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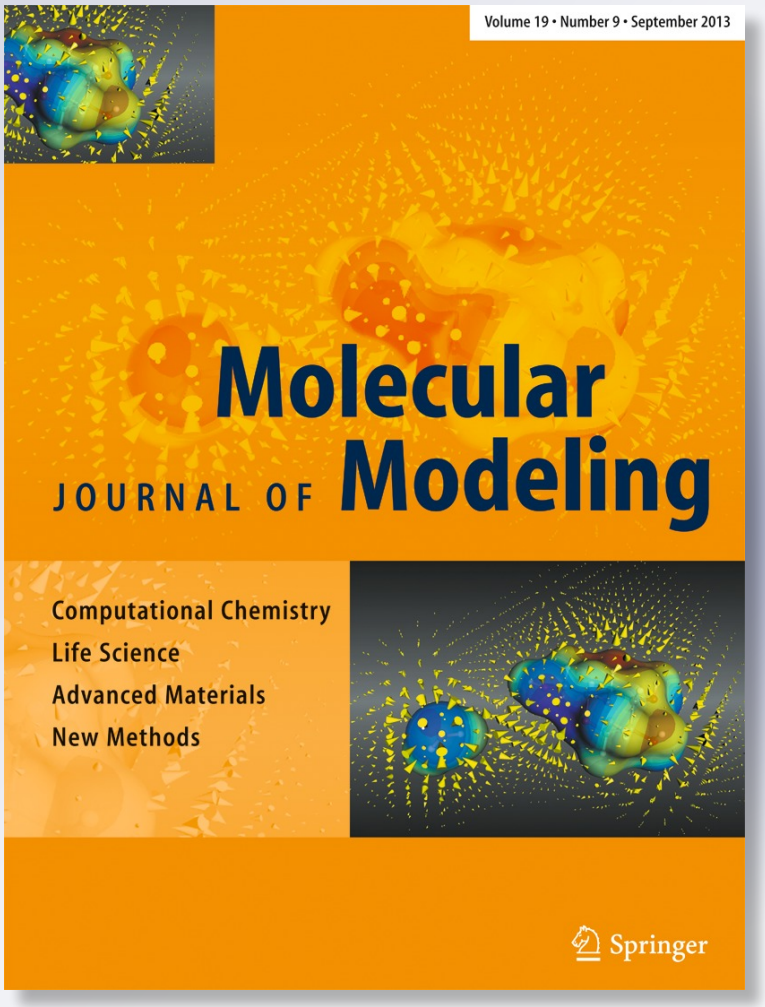

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ORIGINAL PAPER

A theoretical study on the halogen bonding interactions of C_6F_5I with a series of group 10 metal monohalides

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Abstract The halogen bonding interactions between C_6F_5I and a series of transition metal monohalides *trans*-[M(X)(2-C_5NF_4)-(PR_3)$_2$] (M = Ni, Pd, Pt; X = F, Cl, Br; R = Me, Cy) have been studied with quantum chemical calculations. Optimized geometries of the halogen bonding complexes indicate that angles C_1-I···X are basically linear (178–180°) and angles I···X-M mainly range from 90 to 150°. The strength of these metal-influenced halogen bonds alters with different metal centers, metal-bound halogen atoms and the substitutes on phosphine ligands. Electrostatic potential and natural bond orbital analysis show that both of the electrostatic and orbital interactions make a contribution to the formation of halogen bonds, while the electrostatic term plays a dominant role. AIM analysis suggests that, for *trans*-[M(F)(2-C_5NF_4)-(PR_3)$_2$] (M = Ni, Pd, Pt) monomers, the formed halogen bonding complexes are stabilized by local concentration of the charge of intermediate character, while for the metal monomers containing chlorine and bromine, a typical closed-shell interaction exist. These results prove that the structures and geometries of these halogen bonding complexes can be tuned by changing the halogen atoms and metal centers, which may provide useful information for the design and synthesis of new functional materials.

Keywords DFT · Halogen bonds · Iodoperfluoroarenes · Metal halide · NBO

Introduction

Halogen bonds are specific noncovalent interactions between a covalently bonded halogen atom in compounds of R-X (X = F, Cl, Br and I) and a Lewis base [1–7]. It has attracted widespread interest of chemists in recent years due to its potential applications in crystal engineering [1, 8, 9], materials science [10], molecular recognition [3, 11] and biological systems [12–14]. Politzer et al. [2] have explained the formation of halogen bonds with the electrostatic potential of covalent halogen atoms. They found that the charge density on the covalent halogen atom is anisotropic distribution, i.e., the electrostatic potential along the extension the C-X bond is positive and perpendicular to covalent bond is negative. The region of positive electrostatic potential is called σ-hole, which can form halogen bond with Lewis bases which are usually N, O and F atoms with lone-pair electrons, or molecules with π electrons such as ethylene, ethyne and benzene [15–17]. Meanwhile, the covalent halogen atoms may also form hydrogen bond as Lewis bases with hydrogen atom [18, 19].

