

The structure, properties, and nature of unconventional π halogen bond in the complexes of Al_4^{2-} and haloalkanes

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Abstract Quantum chemical calculations have been performed to study the all-metal π halogen bonding in Al_4^{2-} –haloalkane complexes. The result shows the existence of the all-metal π halogen bond in the complexes. There are three interaction modes (top, corner, and side) between Al_4^{2-} and haloalkane. The interaction energy of this interaction varies from a positive value to -90.54 kJ mol $^{-1}$ in Al_4^{2-} –I-ethyne-s complex. The interaction strength is affected greatly by the hybridization of C atom and follows the order of $C(sp^3) < C(sp^2) < C(sp)$ in most complexes. The methyl group in the halogen donor plays a negative contribution to the formation of halogen bond. The halogen bonding becomes stronger for the heavier halogen atom. The effect of binding site on the strength of halogen bond is related with the nature of halogen atom. The complexes have been analyzed with electrostatic potential, NICS, ELF, NBO, and AIM.

Keywords All-metal aromatic · Halogen bonding · Hybridization · Mechanism · Methylation

Introduction

Recently, halogen bonds have attracted more attention and lots of investigations have been carried out for halogen bonds due to their extensive applications in molecular

recognition [1, 2], biological systems [3–7] and crystal engineering [8–11]. A survey of structures of protein and nucleic acid clearly demonstrates the potential significance of halogen bonds in ligand binding and molecular recognition, as well as in molecular folding [12]. Thyroid hormones represent a class of naturally iodinated molecules in which halogen bonds appear to play a role in their molecular recognition, as evident by the short I···O contact between tetraiodothyroxine and its transport protein transthyretin [13]. Metrangolo et al. presented a review on the great potential of halogen bonds in the design of new and high-value functional materials [14]. Nowadays it has come to light that this specific interaction has utilization in the context of drug design [12–18]. Auffinger and co-workers screened and assembled a data set of protein and nucleic acid structures to characterize the prevalence and geometry of halogen bonds in biological systems [12]. They also pointed out that halogen bonds offer a new and versatile tool for the design of ligands as drugs and materials in nanotechnology.

Halogen bonding is an important intermolecular interaction between halogen-containing groups and various electronegative groups [19]. It is necessary to point out that electron donation is not an intrinsic necessity for the latter. Halogen bonding shares some similar characteristics with hydrogen bonding in direction and strength [20]. Thus one can easily design a halogen bond by replacing the proton of hydrogen bond with a halogen atom. In nature, halogen bonding is an electrostatically-driven interaction and belongs to a sigma-hole interaction [21–28]. The sigma-hole is a region of positive electrostatic potential on the outermost portion of the covalently-bonded halogen atom [21]. It has been demonstrated that the interaction energies of halogen bonds on several occasions correlate with the magnitude of the positive sigma-hole potential [26].

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The usual electronegative groups in halogen bonds and hydrogen bonds are those containing lone pair electrons such as oxygen and nitrogen. The groups containing π electrons are also good electronegative groups in halogen bonds and hydrogen bonds. The π electrons are usually provided by unsaturated bonds such as alkynes and aromatic compounds such as benzene. In 2001, a series of bimetallic clusters with chemical composition MA_4^- ($M=Li, Na, \text{ and } Cu$) were prepared and studied with photoelectron spectroscopy and *ab initio* calculations [29]. The result indicates that Al_4^{2-} exhibits aromatic characteristics with two delocalized π electrons. Since it was reported that all-metal clusters possess aromaticity, some special π electron donors have also attracted attention in hydrogen bonds [30]. It has been shown that all-metal aromatic systems tend to be more electron deficient compared to the corresponding aromatic hydrocarbons [31]. The electron deficiency results in an interesting new feature in all-metal aromatic systems [32].

In the very last decade, π -halogen bond interactions have received much attention in experimental and theoretical investigations as a result of their extremely important roles in a wide range of biological and chemical fields including crystal engineering, new supramolecular structures, and drug design [33–38]. In particular, they are often involved in protein-ligand interactions of the aromatic amino acids [6, 39, 40]. Furthermore, in most cases, the π -halogen bonded complexes are key intermediates in the electrophilic halogenations of alkenes, alkynes, allenes and aromatic systems [41, 42]. It has been shown that these kinds of interactions can be established between the electron-rich aromatic rings (including ringed anions) and dihalogens as well as organic halides [43]. Now we are interested in the question: Can the all-metal aromatic ring be as π -electron donors to form halogen bonds? Thus, in this paper, we will study the unconventional π halogen bond with Al_4^{2-} cluster as the electron donor and haloalkanes as the halogen donor with quantum chemical calculations. The aims are: (1) to prove that there exists an all-metal aromatic halogen bond; (2) to find out some of the characters of such all-metal aromatic halogen bond; (3) to unveil the nature of π halogen bond in all-metal aromatic halogen bond. We think that the obtained complexes can be taken as the block of the crystal or part of the alloy integrating the halogen-containing clusters.

