The Mulliken and NBO charges of the metal cations (F_1 in Table II) in BC and MBC complexes are summarized in Table II. They indicate a transfer of positive charge from the cation to the aromatic system during the interaction. It was observed that for the MB and MBC systems, the interaction energies separately correlate linearly with the amount of charge transfer for monovalent and divalent cations (M⁺ → ring; M²⁺ → ring, Supplementary material to this paper– Figs. S-1–S-4). However, the same correlation was poor when M⁺ and M²⁺ were treated together (Supplementary material – Figs. S-5 and S-6). This indicates that both charge transfer and interaction energy are group properties and there exists only a group trend.

TABLE II. Mulliken and NBO charges / atomic units of the cations, ring and Cr(CO)₃ computed for the minimum energy structures in both the studied systems; F^* – Mulliken charge on M1, M2, M3, M4 and M5 for comparison,⁴⁷ F_1 – charge on metal; F_2 – charge on benzene ring and F_3 – charge on Cr(CO)₃

System	MB					MBC					
	Mulliken charge			NBO Charge		Mulliken charge			NBO Charge		
	F^*	F_1	F_2	F_1	F_2	F_1	F_2	F_3	F_1	F_2	F_3
B	–	0	0	0	0	–	0.29	–0.29	–	0.26	–0.26
Li ⁺	0.43	0.42	0.58	0.96	0.04	0.59	1.28	–0.87	0.98	0.31	–0.29
Na ⁺	0.65	0.65	0.35	0.97	0.03	0.66	0.35	–0.01	0.98	0.02	0.01
K ⁺	0.84	0.84	0.16	0.98	0.02	0.86	0.14	–0.01	0.99	0.05	–0.04
Mg ²⁺	0.94	0.93	1.07	1.82	0.18	0.88	0.71	0.41	1.79	–0.13	0.34
Ca ²⁺	1.49	1.49	0.51	1.92	0.08	1.46	0.11	0.43	1.93	–0.27	0.35

In the case of monovalent cations, for both BC and MBC complexes, the order of the charge transferred from the cation to the π -system (F_1 in Table II) is

$K^+ < Na^+ < Li^+$ (*i.e.*, from K^+ to Li^+ the charge dispersed from the cation to the π -system increases). This was confirmed by the corresponding change in the charge on the ring (F_2 in Table II) (ring charge – $Li^+-BC > Na^+-BC > K^+-BC$ similar to $Li^+-B > Na^+-B > K^+-B$). This may be due to the smaller surface area available for the cation to interact with the π -system. The strength of interaction decreases as the ionic radius increases from lithium to potassium. However, the amount of charge transferred from the dication complexes to the π -system is slightly higher as compared to that transferred from the mono-cation complexes for both MB and MBC. Among the dication complexes, the Mg^{2+} ion has less Mulliken charge as compared to Ca^{2+} , signifying that higher amount of charge is transferred from the cation to the π -system, which was confirmed by a corresponding change in the charge on the ring (ring charge – $Mg^{2+}-BC > Ca^{2+}-BC$) (F_2 in Table II). As a result, the highest interaction is observed in the case of the Mg^{2+} complexes. Thus, among all complexes, large amount of positive charge is transferred from (Li^+-BC) and ($Mg^{2+}-BC$) ions to the benzene ring and this could explain their corresponding higher interaction energies.

The impact of the $Cr(CO)_3$ moiety in MBC does not alter the trends in the charge transferred from the cations to the π -system but causes a slight change in the magnitude of the charge transferred. Additionally, it is obvious that the $Cr(CO)_3$ moiety functions as a sink for charge and affords stability to the molecule. This is again a demonstration of the cooperative behaviour of both metals towards the sandwiched benzene ring.

Aromaticity

As has already been discussed, it is well established that when a $Cr(CO)_3$ group is complexed to benzene its π -aromaticity decreases.³⁴ In this study, the status of the aromaticity of both M–B and M–BC is worth documenting. For this purpose, two aromaticity indices $NICS_{zz}$ at 0 and 1 Å, and the proton chemical shift values (with TMS as the reference) are tabulated in Table III for both MB and MBC.