In the past decades, numerous experimental and computational studies have been devoted to better understand the structure, directionality and nature of halogen bonds [20–25], and a fair amount is known about this noncovalent interaction. For example, its strength is similar to that of hydrogen bond, and increases in the order of chlorine < bromine < iodine. In general, fluorine does not form halogen bond because it lacks a positive σ-hole. However, when fluorine attaches to a strong electron withdrawing groups, it can display a σ-hole and form halogen bonds with Lewis bases [11, 26]. The structural characterization of halogen

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N. Cheng · Y. Liu (✉) · C. Zhang · C. Liu
Key Laboratory of Theoretical and Computational Chemistry in Universities of Shandong, School of Chemistry and Chemical Engineering, Shandong University, Jinan, Shandong 250100, China
e-mail: yongjunliu_1@sdu.edu.cn

Y. Liu
Northwest Institute of Plateau Biology, Chinese Academy of Sciences, Xining, Qinghai 810001, China

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bonds has been established in a wide range of situations encompassing organic compounds and main group elements.

In recent years, two types of metal-influenced halogen bonds attracted much attention. One type is the halogen bonds of M-C-X···X′ (M represents metal), which exist widely in the supramolecular networks [27, 28]. Many kinds of halogen bonds M-C-X···X′ have been studied from both theoretical and experimental points of view. For example, Xu et al. [29] studied two model complexes PyCl···X (PyCl = NC_5H_4Cl-4; X = F^-, Cl^-, or Br^-) and MPyCl···X (M = Cu^+, Zn^+) by using DFT calculations. They predicted that the anisotropy of electrostatic potential on the outer surface of covalent chlorine is enhanced due to the metal coordination, and the strength and directionality of halogen bond are thus strengthened.

Another type of halogen bonds exists in the metal complexes C-X···X′-M (usually, M is transition metal atom) [30–33]. Unlike the traditional halogen bond, this kind of halogen bond is formed between an organic halide (C-X) and an inorganic metal halide (X′-M), which also plays an important role in supramolecular self-assembly process. In these halogen bond complexes, the group which the covalent halogen is bound to and the halometallate also have significant influence on the strength and directionality of such halogen bonds [28, 29, 34, 35]. Thus we can design or suitably tune the structures and geometries of the metal-influenced halogen bonds by changing the covalent halogen atom X, the metal atom M, and the Lewis base X′. For example, Zordan et al. [36] synthesized a series of *trans*-[MCl_2(3-X′-py)$_2$] compounds (M = Pd, Pt; X′ = Cl, Br, and I). They found that two different networks, propagated through M-Cl···X′-C halogen bonds, exist in the crystals structures of these compounds. The *trans*-[$PdCl_2$(3-I-py)$_2$] and *trans*-[$PtCl_2$(3-X′-py)$_2$] (X′ = Cl, Br) are the pattern of one dimensional tapes, while the *trans*-[$PdCl_2$(3-X′-py)$_2$] (X′ = Cl, Br) and *trans*-[$PtCl_2$(3-X′-py)$_2$] (X′ = Br, I) form the two dimensional layers. In a recent review, Bertani et al. [37] demonstrated that C-X···X′-M synthon is effective in controlling the crystals structures and chemical behavior of supramolecules.

Due to the fluorination of benzene ring, perfluorinated iodoalkanes and iodoarenes have also been identified as halogen bond donors. Substituted iodoperfluoroarenes and 1,4-diiodo-tetrafluorobenzen have been widely used in designing liquid crystal and constructing halogen bond-based supramolecular architectures [38, 39]. Libri et al. studied the strong hydrogen bonds and halogen bonds formed by iodopentafluorobenzene and *trans*-(tetrafluoropyrid-2-yl)-bis(triethylphosphine) fluoronickel (NiF) in solution [40]. Recently, Perutz and co-workers [41] synthesized a series of structurally similar group 10 metal monofluoride compounds (Chart **1**) and studied the thermodynamics characteristics of the halogen bonding interactions between C_6F_5I and these monofluoride complexes by using ^{19}F-NMR titration experiments and computational approaches. They showed that the data for -ΔH^o for the halogen bonding follow a trend Ni < Pd < Pt, and the fluoropyridyl ligand has a negligible influence on the thermodynamic data, but that of the phosphine ligand is significant. Perutz et al. [41] suggested that these group 10 metal fluorides are excellent halogen bond acceptors. But how about the group 10 metal chlorides and bromides? Why the dates of halogen bonding energies follow a trend of Ni > Pd > Pt? To explore the bonding nature of C-X···X′-M halogen bond, the interactions between substituted iodoperfluoroarenes and a series of group 10 metal monohalide compounds *trans*-[M(X)(2-C_5NF_4)-(PR_3)$_2$] (M = Ni, Pd, Pt; X = F, Cl, Br; R = Me, Cy) (Chart **1**) have been systematically studied by using quantum chemistry method. We are interested in the influences of different metal atoms and halogen atoms on the strength and bonding characteristics of halogen bonds. These studies may enrich our understanding on metal-bound halogen bond, and provide useful information for developing new supramolecular synthons C-X···X′-M in supramolecular chemistry and crystal engineering.

