Aromatic π–π interaction mediated by a metal atom: structure and ionization of the bis(η6-benzene)chromium–benzene cluster

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Aromatic π–π interaction in the presence of a metal atom has been investigated experimentally and theoretically with the model system of bis(η6-benzene)chromium–benzene cluster ($Cr(Bz)_2$–Bz) in which a free solvating benzene is non-covalently attached to the benzene moiety of $Cr(Bz)_2$. One-photon mass-analyzed threshold ionization (MATI) spectroscopy and first principles calculations are employed to identify the structure of $Cr(Bz)_2$–Bz which adopts the parallel-displaced configuration. The decrease in ionization potential for $Cr(Bz)_2$–Bz compared with $Cr(Bz)_2$, resulting from the increase of the cation–π stabilization energy upon ionization, is consistent with the parallel-displaced structure of the cluster. Theoretical calculations give the detailed cluster structures with associated energetics, thus revealing the nature of π–π–metal or π–π–cation interactions at the molecular level.

1. Introduction

Non-covalent bonds are ubiquitous in chemistry and biology. These include hydrogen bonds and van der Waals (vdW) interactions in the form of inter- or intra-molecular interaction, of which associated conformations and energetics are crucial factors in determining the directionality of chemical reactions and enzymatic processes. One of the most important and yet least understood non-covalent interactions is the aromatic π–π interaction which plays essential roles in protein folding, base stacking in DNA, molecular recognition, and self-assembling of supramolecules.[1–3] Compared to the hydrogen bond or one-dimensional van der Waals interactions, the aromatic interaction involves spatially delocalized π electrons that give rise to conformational diversity including intriguingly assembled structures.[4] As a prototypical system for the π–π interaction study, the benzene dimer has long been investigated both extensively and intensively.[5–19] Though the T-shaped and stacked structures are competing, most gas-phase spectroscopic experiments have yielded quite contradictory results regarding the most stable structure whereas stacked structures are commonly found in crystals.[20,21]

In theoretical calculations, the dispersion in the π systems has been a cumbersome problem. Thus, the correct estimation of the dispersion energy has been very limited except for coupled cluster theory with single, double and perturbative triple excitations (CCSD(T)) at the complete basis set (CBS) limit. Despite great efforts for decades, even for the most recent high-level theoretical studies it has been a main theme to investigate whether the benzene dimer in the global minimum adopts a T-shaped or parallel-displaced structure because different theoretical methods still often give different results.

Furthermore, for the benzene dimer mediated by a metal atom or ion, it is not clearly known which structure is more stable between the T-shaped edge-to-face structure and displaced stacked structure. The effect of the external cation on the structure of the benzene-dimer has not been much investigated to date, whereas the cation–π interaction[22,23] is being considered to be important in determining secondary or tertiary structures of biological molecules as well as in nano-sized recognition for molecular assembly. It is also noteworthy that many enzymes have a metal playing a key role as a charge carrier to induce the conformational change near the active site for the initiation of biological functions.[24] Thus, the study of the π–π interaction mediated by a metal atom could be quite helpful to understand the biological activity associated with the π–π or π–cation interaction.

Here, a novel model system of the bis(η6-benzene)chromium–benzene cluster ($Cr(Bz)_2$–Bz) in which a benzene molecule solvates the 18-electron organometallic sandwich complexes, bis(η6-benzene)chromium, is introduced for the study of π–π–metal or π–π–cation interaction. In this work, the $Cr(Bz)_2$–Bz cluster is generated in the gas phase on the supersonic jet, where the benzene monomer is attached *via* non-covalent interaction to the benzene ligand of $Cr(Bz)_2$. The $Cr(Bz)_2$–Bz cluster provides an ideal system for the molecular-level investigation of the cation–π interaction especially because the pattern of the conformational change upon the metal charge transfer can be inferred from the structural change of the model system upon the ionization. Previously, one of us reported the MATI spectroscopy.[25] However, here we refined the experimental data, though similar to the previous one, and elucidate the structures and the nature of the π interactions involved in the system using high level quantum

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theoretical calculations. We address the experiment briefly and discuss the chemistry of the present π systems.