TABLE III. Aromaticity indices $NICS_{zz}(0)$, $NICS_{zz}(1)$ and chemical shift, δ / ppm, of the ring protons computed for the minimum energy structures in both systems; TMS as reference – optimized the $NICS$ values were computed at the B3LYP/6-31g(d) level

System	MB			MBC		
	$NICS_{zz}(0)$	$NICS_{zz}(1)$	δ_{Ar-H}	$NICS_{zz}(0)$	$NICS_{zz}(1)$	δ_{Ar-H}
B	-13.70	-28.97	7.20	-6.72	-24.18	5.07
Li^+	-12.39	-32.64	8.18	-7.38	-27.58	5.34
Na^+	-13.53	-35.59	8.09	-8.07	-31.64	5.19
K^+	-14.75	-36.01	7.88	-9.72	-31.87	5.05
Mg^{2+}	-11.61	-45.18	9.42	-8.03	-45.96	5.54
Ca^{2+}	-13.52	-42.33	8.97	-10.39	-43.23	5.43

The $NICS_{zz}(0)$ and (1) of MBC indicate reduced aromaticity when compared to MB. This is further supported by chemical shift values reported in the Table III. The $NICS_{zz}(0)$ (indicative of σ aromaticity) of MB indicates that there is not much change in delocalisation upon cation binding to benzene, contrastingly $NICS_{zz}(0)$ of MBC shows a sizeable enhancement in σ -aromaticity upon metal cation binding to BC. This is also supported by chemical shift values in which Hs of MBC have slightly higher δ values than BC. On cation binding to BC, there is a pronounced increase in $NICS_{zz}(1)$ showing an aromaticity enhancement in contrast to our anticipation that cation positioned over the drained π cloud of η^6 -benzene- $Cr(CO)_3$ would further drain the electron density thereby causing a lowering of π -aromaticity and this denotes the cooperative approach of the metals towards the sandwiched π -cloud.

Theoretical UV-Vis spectral predictions

A UV-visible transition between two levels is possible only when the transition dipole moment (*TDM*) vector is non-zero at least along one of the principal axes.⁴⁸ The maximum absorption wavelength (λ_{max}), oscillator strength (*f*) and their state transition for MB and MBC are presented in Table IV (the transition dipole moment (*TDM*) and root mean square values (*RMS*) are detailed in the Supplementary material, Table S-I. The natural transition orbitals (NTO) responsible for the transition, their corresponding percentage contributions and orbital level contributions for both MB and MBC are provided in Tables S-II and S-III of the Supplementary material).

For MB

The major contribution of NTOs of the transition, *viz.*, HOMO-1 \rightarrow LUMO was observed for B, Li^+B , Na^+B and K^+B (Table S-II). However, in the case of $Mg^{2+}B$ and $Ca^{2+}B$, these orbitals are not involved at all, rather the transition are from a very much lower molecular orbital to very much higher lying molecular orbitals. From Table IV, it could be seen that ($S_0 \rightarrow S_4$) transition ($\pi \rightarrow \pi^*$) is intense with $f = 0.559$ for benzene, but on binding with metal cations, the intensity decreases in the following order $B > Li^+B \approx Na^+B > K^+B > Mg^{2+}B > Ca^{2+}B$. In addition, a large bathochromic shift is observed, except in the case of $B-Li$ where a very slight hypsochromic shift is observed. All the bands lie in the UV region only. The *TDM* of Li^+B and Na^+B are comparable to that of benzene and hence the electronic transitions have greater oscillator strengths than that of benzene (Table S-I). However, K^+B shows relatively lower *TDM* and, consequently, lower oscillator strength and in the case of $Mg^{2+}B$ and $Ca^{2+}B$, the more diminished *f* values result in a very weak band that is a consequence of the diminished *TDM*.