Computational methods

For all monomers and halogen bonding complexes, geometrical optimizations and vibrational frequency calculations were performed by using density functional theory as implemented in the Gaussian 09 program package [42]. The density functional theory (DFT) method has been used in the study of large systems containing metal atoms such as MPyCl···X and PyCl···X (M = Cu, Zn) systems [11], and BHandHLYP functional can provide accurate energetics for noncovalently bonded systems [2, 43, 44]. Therefore, in this study, the BHandHLYP functional was used in conjunction with the SDD effective core potential and associated basis set on I, P, Ni, Pd and Pt and a 6-31G* basis set on the main group atoms C, H, N, F, Cl, and Br. Simultaneously, for all fluorine, chlorine and bromine atoms, diffuse functions were also added. To exam the efficiency of DFT method, a single-point energy calculation at the MP2/def2-TZVP level was also performed. Due to the size of the complexes and the computing cost of MP2, the single-point energy calculation was only applied for the complexes formed by C_6F_5I and *trans*- [Pd(X)(C_5F_4)(PMe_3)$_2$] (X = F and Cl).

The interaction energies of all given complexes (Chart 2) were calculated as the difference between the energy of complexes and the sum of energies of isolated iodoperfluoroarenes and metal halides. The basis set superposition error (BSSE) was eliminated using the Boys and Bernardi [45] counterpoise method. Libri et al. [40] have revealed that the influence of solvation effects on halogen bonding can not be negligible. Thus, after all the stationary points were located, single point electronic energy calculations with the polarized continuum

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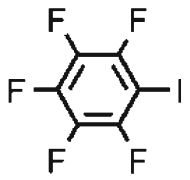
Chart 1 Substituted iodoperfluoroarenes and a series of group 10 metal monohalogenides



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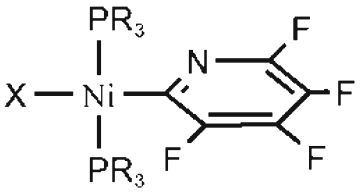
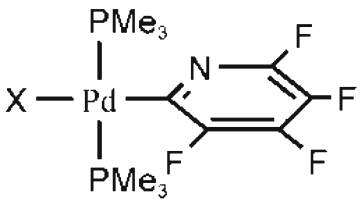
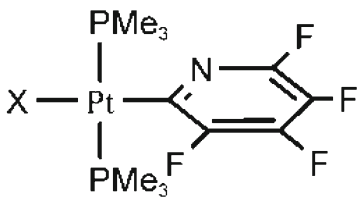


2a: R=Me, X=F ; 2b: R=Me, X=Cl
2c: R=Me, X=Br; 2d: R=Cy, X=F



3a: X=F; 3b: X=Cl; 3c: X=Br



4a: X=F; 4b:X=Cl; 4c: X=Br

model (PCM) were performed at the same level of theory [46, 47]. All interaction energies reported here also were corrected by the effect of zero-point energies. Natural bond orbital (NBO) analysis was performed for our selected systems utilizing the Gaussian NBO module [48] at the same level. To further study the bonding characteristic of the halogen bond, the atoms in molecules (AIM) analysis by means of Bader's "atoms in molecules" theory was carried out with the AIMAll program package [49].

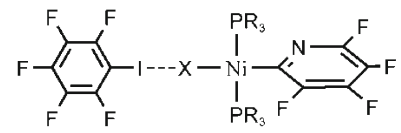
Results and discussion

Geometries and binding energies

Figure 1 depicts the optimized structures of the halogen-bonded complexes. The iodoperfluoroarenes is the halogen bond donor, and the group 10 metal monohalide compounds function as halogen bond acceptors. For a convenient and clear illustration, we number the important atoms, i.e., the carbon atoms bonding with iodine and transition metals are denoted as C_1 and C_2, while the two phosphorus atoms connecting to metals are named as P_1 and P_2, as shown in **1**-**2a**. The interaction energies (ΔE), enthalpies (ΔH), and some key geometrical parameters of the complexes are collected in Table 1. While some important bond distances of monomers (iodoperfluoroarenes and metal halides) are listed in Table S1 of Supporting information. All the optimized structures of metal halide monomers are shown in Fig. S1.