2. Experimental

The $Cr(Bz)_2$ sample was purchased from Aldrich (97%) and used without further purification. The sample was heated to 80 °C, mixed with the Ne carrier gas, and expanded into vacuum through a 0.8 mm diameter nozzle orifice (General Valve 9 Series). The supersonic jet was collimated through a 1 mm diameter skimmer (Precision) prior to being excited with the ultraviolet (UV) laser pulse. The backing pressure behind the nozzle was ~ 1.5 atmosphere and the background pressure of $\sim 10^{-7}$ Torr was maintained when the nozzle was operated at 10 Hz. A tunable UV laser pulse ($\Delta t = \sim 5$ ns, $\Delta \bar{U} \sim 0.4$ cm^{-1}) was generated via frequency doubling of the output of a dye laser (Lambda Physik, Scanmate 2) pumped by the third harmonic of a Nd:YAG laser (Continuum, Precision II) through a BBO crystal placed on a homemade autotracker. High-n,l Rydberg states of molecules were generated by the UV laser pulse and pulsed-field ionized (~ 10 V cm^{-1}) after the delay time of 10–15 μs. This delay time between the laser irradiation and pulsed-field ionization was long enough for the complete separation of MATI ion signals from the prompt ion signals in the time-of-flight mass spectrometry. The resultant MATI ions were accelerated, drifted along the time-of-flight tube and detected by dual microchannel plates. The pulsed electric field scheme employed for the MATI spectroscopy is briefly described in Fig. 1. Ion signals corresponding to the $Cr(Bz)_2$–Bz cluster were digitized by an oscilloscope (LeCroy, LT584M) and monitored as a function of the excitation wavelength to give the MATI spectrum in Fig. 2(a). The MATI spectrum of the bare $Cr(Bz)_2$ taken in an identical experimental condition is also shown in Fig. 2(c) for the comparison.

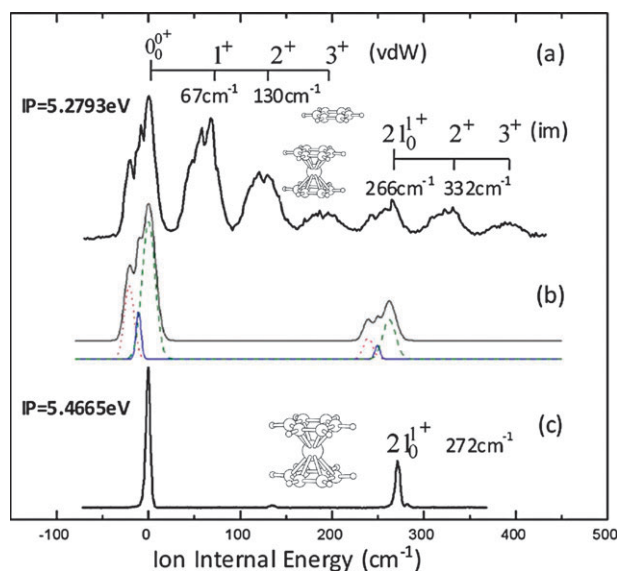**Fig. 2**   MATI spectra of $Cr(Bz)_2$–Bz (a) and $Cr(Bz)_2$ (c) taken in an identical experimental condition. The simulated spectra (b) may represent three structural conformers of the cluster. The relative peak intensity ratios of the three possible conformers are practically same in both the vdW band (the left three overlapped peaks) and the intra-molecular (im) band (the right three overlapped peaks).