Computational details

All calculations were carried out with the Gaussian 09 software package [44]. The geometries of all the monomers and complexes were fully optimized by means of the Moller–Plesset second-order perturbation (MP2) method in conjugation with Dunning's basis set. The aug-cc-pVDZ

[45, 46] basis set is adopted for C, H, Al, and Cl atoms, while the aug-cc-pVDZ-PP basis set for Br [47] and I [48] atoms. The MP2/aug-cc-pVDZ method has been widely used to investigate hydrogen bonding and halogen bonding [49, 50]. Symmetry was disabled in the optimization of complex structures and core electrons were not included in the correlation treatment with MP2 calculations. The optimized structures of complexes of Al_4^{2-} and bromohydrocarbons were shown in Fig. 1. The structures of corresponding monomers were shown in Fig. 2. All optimized structures were characterized as potential energy minima at the same level by verifying that all vibrational frequencies are real. The interaction energy has been calculated as the difference between the energy of the complex and the sum of energy of the monomers. It was corrected for the basis set superposition error (BSSE) using the Boys-Bernardi counterpoise scheme [51]. Table 1 presents the binding distance, C–X bond length change, C–X stretch frequency shift, and interaction energy corrected with BSSE in the complexes.

The electrostatic potential was calculated at the MP2/aug-cc-pVDZ level with WFA Surface analysis suite [52]. The result is shown in Table 2. The natural bond orbital (NBO) analysis was carried out at the HF/aug-cc-pVDZ level for these complexes using the NBO package [53] included in the GAUSSIAN09 suite of programs. Table 3 presents the charge transfer, donor orbital, acceptor orbital, and the corresponding second-order perturbation stabilization energy in the selected complexes.

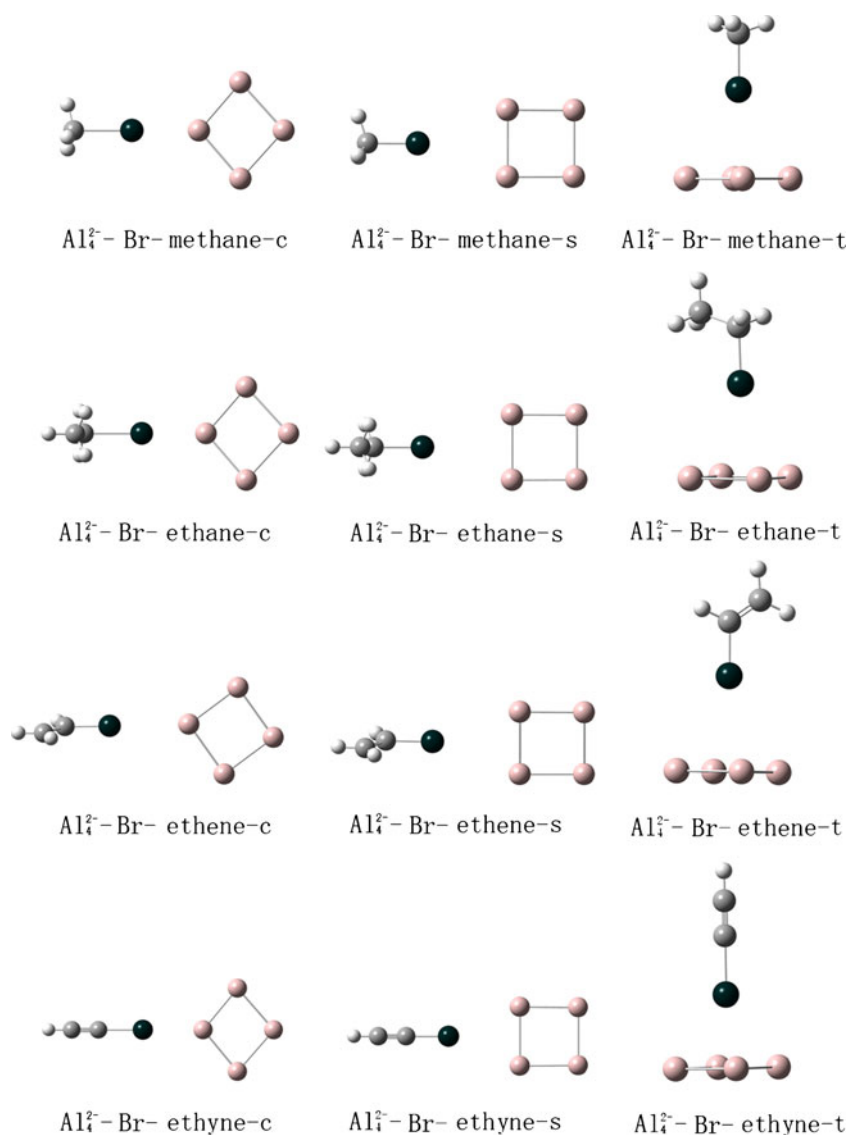
The complexes were also analyzed at the MP2/aug-cc-pVDZ level with atoms in molecules (AIM) using AIM 2000 program [54]. The sketch AIM map of $Al_4^{2-}\cdots X-R$ ($X=Cl, Br, \text{ and } I; R=CH_3, C_2H_5, C_2H_3, \text{ and } C_2H$) complexes was shown in Fig. 3. The topological analysis of the electron localization function (ELF) was performed with Multiwfn 2.01 suite of program [55]. The representation of EFL for Al_4^{2-} block and three selected complexes were shown in Figs. 4 and 5, respectively.