Table 1 shows that the binding distances ($R_{X\cdots I}$) between I and X (X = F, Cl, and Br) are in the range of 2.217 to 3.536 Å, which are clearly shorter than the sum of van der Waals radii of I and X atoms (the sum of van der Waals radii of I···F, I···Cl and I···Br are 3.11, 3.73 and 3.83 Å, respectively), implying a typical halogen bonding interaction between the monomers of iodoperfluoroarenes and metal halides. $R_{X\cdots I}$ of complex **1**–**5** is the shortest, which is consistent with the strongest halogen-bonding interaction of **1**–**5** with the ΔE value of −66.30 kJ mol^{-1}. For the complexes formed by C_6F_5I and *trans*-$[M(X)(C_5F_4)(PMe_3)_2]$ (M = Ni, Pd, Pt), the binding distances $R_{X\cdots I}$ follow the order F < Cl < Br, corresponding to their tendency of ΔE value. We also note that the binding distances $R_{X\cdots I}$ of F complexes (**1**-**2a**, **1**-**3a** and **1**-**4a**) are much shorter than that of other complexes, indicating that the fluorides are

Chart 2 A series of halogen-bonding complexes



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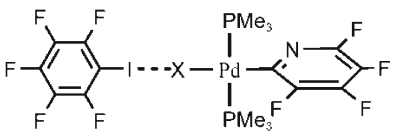

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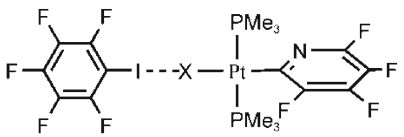

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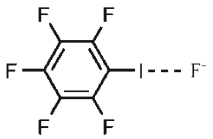

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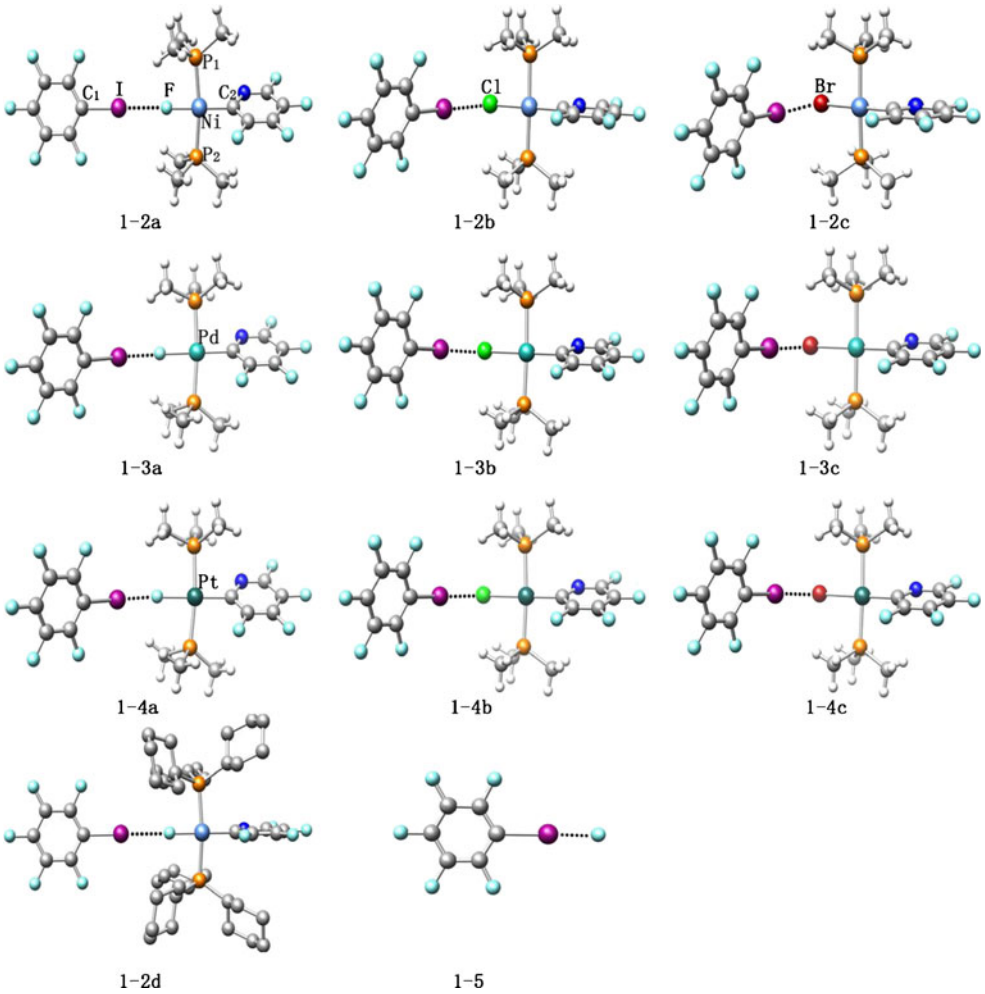