3. Results and discussion

The ionization potential (IP) of $Cr(Bz)_2$–Bz, taken as the peak value of the broad 0–0^+ origin band, is found to be $42\,582 \pm 5$ cm^{-1} (5.2793 ± 0.0006 eV) compared to the IP of $44\,090$ cm^{-1} (5.4665 eV) for bare $Cr(Bz)_2$ (Fig. 2), which is refined from the previous data.[25–27] It should be noted here that this work provides the high-resolution MATI spectrum of the $Cr(Bz)_2$–Bz cluster, much improved from the previously reported low-resolution one.[25] Accordingly, IP and vibrational
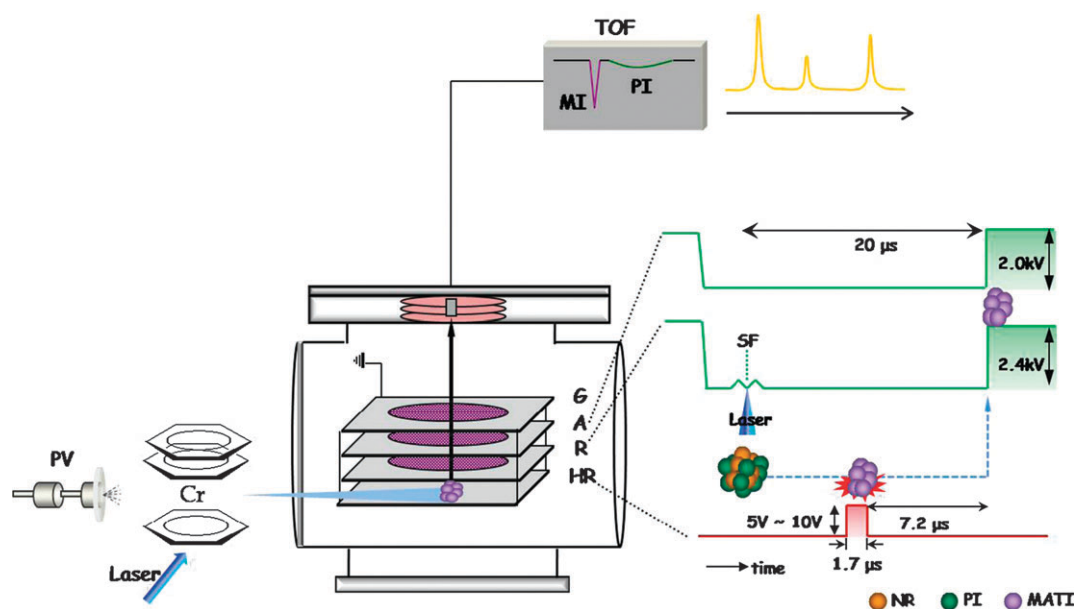

Fig. 1   Experimental setup used for the MATI spectrum. PV: pulsed valve, MCP: microchannel plate, PI: prompt ion, MI: MATI ion, NR: neutral Rydberg, SF: scrambling field, HR: high resolution, R: repeller plate, A: accelerator plate, G: ground.

frequency values have been refined from previously reported values.[25] The closely spaced peaks in the apparently broad origin band, which become resolved in the high-resolution MATI spectrum here, might be ascribed to different structural isomers of the $Cr(Bz)_2$–Bz cluster (*vide infra*). The change in IP (δIP) upon the solvation by an extra benzene molecule is then estimated to be -0.1872 eV. This red IP shift of ~ 1508 cm^{-1} indicates that the $Cr(Bz)_2$–Bz cluster is more stabilized with respect to the asymptotic limit of the $Cr(Bz)_2$ + Bz dissociation channel when it becomes ionized. Interestingly, many vdW vibrational bands are found to be activated in the cluster MATI spectrum, Fig. 2.