Results and discussion

Existence of all-metal aromatic halogen bond

The occupancy of lone pair anti-bonding orbital of each Al atom in the square Al_4^{2-} block is 0.500. This indicates that the Al_4^{2-} contains two delocalized π -electrons in the HOMO (highest occupied molecular orbital). That is to say, the Al_4^{2-} block follows the rule of $4n + 2$ electrons in aromatic compounds. To investigate the aromaticity in the Al_4^{2-} block, nuclear independent chemical shift (NICS) calculations are performed at the B3LYP/aug-cc-pVDZ level. Two Bq ghost atoms are used to designate the

Fig. 1 The optimized structures of Al_4^{2-} ...halohydrocarbon complexes



positions in the NICS calculations. Both atoms are in the center of the square Al_4^{2-} block and one angstrom apart from the Al atom along the diagonal line direction, denoted as N and M positions, respectively. The NICS value is -36.5 at the N position, which is larger than that in the benzene (-8.0) [56], and -2.3 at the M position. Both negative values confirm the existence of the π and σ aromaticity in the Al_4^{2-} block, respectively. The NICS result can also be seen with the ELF analysis as shown in Fig. 4.

Figure 4 shows the electron localization function of Al_4^{2-} cluster. As shown in Fig. 4, there are three different sites which can provide electrons: top, side, and corner of Al_4^{2-} . Thus three possible isomers would be found for each halogen donor. We denoted the three possible isomers as t (top), c (corner), and s (side), in which the halogen donor points toward the center of Al_4^{2-} plane, the corner of Al_4^{2-} cluster, and the side of Al_4^{2-} cluster, respectively. It is necessary to point out that some isomers are not obtained

for the Cl and I complexes. For the t complexes, Al_4^{2-} ...chloroethane-t and Al_4^{2-} ...iodoethyne-t are absent. For the s complexes, Al_4^{2-} ...chloroethane-s, Al_4^{2-} ...iodoethane-s, and Al_4^{2-} ...iodomethane-s are absent. For the c complexes, all chlorine-containing complexes and Al_4^{2-} ...iodoethyne-c are absent. We think that the negative electrostatic potential on the Cl atom could be partly responsible for the absence of some chlorine-containing complexes. The reason for the absence of some I complexes will be given in later chapter. One can see from Table 1 that the trend is similar for both the MP2/aug-cc-pVDZ and CCSD(T)/aug-cc-pVTZ interaction energies although there is a big difference between them. There appear more positive interaction energies in the Br complexes at the CCSD(T)/aug-cc-pVTZ level. This is inconsistent with the most positive electrostatic potential on the Br atom. Thus the following discussion on the interaction energy is based on the MP2 results.

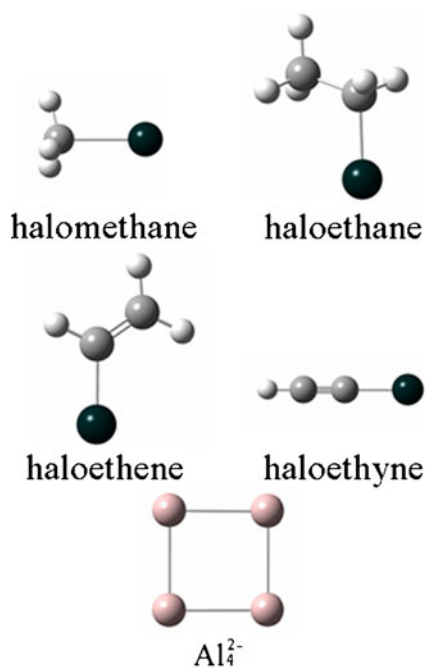


Fig. 2 The optimized structures of Al₄²⁻ and halohydrocarbon monomers

Table 1 Binding distance (R_{XB} , Å), C-X bond length change (Δr , Å), C-X stretch frequency shift ($\Delta\nu$, cm⁻¹), and interaction energy corrected with BSSE (ΔE , kJ mol⁻¹) in the complexes calculated at the MP2/aug-cc-pVDZ level