Fig. 1 The optimized structures of halogen-bonding complexes at BhandHLYP/6-31G*-SDD level

the strongest halogen bonding acceptors. As for the changes of bond lengths of R_{C_1-I}, R_{M-X}, and R_{M-C_2}, Table 1 shows that, after the formation of halogen bonded complexes, all bond lengths R_{C_1-I} and R_{M-X} are elongated, and R_{M-C_2} are contracted.

Politzer et al. have reported that halogen bonding is an electrostatic driven directional molecular interaction [2]. From Table 1, one can see that angles $\theta_{C_1-I\cdots X}$ of all complexes are basically 180°, which is consistent with the linear characteristic of halogen bond. However, the I···X-M moieties of all

Table 1 Corrected interaction energies (ΔE, kJ mol^{-1}), enthalpies (ΔH, kJ mol^{-1}), binding distance (R, Å), changes of key bond lengths (ΔR, Å) and bond angles (θ, degree) in selected halogen-bonded complexes

Complexes	ΔE	ΔH	$R_{X\cdots I}$	ΔR_{C_1-I}	ΔR_{M-X}	ΔR_{M-C_2}	$\theta_{C_1-I\cdots X}$	$\theta_{I\cdots X-M}$
1–2a	−19.87	−15.93	2.725	0.009	0.016	−0.006	180.0	179.9
1–2b	−9.29	−5.22	3.398	0.007	0.010	−0.002	179.4	118.8
1–2c	−6.63	−2.73	3.536	0.008	0.010	−0.002	178.2	92.8
1–2d	−16.59	−11.05	2.753	0.008	0.021	−0.006	179.9	179.7
1–3a	−23.68	−20.00	2.372	0.015	0.021	−0.004	179.9	147.3
1–3b	−10.49	−6.43	3.370	0.009	0.011	−0.003	179.5	117.0
1–3c	−8.98	−4.89	3.499	0.010	0.010	−0.003	179.1	103.8
1–4a	−22.24	−18.26	2.688	0.013	0.019	−0.004	179.5	142.7
1–4b	−10.27	−6.02	3.384	0.008	0.008	−0.002	179.3	115.0
1–4c	−9.01	−4.71	3.503	0.010	0.007	−0.001	178.8	106.4
1–5	−66.30	−61.28	2.217	0.151			180.0	

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metal complexes except nickel fluoride complexes are distinctly bent, agreeing well with the calculation results of Perutz et al. and the observation in a survey of H···X-M angles for hydrogen bonding involving metal halides [41, 50]. The reason that the I···X-M angles are bent is that the interactions are with the sides of the halogen X. Such angles also agree with some experimental results of M-X···X angles [33, 41].

Table 1 shows that the interaction enthalpy (ΔH) of complex **1**-**2a** is 15.93 kJ mol^{-1}, agreeing well with the experimental value of 16 kJ mol^{-1} [40]. Although there is a difference of 4 kJ mol^{-1} between interaction enthalpy (ΔH) and interaction energy (ΔE), both of them give the similar tendency of halogen bonding. Thus, we just analyze these halogen bonded complexes based on their interaction energies (ΔE) in the following sections. For all these metal-influenced complexes **1**–**2**, **1**–**3**, and **1**–**4**, the interaction energies follow the order of F < Cl < Br. The fluorides correspond to the strongest halogen bonds, and bromides correspond to the weakest halogen bonds. As for the influence of metal atoms, one can see that there are only several kJ mol^{-1} differences of interaction energies between these complexes. The interaction energies of fluoride complex follow the order of Pd < Pt < Ni. The influence of phosphine ligand is also not very significant. By changing the substitute on phosphine ligand from methyl (Me) to cyclohexyl (Cy), the interaction energy only changes from −19.87 to −16.59 kJ mol^{-1}.

To assess the efficiency of DFT method, the interaction energies of 1-3a and 1-3b were also calculated at the MP2/def2-TZVP level on the BHandHLYP optimized geometries. After the corrections of zero-point vibrational energies (ZPE) and BSSE, the interaction energies ΔE_{MP2} of complexes 1-3a and 1-3b including solvation effect are −33.49 and −22.78 kJ mol^{-1}, respectively. With respect to the MP2 results, BhandLYP method underestimates the interaction energies of halogen bonds, but both of the MP2 and BhandLYP methods give the same trend of interaction energies. Thus, we used the BhandLYP method for the calculation of interaction energies.