The progression of the band with a fundamental frequency of ~ 67 cm^{-1} (as compared with ~ 65 cm^{-1} in the previous work[25]) is ascribed to the vdW mode reflecting the structural change of the cluster upon ionization. The band at 266 cm^{-1} is the intramolecular (im) Bz–Cr–Bz symmetric stretching mode, which corresponds to the 272 cm^{-1} band of the bare $Cr(Bz)_2$ as shown in Fig. 2(c). The experimental finding that all the MATI bands of the cluster are much broader than the MATI peak of the bare $Cr(Bz)_2$ indicates that there should be at least several structural isomers of the cluster in the molecular beam. The relative population of those isomers is responsible for the band shape. Other possible origins of the broadness are either the ultrashort lifetime or vdW bands with a very low frequency. However, as manifested in the large IP shift upon clustering, the Bz–$Cr(Bz)_2$ stabilization energy should generate a deep well in the potential energy surface for the ground cationic state of the cluster, excluding the possibility of the lifetime broadening effect in the MATI spectrum. The vdW bands with a fundamental frequency of less than 10 cm^{-1} contributing to the broad MATI bands are also less likely since the observed spectral pattern with a narrow Frank–Condon window is not expected for the vdW mode residing in such a shallow potential energy surface.

Nonetheless, the origin of the strongest band in the MATI spectrum indicates that the $Cr(Bz)_2$–Bz cluster does not experience any drastic structural change upon ionization, contrary to the case of the benzene dimer. It is noteworthy that the high-resolution ionization spectroscopy of the benzene dimer had not been possible due to the substantial geometrical change induced by the ionization. In the $Cr(Bz)_2$–Bz cluster, since an electron is removed from the nonbonding d_{z^2} orbital of Cr in the ionization process, the effect of ionization on the metal–ligand bonding in terms of the structural change is expected to be not large, despite that the increase of the total charge of the $Cr(Bz)_2$ moiety should contribute significantly to the charge-resonance stabilization of the whole cluster.

For the quantitative description of the cluster structure, theoretical calculations are carried out, while the computation for the structure of this large metal-containing cluster is quite challenging. For geometry optimization, we have employed density functional theory (DFT) using M062X[28] and MPWB1K[29] which can properly deal with the dispersion energy, and *ab initio* theory using the second-order Møller–Plesset (MP2) method. A single-point energy calculation for coupled cluster theory with single, double and perturbative triple excitations [CCSD(T)] is performed on a selected geometry. The CRENBL-ECP basis set[30] was used for Cr, whereas the

aug-cc-pVDZ basis set (shortened as aVDZ) was used for the remaining atoms, and the aVDZ' basis set (in which a set of the outmost diffuse d functions for carbon and sp function of hydrogen are deleted from the aVDZ basis set)[31] is used for the CCSD(T) calculation. Frequencies for the cationic complexes were calculated at the M062X and MPWB1K/aVDZ levels. For DFT geometry optimization and frequency calculations, ultrafine or more integral grids are used.[32] The frequencies are exponentially scaled[33,34] as $\nu_i^s = \nu_i e^{-\alpha \nu_i}$, where ν_i^s and ν_i are scaled and unscaled frequencies corresponding to the vibrational mode i. The exponent α, a single parameter, was chosen to optimally fit the theoretical frequencies with the experimental frequencies of C–H stretching mode of $Bz_2(Cr)$.[35] This method scales down lower vibrational frequencies slightly less than higher frequencies; thus, the frequencies often turned out to be better than the constant-scaled values. We note that in the present system the MPWB1K/aVDZ energies are much less reliable than the M062X/aVDZ energies, as compared with the CCSD(T) energies. Thus, the MPWB1K energies are not reported here except for the frequencies which are somewhat more reliable. All the calculations were carried out using a Gaussian suite of programs.[36] In order to compare the strength of benzene–benzene interaction in neutral and cationic forms of $Cr(Bz)_2$–Bz, we have calculated the neutral and cationic forms of $Cr(Bz)_2$ in eclipsed stacked structure S as the lowest energy conformer (Table 1). For both neutral and cationic states of the $Cr(Bz)_2$–Bz cluster, three parallel-displaced (PD) isomers (S-PD1, S-PD2, S-PD3) and one T-shaped isomer (S-T) are investigated (Fig. 3).