	ΔE_{MP2}	$\Delta E_{CCSD(T)}^a$	R_{XB}	$\Delta r(C-X)^b$	$\Delta\nu(C-X)^b$
Al ₄ ²⁻ ...Cl-methane-t	7.69	13.16	3.770	0.001(1.797)	-24(750)
Al ₄ ²⁻ ...Cl-ethene-t	-3.93	2.43	3.738	-0.009(1.745)	-9(733)
Al ₄ ²⁻ ...Cl-ethyne-t	-28.25	-20.69	3.546	0.010(1.657)	-66(754)
Al ₄ ²⁻ ...Br-methane-t	-7.26	3.37	3.185	0.075(1.942)	-194(634)
Al ₄ ²⁻ ...Br-ethane-t	-6.11	4.18	3.299	0.043(1.955)	-104(596)
Al ₄ ²⁻ ...Br-ethene-t	-18.53	-8.51	3.376	0.025(1.889)	-283(629)
Al ₄ ²⁻ ...Br-ethyne-t	-51.39	-40.35	2.637	0.315(1.798)	-280(611)
Al ₄ ²⁻ ...I-methane-t	-43.10	-25.21	2.877	0.295(2.149)	-246(558)
Al ₄ ²⁻ ...I-ethane-t	-37.55	-16.17	2.899	0.286(2.164)	-211(534)
Al ₄ ²⁻ ...I-ethene-t	-46.12	-30.28	2.979	0.216(2.099)	-203(557)
Al ₄ ²⁻ ...Cl-methane-s	11.5	11.06	4.222	-0.004(1.797)	-1(750)
Al ₄ ²⁻ ...Cl-ethene-s	0.71	1.12	3.984	-0.011(1.745)	1(733)
Al ₄ ²⁻ ...Cl-ethyne-s	-22.88	-21.61	3.642	0.008(1.657)	-57(754)
Al ₄ ²⁻ ...Br-methane-s	-1.34	0.23	3.533	0.038(1.942)	-81(634)
Al ₄ ²⁻ ...Br-ethane-s	0.59	1.99	3.608	0.021(1.955)	-21(596)
Al ₄ ²⁻ ...Br-ethene-s	-12.20	-10.01	3.558	0.015(1.889)	-57(629)
Al ₄ ²⁻ ...Br-ethyne-s	-43.80	-38.24	3.182	0.096(1.798)	-276(611)
Al ₄ ²⁻ ...I-ethene-s	-38.00	-31.53	3.264	0.145(2.099)	-199(557)
Al ₄ ²⁻ ...I-ethyne-s	-90.54	-90.94	3.023	0.357(2.002)	-309(522)
Al ₄ ²⁻ ...Br-methane-c	-14.89	-0.72	2.714	0.410(1.942)	-191(634)
Al ₄ ²⁻ ...Br-ethane-c	-11.95	7.27	2.692	0.462(1.955)	-113(596)
Al ₄ ²⁻ ...Br-ethene-c	-9.82	-7.78	3.392	0.031(1.889)	-89(629)
Al ₄ ²⁻ ...Br-ethyne-c	-50.17	-53.21	2.832	0.290(1.798)	-328(611)
Al ₄ ²⁻ ...I-methane-c	-43.17	-34.44	3.010	0.287(2.149)	-183(558)
Al ₄ ²⁻ ...I-ethane-c	-37.92	-27.13	3.003	0.289(2.164)	-227(534)
Al ₄ ²⁻ ...I-ethene-c	-43.07	-38.08	3.092	0.191(2.099)	-196(557)

^a The CCSD(T)/aug-cc-pVTZ results are obtained with a single-energy calculation on the MP2/aug-cc-pVDZ geometries

^b The data in parentheses in the fourth and fifth lines are the C-Br bond length and its stretch frequency in the monomers, respectively

Table 2 The most positive electrostatic potentials ($V_{s,max}$, kcal mol⁻¹) on surface of halogen atom and the most negative electrostatic potentials ($V_{s,min}$, kcal mol⁻¹) on surface of Al₄²⁻ in the monomers calculated at the B3PW91/6-31 G(d,p) level

	$V_{s,max}$		$V_{s,min}$
Cl-methane	-1.5	Al ₄ ²⁻ (c)	-137.5
Cl-ethane	-4.4	Al ₄ ²⁻ (s)	-153.0
Cl-ethene	4.1	Al ₄ ²⁻ (t)	-154.2
Cl-ethyne	25.9		
Br-methane	9.4		
Br-ethane	6.7		
Br-ethene	15.4		
Br-ethyne	37.4		
I-methane	17.9		
I-ethane	14.7		
I-ethene	23.3		
I-ethyne	43.5		

Surface defined by 0.001 electrons/bohr³ contour of electronic density

In the c complexes, the binding distance is calculated to be 2.7–3.4 and 3.0–3.1 Å for the Al⋯Br and Al⋯I contacts,

Table 3 Charge transfer (CT, e), donor orbital, acceptor orbital, and the corresponding second-order perturbation stabilization energy (E^2 , kcal mol⁻¹) in the selected complexes calculated at the HF/aug-cc-pVDZ level