For further understanding the formation of halogen bonds, electrostatic potential analysis was applied to all monomers. The electrostatic potentials of C_6F_5I (**1**) and some selected metal halide monomers are shown in Fig. 2. It can be seen that there is a positive electrostatic potential cap (σ-hole) on the molecular surface of monomer **1** along the C_1-I bond, but for the metal monohalides, there are negative electrostatic regions on the outermost portions of halogen atoms X. Table 2 lists the most positive electrostatic potentials (V_{max}) for iodine atom, and the most negative electrostatic potential (V_{min}) for X atoms in the metal halide monomers. The V_{max} value for iodine atom is 37.3 kcal mol^{-1}. The V_{min} values for X atoms follow the order of F < Cl < Br, which is consistent with their binding energies of the halogen bond complexes, which indicates that the contribution of electrostatic interaction is significant.

NBO analysis

To have a deeper understanding of the nature and properties of noncovalent interactions, we perform a NBO analysis at the BhandHLYP/6-31G(d)-SDD level of theory. The important donor-acceptor orbital interactions and corresponding second-order perturbation stabilization energies E(2) are given in Table 3. There are four types of orbital interactions: LP(1)X → σ*(C-I), LP(2)X → σ*(C-I), LP(3)X → σ*(C-I), and LP(4)X → σ*(C-I). They indicate that the electron transfer always occurs from the lone electron pairs of X to C-I antibonding σ* orbital. The stabilization energy E(2) of the LP(3)X → σ*(C-I) orbital interaction is larger than that of the LP(1)X or LP(2) → σ*(C-I) in all complexes except

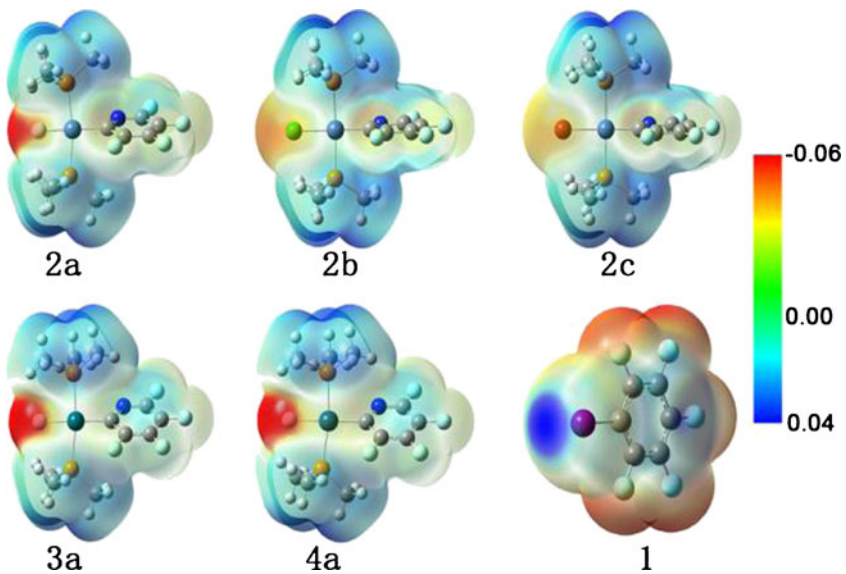

Fig. 2 Calculated electrostatic potential on the 0.001 a.u. molecular surface of selected monomers

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Table 2 The most positive electrostatic potentials (V_{max}, kcal mol^{-1}) on 0.001 a.u. surface of I atom in C_6F_5I, and the most negative electrostatic potentials (V_{min}, kcal mol^{-1}) on 0.001 a.u. outer surface of halogen atom in metal monohalogenides

Complexes	V_{max}	V_{min}
1	37.3	
2a		−43.7
2b		−30.7
2c		−27.1
2d		−44.4
3a		−50.7
2b		−34.3
3c		−30.1
4a		−48.8
4b		−32.6
4c		−28.9
5		−173.7

Table 4 Bond critical point properties (in a.u.) for halogen bond in studied complexes