Overall, we find that in the present system the M062X/aVDZ (MP2/aVDZ) energies are in reasonable agreement with the CCSD(T)/CBS energies. Thus, our dicussion will be based on the M062X/aVDZ (MP2/aVDZ) energies, unless otherwise specified. For the neutral $Cr(Bz)_2$–Bz cluster, the S-PD3-like configuration (nearly in between SPD1 and SPD3 configurations), which is isoenergetic to the S-PD3 configuration, is the most stable with binding energy of 3.99 (4.91) kcal mol^{-1}, but practically isoenergetic to S-PD1 and SPD-2 configurations within 0.01 kcal mol^{-1}. Given that the binding energy difference between CCSD(T)/aVDZ' and CCSD(T)/CBS for the parallel displaced benzene dimer is 1.8 kcal mol^{-1}, we apply this correction to the CCSD(T)/aVDZ' energy of the neutral S-PD3(-1.8 kcal mol^{-1}) to get the estimated CCSD(T)/CBS binding energy of 3.6 kcal mol^{-1},[19,37] which is close to the M062X/aVDZ energy. There are no significant energy barriers between S-PD1, S-PD2 and S-PD3; hence, the structure would have wide-ranging parallel displaced configurations. The S-PD3 like structure is more stable than the T-shaped S–T isomer by 1.7 and 1.0 kcal mol^{-1} in binding energies without and with zero point energy correction ($-\Delta E_e$ and $-\Delta E_o$), respectively.

The MPWB1K/aVDZ-predicted adiabatic IP of $Cr(Bz)_2$ is 5.331 eV, which is close to the experimental value of 5.4665 eV. However, this MPWB1K/aVDZ fails to predict the correct structure because it favors the S-T structure more than the S-PD3. Meanwhile, M062X/aVDZ-predicted IP of $Cr(Bz)_2$ is 5.083 eV which is underestimated in comparison with both MPWB1K/aVDZ and experimental values. However, at the M062X/aVDZ (MPWB1K/aVDZ) level the changes in IP
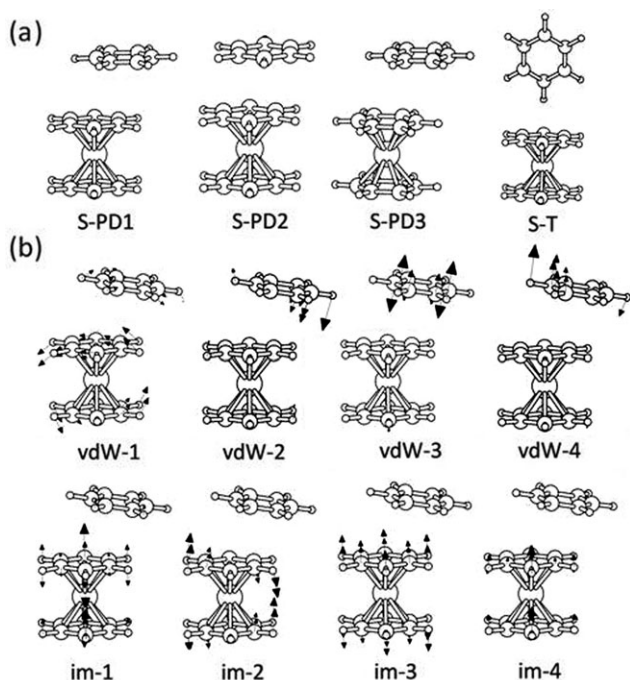
Fig. 3 (a) Structures of three different parallel displaced (PD) isomers and one T-shaped isomer of the neutral and cationic states of the S-type $Cr(Bz)_2$–Bz. Geometrical parameters are in Table 2. (b) The van der Waals modes (vdW1-4) between the extra benzene and $CrBz_2$ and the intramolecular (im) vibrational modes (im-1 to im-4) in $CrBz_2$ for the S-PD1 cationic isomer. The $Cr(Bz)_2$ for S-PD2 and S-PD3 also show the similar vibrational modes. Only the vdW-modes which affect the distance and/or angle between the interacting benzene rings by virtue of its vibrational directions are considered, whereas the vdW-modes form which the vibrational direction is toward the interchangeable PD-isomers (~ 27 cm^{-1}) are not considered.