	CT	Donor orbital	Acceptor orbital	E^2
Al ₄ ²⁻ ⋯Br-ethene-c	0.037	n(Al)	σ*(Br-C)	5.88
Al ₄ ²⁻ ⋯Br-ethene-s	0.031	σ(Al-Al)	σ*(Br-C)	4.18
Al ₄ ²⁻ ⋯Br-methane-t	0.133	π*(Al)	σ*(Br-C)	7.44
Al ₄ ²⁻ ⋯Br-ethane-t	0.087	π*(Al)	σ*(Br-C)	4.74
Al ₄ ²⁻ ⋯Br-ethene-t	0.072	π*(Al)	σ*(Br-C)	3.47
Al ₄ ²⁻ ⋯Br-ethyne-t	0.672	π*(Al)	σ*(Br-C)	894.56
Al ₄ ²⁻ ⋯Cl-ethyne-s	0.011	σ(Al-Al)	σ*(Cl-C)	2.05
Al ₄ ²⁻ ⋯Br-ethyne-s	0.130	σ(Al-Al)	σ*(Br-C)	13.48
		n(Al)	σ*(Br-C)	7.20
Al ₄ ²⁻ ⋯I-ethyne-s	0.675	σ(Al-Al)	n(I)	87.69
		n(I)	π*(Al)	58.06

respectively. Both ranges are smaller than the sum of the van der Waals Radii of Al and X atoms (about 4.5 Å). This indicates that there is an attractive force named halogen bond, which is responsible for the stability of the complexes. In some complexes such as Al₄²⁻⋯Cl-methane-t, Al₄²⁻⋯Cl-methane-s, Al₄²⁻⋯Cl-ethene-s, Al₄²⁻⋯Br-ethane-s, the interaction energies are positive, indicating that these complexes are unstable. This is consistent with the negative electrostatic potential on the Cl atom in Cl-methane and the small positive electrostatic potential on the

Cl atom in Cl-ethene and Br atom in Br-ethane. The interaction energy is changed greatly from 11.50 kJ mol⁻¹ in Al₄²⁻⋯Cl-methane-s complex to -90.54 kJ mol⁻¹ in Al₄²⁻⋯I-ethyne-s complex. The interaction energy in some complexes is so large that such complexes can exist. The existence of all-metal π halogen bond is also evidenced with critical points in the complexes as shown in Fig. 3.

Upon complexation, the C-X bond is elongated in most complexes and the corresponding stretch vibration displays a red shift. In three complexes (Al₄²⁻⋯Cl-ethene-t, Al₄²⁻⋯Cl-methane-s, and Al₄²⁻⋯Cl-ethene-s), the C-X bond is shortened and the respective stretch vibration exhibits a very small shift. This is consistent with the positive interaction energy in the three complexes. The biggest red shift is 66, 328, and 309 cm⁻¹ for the Cl, Br, and I complexes, respectively. Considering the large atomic mass of the halogen atoms (Cl, Br, I), the red shifts predicted could likely be observed experimentally via spectroscopic methods. This means that such complexes can be studied with spectroscopic methods in future. The red shift of C-Br stretch vibration can be explained with the charge transfer into anti-bonding C-Br orbital as shown in Table 3. However, such explanation is negated by the fact that a blue shift is sometimes observed for the C-Br bond.

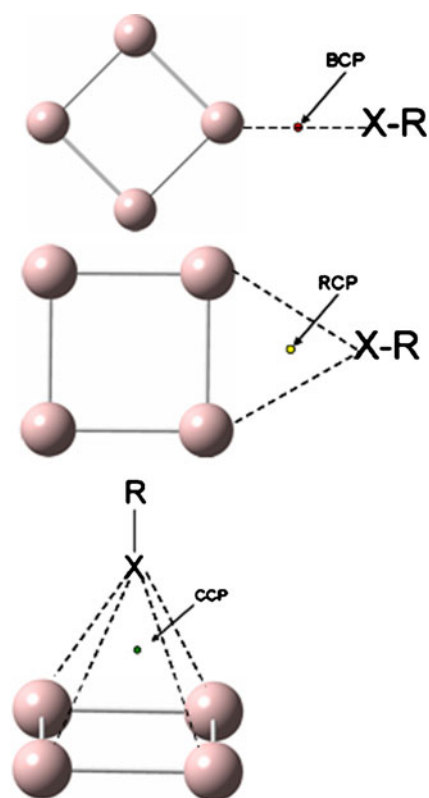


Fig. 3 Sketch AIM map of Al₄²⁻⋯X-R (X=Cl, Br, and I; R=CH₃, C₂H₅, C₂H₃, and C₂H) complexes in three positions

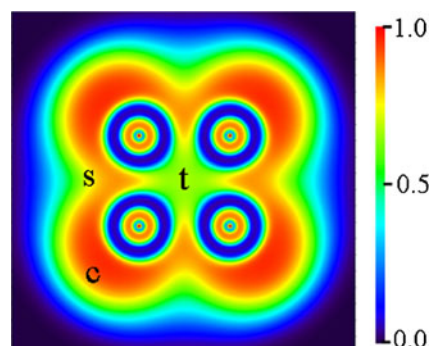
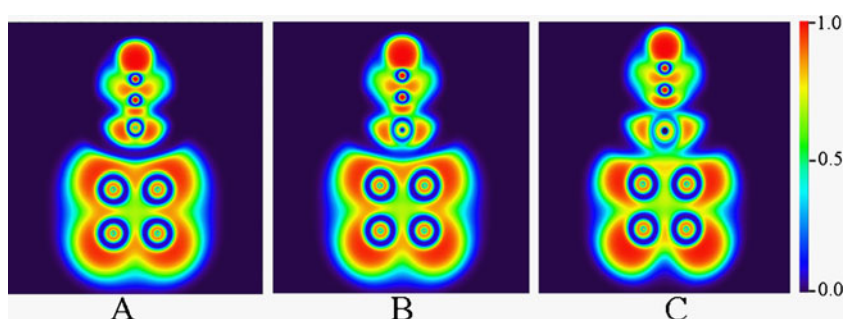