TABLE IV. Computed λ_{\max} (maximum absorption wavelength), nm, and f (oscillator strength) between the ground and n^{th} excited state of all the systems under study

System	MB			MBC		
	State transition	λ_{\max}	f	State transition	λ_{\max}	f
B	$S_0 \rightarrow S_4$	168.03	0.5588	$S_0 \rightarrow S_8$	328.93	0.0016
Li^+	$S_0 \rightarrow S_6$	165.65	0.5223	$S_0 \rightarrow S_6$	352.21	0.0025
Na^+	$S_0 \rightarrow S_5$	168.36	0.5276	$S_0 \rightarrow S_9$	351.84	0.0015
K^+	$S_0 \rightarrow S_{10}$	169.76	0.3436	$S_0 \rightarrow S_{10}$	339.76	0.0013
Mg^{2+}	$S_0 \rightarrow S_8$	174.03	0.0109	$S_0 \rightarrow S_3$	792.33	0.0484
Ca^{2+}	$S_0 \rightarrow S_{10}$	173.55	0.0069	$S_0 \rightarrow S_3$	667.06	0.0174

For MBC

The *TDM* for MBC is reduced and hence, the f values are much lower than their MB counterparts but λ_{\max} shows a large bathochromic shift (Table S-I). This bathochromic shift is the immediate consequence of the narrowing of the frontier orbital energy gap that was already discussed in the interaction energy section. The intensity of the band is in the order $\text{Mg}^{2+}\text{-BC} > \text{Ca}^{2+}\text{-BC} > \text{Li}^+\text{-BC} > \text{Na}^+\text{-BC} \approx \text{BC} > \text{K}^+\text{-BC}$ (Table IV). The order of bathochromic shift of λ_{\max} is $\text{BC} < \text{K}^+\text{-BC} < \text{Na}^+\text{-BC} < \text{Li}^+\text{-BC} \ll \text{Ca}^{2+}\text{-BC} \ll \text{Mg}^{2+}\text{-BC}$ (Table IV). All these lie in the visible region. From the NTOs and their molecular orbital contribution (Table S-III), there is a striking observation in the case of $\text{Mg}^{2+}\text{-BC}$ and $\text{Ca}^{2+}\text{-BC}$. It could be seen that in both these complexes only one orbital, namely HOMO-2 \rightarrow LUMO, is responsible for the electronic transition $S_0 \rightarrow S_3$ (λ_{\max}). The NTO picture (Table S-III) of the aforementioned transition shows that $\text{Cr}(\text{CO})_3$ and the metal ion contribute largely in the donor (hole) while the acceptor (particle) has the lobe mainly on the metal cation, ensuring its contribution in the LUMO.

CONCLUSIONS

The intricacies of cation (Li^+ , Na^+ , K^+ , Mg^{2+} and Ca^{2+}) interactions with the π -cloud of (η^6 -benzene)tricarbonylchromium were explored through density functional studies. The studies revealed that the *BSSE* corrected binding energies of the cation bound BCs are very high compared to that of the cation-benzene interaction. The sizeable reduction in hardness of cation-BC relative to BC is yet another intriguing observation. The most stable (larger interaction energy) $\text{Mg}^{2+}\text{-BC}$ is the most reactive (lowest frontier orbital energy gap). This inverse relation could be attributed to synergistic interaction of the two metal acids (M^{n+} and the $\text{Cr}(\text{CO})_3$ moiety) in activating the benzene ring, evidencing a cooperative behaviour of the acids towards the common π -base. Furthermore, the aromaticity studies through NICS_{zz} indicated an enhancement of aromaticity due to cation binding with BC. Hence, delocalisation validates the stability of the cation-bound BC. TDDFT studies revealed that for MBC, very weak bands are obtained and

the low intensity is due to a low transition dipole moment. Furthermore, the reduction in the frontier orbital energy gap led to a large bathochromic shift of the λ_{\max} value.

SUPPLEMENTARY MATERIAL

Figures containing the interaction energy vs. charge transfer and tables containing state transitions, λ_{\max} , f , TDM , RMS and NTO are available electronically at the pages of the journal website: <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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ИЗВОД

СТРУКТУРНИ И ЕЛЕКТРОНСКИ ЕФЕКТИ КАТЈОНА КОЈИ ВЕЗУЈУ (Li⁺, Na⁺, K⁺, Mg²⁺ и Ca²⁺) НА π -СИСТЕМ (η^6 -БЕНЗЕН)Cr(Co)₃ КОМПЛЕКСА: ТЕОРИЈСКА СТУДИЈА

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За катјоне који се везују за π -електроне бензена је познато да показују периодни тренд у енергијама интеракције. У овом раду износимо хемију катјон– π -интеракција у бензеновом прстену везаном за треноги Cr(CO)₃. У супротности са претпостављеном дестабилизацијом због надметања између две Луисове киселине за заједничку усендвичену базу, опажено је да везивање катјона са ВС показује сличан тренд као код бензена. Даље је нађено да смањивање јаза између орбитала веома значајно активира бензенов прстен. $NICS_{zz}$ индекс пружа овој тврдњи довољан доказ. Такође TDDFT студије указују да батохромни помак при везивању катјона јесте непосредна последица смањивања јаза између граничних орбитала.