Complexes	ρ_b	$\nabla^2\rho_b$	V_b	G_b	H_b	$\lvert V_b\rvert/G_b$
1–2a	0.0224	0.0900	−0.0206	0.0204	−0.0002	1.0098
1–2b	0.0109	0.0395	−0.0061	0.0077	0.0016	0.7922
1–2c	0.0107	0.0332	−0.0053	0.0066	0.0013	0.8030
1–2d	0.0212	0.0848	−0.0193	0.0191	−0.0002	1.0105
1–3a	0.0256	0.1004	−0.0235	0.0227	−0.0008	1.0352
1–3b	0.0116	0.0417	−0.0066	0.0082	0.0016	0.8049
1–3c	0.0114	0.0354	−0.0058	0.0071	0.0013	0.8169
1–4a	0.0248	0.0972	−0.0227	0.0220	−0.0007	1.0318
1–4b	0.0113	0.0407	−0.0063	0.0080	0.0017	0.7875
1–4c	0.0113	0.0352	−0.0057	0.0070	0.0013	0.8143
1–5	0.0726	0.3389	−0.0643	0.0560	−0.0083	1.1482

complex **1**–**5**. Nevertheless, the stabilization energy E(2) of LP(4)X → σ*(C-I) orbital interaction is extremely large in complexes **1**–**5**. Table 3 shows that the largest stabilization energy E(2) of each complex correlates at some extent with the corresponding interaction energy, which implies that orbital interaction plays a role in the formation of halogen bond.

As we know, the charge transfer is the concomitant of orbital interaction. Table 3 lists the charge transfer (CT) between monomer C_6F_5I and metal monohalides upon forming complexes. With the increase of atomic number of X, the charge transfer gradually increases for complexes

Table 3 Stabilization energies (E(2), kJ mol^{-1}), charge transfer (CT, e), and differences between NBO electron density in the complexes and isolated C_6F_5I in C-I sigma bonding (σ) and sigma antibonding (σ*) orbitals in complexes

Complexes	E(2)	CT	Δσ(C-I)	Δσ*(C-I)
1–2a	25.22[c]	0.0157	−0.0055	0.0212
1–2b	3.18[a], 15.93[c]	0.0226	−0.0030	0.0240
1–2c	1.76[a], 19.45[c]	0.0237	−0.0029	0.0317
1–2d	23.67[c]	0.0059	−0.0061	0.0211
1–3a	1.25[b], 30.57[c]	0.0241	−0.0067	0.0283
1–3b	1.80[b], 17.82[c]	0.0271	−0.0035	0.0273
1–3c	1.76[a], 20.41[c]	0.0348	−0.0033	0.0349
1–4a	2.93[b], 31.03[c]	0.0214	−0.0064	0.0265
1–4b	2.47[a], 17.90[c]	0.0258	−0.0031	0.0262
1–4c	2.38[a], 20.49[c]	0.0343	−0.0030	0.0340
1–5	46.75[a], 223.40[d]	0.1962	−0.0324	0.1725

[a] the LP(1)X→σ*(C-I)orbital interaction. [b] the LP(2)X→σ*(C-I)orbital interaction

[c] the LP(3)X→σ*(C-I) orbital interaction. [d] the LP(4)X→σ*(C-I) orbital interaction

X = F, Cl, Br

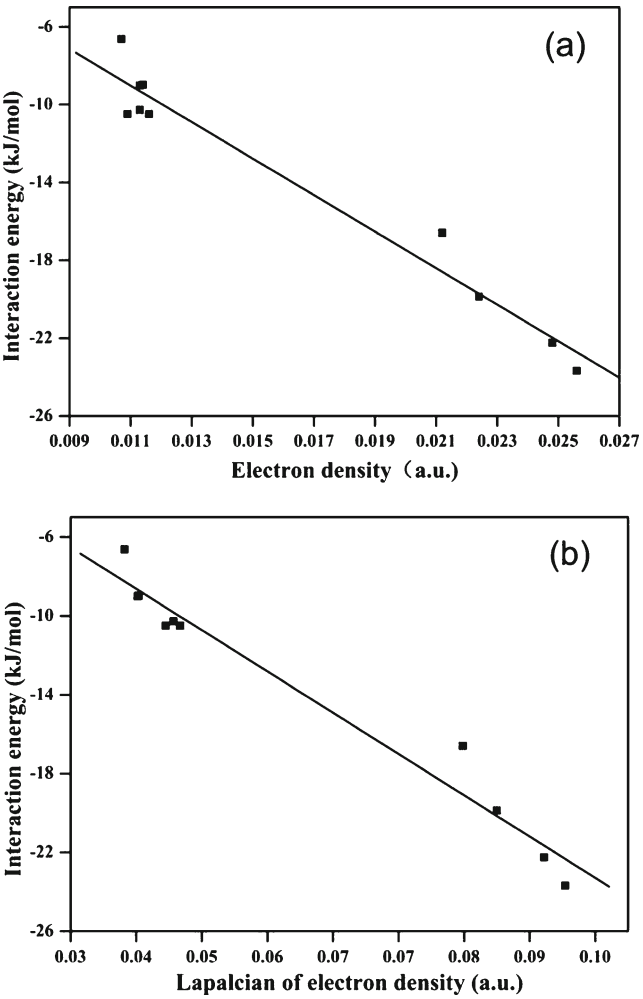

Fig. 3 **a** The relationship between the interaction energies and the electron density at bond critical points; **b** The relationship between the interaction energies and the Lapalcian of electron density at bond critical points