Fig. 4 Representation of electron localization function for Al₄²⁻ block

Fig. 5 Representation of electron localization function for $\text{Al}_4^{2-}\cdots\text{Cl-ethyne-s}$ (a), $\text{Al}_4^{2-}\cdots\text{Br-ethyne-s}$ (b), and $\text{Al}_4^{2-}\cdots\text{I-ethyne-s}$ (c) complexes



Hybridization effect

It has been demonstrated that the strength of C-H hydrogen bond is related with hybridization and it increases in order of $\text{C}(\text{sp}^3)\text{-H}<\text{C}(\text{sp}^2)\text{-H}<\text{C}(\text{sp})\text{-H}$ for $\text{C-H}\cdots\text{O}$, $\text{C-H}\cdots\text{N}$, $\text{C-H}\cdots\text{F}$, and $\text{C-H}\cdots\text{S}$ hydrogen bonds [57–61]. Thus we consider the effect of hybridization on the strength of all-metal π halogen bond.

In most cases, the interaction energy in the $\text{C}(\text{sp})$ complex is largest, followed by the $\text{C}(\text{sp}^2)$ complex, and that in the $\text{C}(\text{sp}^3)$ complex is smallest. This is similar to that in C-H hydrogen bonds [57–61] and Au-bonding [62]. One exception is that the interaction energy in $\text{Al}_4^{2-}\cdots\text{Br-ethene-c}$ complex is less negative than that in the corresponding $\text{C}(\text{sp}^3)$ complex. The interaction energy in $\text{Al}_4^{2-}\cdots\text{Br-ethene-c}$ complex is about three times as much as that in $\text{Al}_4^{2-}\cdots\text{Br-ethane-c}$ complex, indicating that the hybridization has a great effect on all-metal π halogen bond complexes.

The binding distance decreases in order of $\text{C}(\text{sp}^3)\text{-X}<\text{C}(\text{sp}^2)\text{-X}<\text{C}(\text{sp})\text{-X}$ in most complexes although it is abnormal in $\text{Al}_4^{2-}\cdots\text{Br-t}$, $\text{Al}_4^{2-}\cdots\text{I-t}$, $\text{Al}_4^{2-}\cdots\text{Br-c}$, and $\text{Al}_4^{2-}\cdots\text{I-c}$ complexes. In the $\text{Al}_4^{2-}\cdots\text{Br-t}$ complex, the binding distance in $\text{Al}_4^{2-}\cdots\text{Br-ethane-t}$ complex is smaller than that in $\text{Al}_4^{2-}\cdots\text{Br-ethene-t}$ complex. In the $\text{Al}_4^{2-}\cdots\text{I-t}$, $\text{Al}_4^{2-}\cdots\text{Br-c}$, and $\text{Al}_4^{2-}\cdots\text{I-c}$ complexes, the binding distance is smallest in the $\text{C}(\text{sp}^3)$ complex. Clearly, there appears some inconsistency of the binding distance with the interaction energy in these complexes.

Taking the $\text{Al}_4^{2-}\cdots\text{Br-t}$ complex as an example, the dominant orbital interaction is $\pi^*(\text{Al})\rightarrow\sigma^*(\text{Br-C})$ (Table 3). The corresponding stabilization energy is $894.56\text{ kcal mol}^{-1}$ in $\text{Al}_4^{2-}\cdots\text{Br-ethyne-t}$ complex, and the charge transfer in the complex is also very big (0.672 e). This shows that the charge transfer interaction plays a main role in $\text{Al}_4^{2-}\cdots\text{Br-ethyne-t}$ complex. The stabilization energy and charge transfer in $\text{Al}_4^{2-}\cdots\text{Br-ethene-t}$ and $\text{Al}_4^{2-}\cdots\text{Br-ethane-t}$ complexes are small, but they are inconsistent with the interaction energies in both complexes. However, the interaction energies in both complexes are consistent with the most positive electrostatic potential associated with Br atom, which is 6.7 and $15.4\text{ kcal mol}^{-1}$ in Br-ethane and Br-

ethene, respectively. This provides further evidence that the electrostatic interaction is of greater importance in such complexes.