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REFERENCES

1. G. Weber, *Protein interactions*, Chapman & Hall, London, 1992
2. H. Rubin, *Touchstone of life: molecular information, cell communication, and the foundations of life*, Oxford University Press, New York, 1999
3. A. Subha Mahadevi, G. N. Sastry, *Chem. Rev.* **113** (2013) 2100
4. B. H. Hong, S. C. Bae, C. W. Lee, S. Jeong, K. S. Kim, *Science* **294** (2001) 348
5. D. A. Dougherty, *J. Nutr.* **137** (2007) 1504S
6. M. M. Torrice, K. S. Bower, H. A. Lester, D. A. Dougherty, *Proc. Natl. Acad. Sci. U.S.A.* **106** (2009) 11919
7. P. Lhoták, S. Shinkai, *J. Phys. Org. Chem.* **10** (1997) 273
8. E. T. Kool, M. L. Waters, *Nat. Chem. Biol.* **3** (2007) 70
9. J. C. Ma, D. A. Dougherty, *Chem. Rev.* **97** (1997) 1303
10. D. A. Dougherty, *Acc. Chem. Res.* **46** (2013) 885
11. J. D. Cox, J. A. Hunt, K. M. Compher, C. A. Fierke, D. W. Christianson, *Biochemistry* **39** (2000) 13687
12. J. Sunner, K. Nishizawa, P. Kebarle, *J. Phys. Chem.* **85** (1981) 1814
13. S. E. Wheeler, K. N. Houk, *J. Am. Chem. Soc.* **131** (2009) 3126