Table 1 Interaction energies (ΔE), distance from Cr to the benzene centroid ($[R_{Cr}]$), and ionization potential (IP) of the eclipsed stacked structure S of the neutral and cationic states of $Cr(Bz)_2$ at the M062X/aVDZ level

Isomer	Eclipsed stacked structure: S
Structure	
Neutral (ΔE [R_{Cr}])	-19.40 kcal mol^{-1} [1.644 Å]
IP {Exptl. 5.4665 eV}	5.083 eV
Cation (ΔE [R_{Cr}])	-52.55 kcal mol^{-1} [1.688 Å]

(δIP) of the PD isomers (S-PD1, S-PD2, S-PD3) and the T-shaped isomer (S-T) of $Cr(Bz)_2$–Bz with respect to the IP of $Cr(Bz)_2$ upon attaching a solvent benzene molecule are -0.167 (-0.157), -0.166 (-0.158), -0.165 (-0.157) and 0.035 (0.035) eV, respectively. The δIPs of the PD isomers are in good agreement with the experimental δIP of -0.1872 eV. Thus, this negative δIP in the experiment, which agrees with the negative δIP of the parallel displaced structure PD isomers against the positive δIP of the T-shaped structure in the calculation, clearly demonstrates that the $Cr(Bz)_2$–Bz cluster in the neutral state has the parallel displaced structure.

The cationic ground state of $Cr(Bz)_2$–Bz shows three nearly isoenergetic PD isomers, which are 5 and 6 kcal mol^{-1} more stable than the T-shaped S-T structure (Table 2) at the M062X/aVDZ and MP2/aVDZ levels. Unlike in the case of neutral PD isomers, the optimized geometries of the structural isomers which lie in between the two out of S-PD1, S-PD2 and S-PD3 configurations are found to have a barrier of ~ 0.02 kcal mol^{-1}. Since the potential surface where these isomers are located is nearly flat, the van der Waals interaction modes between $Cr(Bz)_2$ and a benzene molecule (vibrational frequency of ~ 27 cm^{-1}; the corresponding zero point energy: ~ 0.04 kcal mol^{-1}) put the barriers below the zero point vibration energy of the potential surface. Thus, the conformations including the S-PD1, S-PD2 and S-PD3 configurations and the conformations along their transition paths would be quantum statistically[38] populated. In this case, the three conformations would still be slightly more populated than other wide-ranging configurations. This might lead us to speculate if the three peaks with substantial overlaps would correspond to the three more populated conformations of S-PD1, S-PD2 and S-PD3, *i.e.*, if the three structures could give three peaks with each separated by ~ 0.001 eV (~ 10 cm^{-1} or ~ 0.03 kcal mol^{-1}).

Since the experiment indicates that there exists no drastic ionization-driven structural change, the parallel-displaced structure is most likely to be the minimum energy structure of the $Cr(Bz)_2$–Bz cluster in the neutral state. Energetically, the binding energy of the most stable stacked benzene molecule in the cluster (S-PD3) increases from 3.6 kcal mol^{-1} to 7.8 kcal mol^{-1} upon ionization. The increase of binding energies upon ionization stems from the fact that the benzene ring in $Cr(Bz)_2$ is positively charged by the ionization of Cr, resulting in the typical π^+–π interaction having ~ 8 kcal mol^{-1}.[39] However, the charge resonance stabilization here would not be as strong as in the case of cationic benzene dimer.[40,41] On the other hand it could to some extent be treated as the co-operativity between cation–π and π–π interactions as in the case of cation–π–π ternary complexes.[42]