Methylation effect

Methylation has been widely concerned for a long time [63–65]. In a very recent investigation performed by Assaf Zemach et al. [66], it has demonstrated that extant DNA methylation systems are mosaics of conserved and derived features and gene body methylation is an ancient property of eukaryotic genomes. In our previous works [67, 68], we reported that the methyl group in hydrogen bonds is electron-donating in the proton acceptor and electron-withdrawing in the proton donor. Thus we are interested in the role of methyl group in the all-metal π halogen bonds. One can see from Table 1 that the interaction energy is less negative in the ethane complex than that in the methane complex, indicating that the methyl group in the halogen donor plays a negative contribution to the formation of all-metal π halogen bond. This is different from that in $\text{OH}\cdots\text{O}$ hydrogen bond in dimethylsulfoxide-methanol complex [61] but is the same as that in $\text{CH}\cdots\text{O}$ hydrogen bond in ethyne-methanol complex [62].

For the t and s complexes, the binding distance is bigger in the ethane complex than that in the methane complex, whereas for the c complex, the former is smaller than the latter. The elongation of C–X bond is smaller in the ethane complex than that in the methane complex for the t and s complexes, while the former is larger than the latter for the c complex. The red shift of C–X stretch vibration is smaller in the ethane complex than that in the methane complex except in $\text{Al}_4^{2-}\cdots\text{I-ethane-c}$ and $\text{Al}_4^{2-}\cdots\text{I-methane-c}$ complexes.

The NPA charge on the methyl group is -0.124 e in bromoethane and it is changed to be -0.002 e in $\text{Al}_4^{2-}\cdots\text{Br-ethane-t}$ complex. The decrease of negative charge on the methyl group means that the methyl group is electron-donating in formation of halogen bond. This means the charge (-0.054 e) on Br atom in bromoethane is more negative than that (-0.030 e) in bromomethane. Simulta-

neously, the most positive electrostatic potential associated with Br atom in bromoethane ($6.7 \text{ kcal mol}^{-1}$) is smaller than that in bromomethane ($9.4 \text{ kcal mol}^{-1}$). The electron-donating of methyl group in the halogen donor is thus unfavorable to the formation of halogen bond. The orbital interaction also supports the above conclusion. The stabilization energy due to the $\pi^*(\text{Al}) \rightarrow \sigma^*(\text{Br-C})$ in $\text{Al}_4^{2-} \cdots \text{Br-ethane-t}$ complex is smaller than that in $\text{Al}_4^{2-} \cdots \text{Br-methane-t}$. The charge transfer in the former is also smaller than that in the latter.

Position influence

Half of the Cl complexes are absent, especially for the c complexes. Hu et al. [69] reported that the all metal hydrogen bond is formed in complex of Al_4^{2-} and HF. A hydrogen bond is also found in $\text{Al}_4^{2-} \cdots \text{chloroethane}$ complex and the interaction energy is calculated to be $-49.14 \text{ kJ mol}^{-1}$, which is larger than that in HF dimer ($-28.0 \text{ kJ mol}^{-1}$). On the other hand, the interaction energies in $\text{Al}_4^{2-} \cdots \text{Cl-methane-s}$, $\text{Al}_4^{2-} \cdots \text{Cl-methane-t}$, and $\text{Al}_4^{2-} \cdots \text{Cl-ethene-t}$ complexes are positive, indicating that these molecular pairs are unfavorable. The interaction energy is $-28.25 \text{ kJ mol}^{-1}$ in $\text{Al}_4^{2-} \cdots \text{Cl-ethyne-t}$ complex, while it is $-22.88 \text{ kJ mol}^{-1}$ in $\text{Al}_4^{2-} \cdots \text{Cl-ethyne-s}$ complex. In general, one can see that the Cl-t complex is the most stable, followed by the Cl-s one, and the Cl-c one is the most unstable.

As to $\text{Al}_4^{2-} \cdots \text{I-ethene}$ complex, the interaction energy is -38.00 , -43.07 , and $-46.12 \text{ kJ mol}^{-1}$ in $\text{Al}_4^{2-} \cdots \text{I-ethene-s}$, $\text{Al}_4^{2-} \cdots \text{I-ethene-c}$, and $\text{Al}_4^{2-} \cdots \text{I-ethene-t}$ complexes, respectively. Obviously, the interaction strength is smallest in the s complex and largest in the t complex. For $\text{Al}_4^{2-} \cdots \text{I-ethyne}$ complex, however, only one isomer ($\text{Al}_4^{2-} \cdots \text{I-ethyne-s}$ complex) is obtained and its interaction energy is $-90.54 \text{ kJ mol}^{-1}$. The reason for the absence of $\text{Al}_4^{2-} \cdots \text{I-ethyne-c}$ and $\text{Al}_4^{2-} \cdots \text{I-ethyne-t}$ complexes may be that a reaction occurs between them due to the strong interaction. For $\text{Al}_4^{2-} \cdots \text{I-methane}$ complex, the s complex is absent due to the extremely weak interaction, and the interaction energies are -43.17 and $-43.10 \text{ kJ mol}^{-1}$ in the c and t complexes, respectively.

For the Br complexes, the sequence of interaction strength is apparently relevant to the hybridization. The interaction strength in the sp^3 hybridization complexes is sequenced in the order: $s < t < c$. For the sp^2 hybridization complexes, it follows the order of $c < s < t$. As to the sp hybridization complexes, the sequence is similar to the I complexes.