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C_6F_5I *trans*-[M(X)(C_5F_4)(PMe_3)$_2$]. For example, the CT value of **1-2a** is 0.0157, while that of **1-2c** is 0.0237. However, the CT values do not directly correct with interaction energies, i.e., the largest CT value does not correspond to the smallest interaction energy, which means the charge transfer plays a minor role in the formation of halogen bond. In addition, these orbital interactions in all complexes also cause an increase of electron density for σ*(C-I) and a decrease of electron density for σ(C-I). From Table 3, one can see the overall electron-density changes of σ(C-I) are very small. The electron-density increase of σ*(C-I) contributes mainly to the elongation of C-I bond.

AIM analysis

The AIM topological analysis has been widely used in the study of noncovalent interactions, such as hydrogen and halogen bonds. It is another effective method for understanding the nature of halogen bond. Therefore, we analyze the electron density (ρ_b) and corresponding Laplacian ($\nabla^2\rho_b$) at the bond critical point (BCP) of halogen bonds for all complexes. The calculation results are listed in Table 4. Koch and Popelier [51] have proposed that for closed-shell interaction, both the parameters of ρ_b and $\nabla^2\rho_b$ are positive and should be within the range of 0.002–0.035 a.u. and 0.024–0.139 a.u., respectively. Table 4 shows that all the values of ρ_b and $\nabla^2\rho_b$, except that of complex **1**–**5**, are within the proposed range. However, ρ_b at BCP of the complex **1**–**5** is beyond the above range. We found that the halogen bond in **1**–**5** has the small interaction distance R, large interaction energy ΔE, large ρ_b, positive $\nabla^2\rho_b$ and negative H_b(total energy density). These characteristics indicate that a strong intermolecular interaction is formed in complex **1**–**5**. All these topological parameters can well describe the interaction strength of the halogen bond, because they relate directly with the interaction energy. The linear relationship between ρ_b and ΔE is shown in Fig. 3a, and that of $\nabla^2\rho_b$ and ΔE is shown in Fig. 3b.

Moreover, it may be insufficient to characterize an intermolecular interaction only based on the values of ρ_b and the sign of $\nabla^2\rho_b$, therefore, the local potential energy density (V_b), local kinetic energy (G_b) and total energy density ($H_b=V_b+G_b$) at BCPs are also listed in Table 4. H_b is a more precise index to characterize weak interaction. Later, Jenkins and Morrison [52] used the ratio $|V_b|/G_b$ to describe the noncovalent interaction. For complexes involving metal monofluorides (**1-2a**, **1-2d**, **1-3a**, **1-4a**, and **1**–**5**), Table 4 shows that the values of $|V_b|/G_b$ is between 1 and 2 ($1<|V_b|/G_b<2$), and H_b is negative, which indicates that these monofluorides complexes are stabilized by local concentration of the charge of intermediate character. For the other complexes, the values of $|V_b|/G_b$ are less than 1 ($|V_b|/G_b<1$) and $\Delta H_b>0$, implying that these complexes are closed-shell interactions.

Conclusions

In this paper, a series of metal-influenced halogen bonding complexes formed by C_6F_5I and *trans*-[M(X)(2-C_5NF_4)-(PR_3)$_2$] (M = Ni, Pd, Pt; X = F, Cl, Br; R = Me, Cy) has been studied with quantum chemical calculation. The interaction energies of the metal-influenced halogen bonds in these complexes do not monotonicly depend on the atom number of group 10 metals. The data of -ΔE for the halogen bonds follow the trend Ni < Pt < Pd when X is F and Cl. Electrostatic potential and NBO analysis show that both of the electrostatic and orbital interactions contribute to the formation of halogen bonds, but the electrostatic interaction plays a dominant role. AIM calculation indicates that for *trans*-[M(F)(2-C_5NF_4)-(PR_3)$_2$] (M = Ni, Pd, Pt) monomers, the formed halogen bonding complexes are stabilized by local concentration of the charge of intermediate character, while for the metal monomers containing chlorine and bromine, a typical closed-shell interaction exist. All these results show that the metal-bound halogen atoms can be halogen bond acceptors, and the interaction strength and structures of these complexes can be controlled by changing the metal and halogen atoms. The present study may help to understand the nature of C-I···X-M halogen bond and provide useful information for the design and synthesis of new functional materials.

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