Upon ionization, the structural change of the $Cr(Bz)_2$–Bz cluster can then be found from the comparison of their structures (Table 2). The vertical distances ($R_\perp$) between the extra benzene monomer and the nearest benzene ligand of $Cr(Bz)_2$ is shortened by 0.17–0.19 Å at both M062X/aVDZ and MP2/aVDZ levels. In all the PD isomers in the neutral $Cr(Bz)_2$–Bz, the extra benzene monomer with respect to the benzene ligand of $Cr(Bz)_2$ has negligible tilted angle ($\sim 0°$ with respect to the perfect PD plane at the MP2/aVDZ level). On the other hand, in the cationic $Cr(Bz)_2$–Bz, due to the slightly positive charge of the benzene ligand of $Cr(Bz)_2$ the extra benzene monomer becomes tilted out from the perfect PD plane ($\sim -8°$). Thus, the close-up and tilting-out motion of the solvent benzene is most likely to be strongly activated in the MATI spectrum. Normal-mode analysis shows that the vdW mode calculated at 70–72 cm^{-1} (vdW-2 mode, Table 2 and Fig. 3) which is associated with the close-up and tilting-out motion could be correlated to the experimental 67 cm^{-1} band. The first, second and third overtones of this vdW-2 mode reflect the structural change of the cluster upon ionization along the tilting angle of the benzene solvent.

Table 2 M062X/aVDZ (MP2/aVDZ) geometrical parameters (R/Å, θ/°), binding energies (kcal mol^{-1}) without ($-\Delta E_e$) and with zero-point energy correction ($-\Delta E_o$) and binding free energies ($-\Delta G_{100}$ at 100 K) of the neutral and cationic Cr(Bz)$_2$–Bz clusters, ionization potential changes in eV (δIP with respect to the IP of Cr(Bz)$_2$) for the important neutral conformations, and selected low vibrational frequencies (cm^{-1}) of the cation conformations along with the experimental frequencies of the cation and the δIP of the neutral[a]

Neutral	R_{Cr}	$R_\perp$	R_d	θ	$-\Delta E_e$[b]	$-\Delta E_o$	δIP
S-PD1	1.649 (1.579)	3.369 (3.37)	1.532 (1.380)	0.6 (−1.1)	3.98 (10.3/4.19)	3.90	−0.167
S-PD2	1.649 (1.579)	3.367 (3.38)	1.530 (1.377)	−0.1 (−1.5)	3.97 (10.3/4.70)	3.85	−0.166
S-PD3	1.649 (1.581)	3.386 (3.39)	1.547 (1.518)	1.2 (0.0)	**3.99 (10.4/4.91)**	3.95	−0.165
S-T	1.641 (1.577)	4.849 (4.95)	0.000	90.0	2.30 (7.4/3.16)	2.93	0.035
Expt.							−0.1872

Cation	R_{Cr}	$R_\perp$	R_d	θ	$-\Delta E_e$	$-\Delta E_o$	$-\Delta G_{100}$
S-PD1	1.695 (1.512)	3.190 (3.20)	1.723 (1.643)	−8.1 (−8.9)	7.82 (14.5/8.64)	7.45	4.98
S-PD2	1.696 (1.512)	3.185 (3.21)	1.741 (1.620)	−8.2 (−8.8)	7.79 (14.5/8.63)	7.51	4.64
S-PD3	1.695 (1.513)	3.193 (3.22)	1.737 (1.582)	−7.6 (−8.3)	7.80 (14.5/8.60)	7.52	4.62
S-T	1.690 (1.514)	4.895 (5.00)	0.000	90.0	2.65 (10.0/2.71)	2.34	−0.12

Cation	Wavenumbers/cm^{-1}							
	vdW-1	vdW-2	vdW-3	vdW-4	im1	im2	im3	im4
S-PD1	34	72	82	86	138	139	236	298
S-PD2	30	72	82	86	138	139	236	298
S-PD3	33	70	80	88	135	138	236	296
Expt.		67					266	