14. A. Hassan, T. C. Dinadayalane, J. Leszczynski, *Chem. Phys. Lett.* **443** (2007) 205
15. T. C. Dinadayalane, A. Hassan, J. Leszczynski, *J. Mol. Struct.: THEOCHEM* **976** (2010) 320
16. S. D. Zaric, *Chem. Phys. Lett.* **311** (1999) 77
17. W. Zhu, X. Tan, J. Shen, X. Luo, F. Cheng, P. C. Mok, R. Ji, K. Chen, H. Jiang, *J. Phys. Chem., A* **107** (2003) 2296
18. J. F. Gal, P. C. Maria, M. Decouzon, O. M6, M. Y6ñez, J. L. M. Abboud, *J. Am. Chem. Soc.* **125** (2003) 10394
19. O. M6, M. Y6ñez, J. F. Gal, P. C. Maria, M. Decouzon, *Chem.-Eur. J.* **9** (2003) 4330
20. J. F. Gal, P. C. Maria, M. Decouzon, O. M6, M. Y6ñez, D. Kuck, *Chem.-Eur. J.* **12** (2006) 7676
21. a) C. Garau, A. Frontera, D. Qui6noro, P. Ballester, A. Costa, P. M. Dey6, *Chem. Phys. Lett.* **392** (2004) 85; b) C. Estarellas, D. Escudero, A. Frontera, D. Qui6noro, P. M. Dey6, *Theor. Chem. Acc.* **122** (2009) 325; c) A. Frontera, D. Qui6noro, P. Ballester, A. Costa, P. M. Dey6, *New J. Chem.* **31** (2007) 556; d) A. Frontera, D. Qui6noro, P. M. Dey6, *WIREs Comput. Mol. Sci.* **1** (2011) 440
22. a) R. Amunugama, M. T. Rodgers, *Int. J. Mass Spectrom.* **222** (2003) 431; b) R. Amunugama, M. T. Rodgers, *J. Phys. Chem., A* **106** (2002) 9718
23. a) Y.-C. Lin, R. C. Dunbar, *Organometallics.* **16** (1997) 2691; b) R. C. Dunbar, J. D. Steill, J. Oomens, *J. Am. Chem. Soc.* **133** (2011) 9376
24. A. J. Pearson, *Metallo-Organic Chemistry*, Wiley, New York, 1985
25. a) F. J. McQuillin, D. G. Parker, G. R. Stephenson, *Transition Metal Organometallics for Organic Synthesis*, Cambridge University Press, Cambridge, 1991; b) B. L. Feringa, *Molecular Switches*, Wiley-VCH, Weinheim, 2001; c) N. L. Wagner, F. E. Laib, D. W. Bennett, *Inorg. Chem. Commun.* **3** (2001) 87; d) R. A. van Delden, M. K. J. ter Wiel, M. M. Pollard, J. Vicario, N. Koumura, B. L. Feringa, *Nature* **437** (2005) 1337; e) T. J. J. Muller, A. Netz, M. Ansorge, *Organometallics* **18** (1999) 5066
26. A. A. Low, M. B. Hall, *Int. J. Quant. Chem.* **77** (2000) 152
27. C. H. Suresh, N. Koga, S. R. Gadre, *Organometallics* **19** (2000) 3008
28. a) A. Kalpana, L. Akilandeswari, *Comput. Theor. Chem.* **1069** (2015) 125; b) A. Kalpana, L. Akilandeswari, *Comput. Theor. Chem.* **1084** (2016) 103
29. a) A. Boldyrev, L. S. Wang, *Chem. Rev.* **105** (2005) 3716; b) D. D. Yu. Zubarev, B. B. Averkiev, H.-J. Zhai, L. S. Wang, A. I. Boldyrev, *Phys. Chem. Chem. Phys.* **10** (2008) 257; c) T. R. Galeev, A. Boldyrev, *Annu. Rep. Prog. Chem., C* **107** (2011) 124
30. a) A. C. Tsipis, *Phys. Chem. Chem. Phys.* **11** (2009) 8244; b) A. C. Tsipis, I. G. Depastas, E. E. Karagiannis, C. A. Tsipis, *J. Comput. Chem.* **31** (2010) 431; c) A. C. Tsipis, I. G. Depastas, C. A. Tsipis, *Symmetry* **2** (2010) 284
31. D. V. Simion, T. S. Sorensen, *J. Am. Chem. Soc.* **118** (1996) 7345
32. R. H. Mitchell, *Chem. Rev.* **101** (2001) 1301
33. P. V. R. Schleyer, B. Kiran, D. V. Simion, T. S. Sorensen, *J. Am. Chem. Soc.* **124** (2002) 11983
34. F. Feixas, J. O. C. Jimenez-Halla, E. Matito, J. Poater, M. Sola, *Pol. J. Chem.* **81** (2007) 783
35. *Gaussian 09, Revision A.1*, Gaussian, Inc., Wallingford, CT, 2009.
36. a) A. D. Becke, *J. Chem. Phys.* **98** (1993) 1372; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev., B* **37** (1988) 785
37. S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **132** (2010) 154104
38. S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **32** (2011) 1456

39. P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* **28** (1973) 213
40. P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **82** (1985) 299
41. S. F. Boys, R. Bernardi, *Mol. Phys.* **19** (1979) 553
42. a) J. P. Foster, F. Weinhold, *J. Am. Chem. Soc.* **102** (1980) 7211; b) A. D. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **88** (1988) 899; c) E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold, *NBO 3.1 Program Manual*, Theoretical Chemistry Institute and Department of Chemistry, University of Wisconsin, Madison, WI, 1988
43. P. V. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. v. E. Hommes, *J. Am. Chem. Soc.* **118** (1996) 6317
44. K. Wolinski, J. F. Hinton, P. Pulay, *J. Am. Chem. Soc.* **112** (1990) 8251
45. L. V. Skripnikov, *Chemissian Visualization Computer Program*, www.chemissian.com, 2009
46. W. Yang, R. G. Parr, *Proc. Natl. Acad. Sci. U.S.A.* **82** (1985) 6723
47. a) A. Srinivas Reddy, G. N. Sastry, *J. Phys. Chem., A* **109** (2005) 8893; b) A. Srinivas Reddy, Hendrik Zipse, G. N. Sastry, *J. Phys. Chem., B* **111** (2007) 11546
48. F. Albert Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, 6th ed., Wiley, New York, 1999.