The type of the orbital interaction is different in the c, s, and t isomers. The donor orbital is $n(\text{Al})$, $\sigma(\text{Al-Al})$, and $\pi^*(\text{Al})$ in $\text{Al}_4^{2-} \cdots \text{Br-ethene-c}$, $\text{Al}_4^{2-} \cdots \text{Br-ethene-s}$, and $\text{Al}_4^{2-} \cdots \text{Br-ethene-t}$ complexes, respectively. The corresponding stabilization energy shows a reverse change with the interaction

energy. The charge transfer is $0.072 e$ in the t complex, while it is smaller in the s complex than that in the c complex. The most negative electrostatic potentials at the t, s, and c sites are -154.2 , -153.0 , and $-137.5 \text{ kcal mol}^{-1}$, respectively, which is consistent with the interaction energy in the Br-ethene complexes. This also shows that the electrostatic interaction plays a main role in the Br-ethene complexes.

Halogen effect

It has been demonstrated that the strength of halogen bond is dependent mainly on the nature of halogen atom [26]. F atom seldom participates in halogen bonding although it can form a halogen bond when it adjoins with an electron-withdrawing group [50]. In general, the strength of halogen bond increases in order of $\text{Cl} < \text{Br} < \text{I}$ in conventional halogen bonds. One can see that the interaction energy is most negative in the I-containing complex, followed by the Br complex, and the Cl complex gives the least negative interaction energy. The binding distance also follows the same change in most complexes except in the c complex. This indicates that in the all-metal π halogen bond the strength follows the increased order: $\text{Cl} < \text{Br} < \text{I}$, which is like that in conventional halogen bonds [26].

The strength of halogen bond can also be understood with the orbital interaction besides the electrostatic potential on halogen atom. In $\text{Al}_4^{2-} \cdots \text{Cl-ethyne-s}$ complex, the $\sigma(\text{Al-Al}) \rightarrow \sigma^*(\text{Cl-C})$ orbital interaction is a main one and its stabilization energy is $2.05 \text{ kcal mol}^{-1}$. In $\text{Al}_4^{2-} \cdots \text{Br-ethyne-s}$ complex, besides the $\sigma(\text{Al-Al}) \rightarrow \sigma^*(\text{Br-C})$ orbital interaction, there is a $n(\text{Al}) \rightarrow \sigma^*(\text{Br-C})$ orbital interaction. One can see that the former is stronger than the latter according to the stabilization energy. Both types of stabilization energies are larger than that in $\text{Al}_4^{2-} \cdots \text{Cl-ethyne-s}$ complex. In $\text{Al}_4^{2-} \cdots \text{I-ethyne-s}$ complex, however, the acceptor orbital is π -character lone pair orbital from I atom not the $\sigma^*(\text{I-C})$ orbital, and its stabilization energy is larger than that of the $\sigma(\text{Al-Al}) \rightarrow \sigma^*(\text{Br-C})$ orbital interaction. Additionally, there is also another orbital interaction with $n(\text{I})$ as the donor orbital and $\pi^*(\text{Al})$ as the acceptor orbital. This shows that the $\text{Al}_4^{2-} \cdots \text{I-ethyne-s}$ interaction exhibits a certain degree of feedback-bond. The charge transfer also supports the strength of halogen bond in $\text{Al}_4^{2-} \cdots \text{Cl-ethyne-s}$, $\text{Al}_4^{2-} \cdots \text{Br-ethyne-s}$, $\text{Al}_4^{2-} \cdots \text{I-ethyne-s}$ complexes. This shows that the charge transfer interaction is also important in the complexes like the electrostatic interaction.

The difference of interaction strength in the above three complexes can also be seen with ELF as shown in Fig. 5. For $\text{Al}_4^{2-} \cdots \text{Cl-ethyne-s}$ complex, the electron localization area is separated into two parts, indicating that the interaction is electrostatic. For $\text{Al}_4^{2-} \cdots \text{I-ethyne-s}$ complex, however, the electron localization area is connected together, showing the interaction is partially covalent.

Conclusions

In the present work, the complexes of Al_4^{2-} and halo-hydrocarbon have been studied with quantum chemical calculations at the MP2/aug-cc-pVDZ level. NICS analysis indicates that there are π - and σ -aromaticity in the Al_4^{2-} block. The results show that there is an all-metal π halogen bonding in the complexes. The all-metal π halogen bonding could be very strong, for example, the interaction energy amounts to $-90.54 \text{ kJ mol}^{-1}$ in $Al_4^{2-}\cdots I$ -ethyne-s complex. The strength of halogen bonding interaction follows the order of $C(sp^3) < C(sp^2) < C(sp)$, and the effect of hybridization on it is more prominent than on hydrogen bonds. The methyl group in the halogen donor is electron-donating, and thus it weakens the strength of halogen bond. As expected, the strength of the halogen bond is also dependent on the nature of halogen atom and interaction sites. The analyses of electrostatic potentials, NBO, and ELF shows that the electrostatic interaction and charge transfer interaction play different contributions in different complexes and some complexes exhibit a character of partially covalent bond.

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