[a] MP2/aVDZ energies are given in BSSE-uncorrected/-corrected energies. ΔE: interaction energy of the extra benzene with Cr(Bz)$_2$. R_{Cr}: distance from Cr to the benzene centroid, $R_\perp$: vertical stacking distance from the plane of top benzene in Cr(Bz)$_2$ to the centroid of the extra benzene, R_d: off-center distance, (all distances in Å); θ: out-of-plane tilted angle (in degrees) of the extra benzene with respect to the PD plane. At the M062X/aVDZ level, in the case of the neutral state, an S-PD3 like structure between S-PD3 and S-PD1 is predicted to be on the global minimum of the energy hypersurface, while in the cationic state the S-PD3 structure is predicted to be on the global minimum. The frequencies are exponentially scaled[33,34] to match the experimental frequencies of Cr(Bz)$_2$:[35] scale factor $\alpha = 1.998 \times 10^{-5}$. [b] Given that the binding energy difference between CCSD(T)/aVDZ′ and CCSD(T)/CBS for the parallel displaced benzene dimer is 1.8 kcal mol^{-1}, we apply this correction to the CCSD(T)/aVDZ′ − ΔE_e of the neutral S-PD3 (−1.8 kcal mol^{-1}) to get the estimated CCSD(T)/CBS binding energy of 3.6 kcal mol^{-1}.[19,37]

Upon ionization, the distance from Cr to the benzene centroid (R_{Cr}) in the PD structures is slightly elongated by ~0.05 Å at the M062X/aVDZ level, whereas it is shortened by ~0.07 Å at the MP2/aVDZ level. Upon considering the decrease in frequency of the intramolecular Bz–Cr–Bz symmetric stretching mode (im3) from Cr$^+$(Bz)$_2$ (272 cm^{-1}) to Cr$^+$(Bz)$_2$–Bz (266 cm^{-1}), R_{Cr} is likely to be slightly elongated upon complexation with another benzene. According to M06X2/aVDZ calculations, the im symmetric stretching mode changes from Cr$^+$(Bz)$_2$ (236 cm^{-1}) to Cr$^+$(Bz)$_2$–Bz (236 cm^{-1}). The MPWB1K/aVDZ im3 Bz–Cr–Bz symmetric stretching frequency changes from Cr$^+$(Bz)$_2$ (266 cm^{-1}) to Cr$^+$(Bz)$_2$–Bz (266 cm^{-1}). Thus, this im3 band involving with the vertical distance contraction in the Cr(Bz)$_2$ would be strongly activated in the MATI spectrum.

4. Conclusion

In summary, the novel type of the aromatic π–π interaction mediated by a metal has been investigated with the model system of the Cr$^+$(Bz)$_2$–Bz cluster. The free solvating benzene is non-covalently attached to the benzene moiety of Cr$^+$(Bz)$_2$ and the minimum energy geometry adopts the parallel-displaced structure according to M062X and MP2 calculations, in contrast to the T-shaped benzene dimer. Upon the ionization the solvent benzene becomes slightly closed up but tilted out with respect to the benzene plane of Cr(Bz)$_2$, which is well supported by the experiment. The IP of the Cr(Bz)$_2$–Bz cluster is found to decrease relative to that of Cr(Bz)$_2$.

The parallel-displaced structure gives a decreased IP, consistent with the experiment, resulting from the cluster stabilization energy upon ionization due to the stronger cation–π interaction in the cationic ground state. This is in contrast to the T-shaped structure which would give the IP increase upon ionization because of the Coulomb repulsion between the slightly positively charged H atom of the free solvating benzene molecule and the Cr cation. This work explains the van der Waals vibrational mode regarding the π–π interaction where a neutral benzene interacts with a cationic π-system. In conclusion, the study of the non-covalent interaction in the presence of a metal is challenging and yet would be useful for the better understanding of the structure-based biological functions, because the conformational change of the local active site, as the charge is transferred in and out from the metal, may play key roles in complex biological functions. This work opens a new possibility of utilizing the simple organometallic cluster system for the investigation of cation–π or cation–π–π interactions at the molecular level.

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