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Exploring a new kind of aromatic hydrogen bond: hydrogen bonding to all-metal aromatic species†

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Based on the recent advance of the aromaticity concept into all-metal species, we put forward a new kind of hydrogen bond: hydrogen bonding to all-metal aromatic species. The similarities and differences between the hydrogen bonds in all-metal aromatic systems and those in traditional organic aromatic systems are systematically explored: we investigated the interactions between all-metal aromatic complexes Al_4^{2-}/Al_4M (M = Mg^{2+}, Ca^{2+}, $2Na^+$) and H–Y (Y = CH_3, NH_2, OH, F, Cl, Br) as well as those between benzene and H–Y. Geometric configuration calculations, molecular orbital (MO) analysis, nuclear independent chemical shift (NICS) and frequency shift (FS) as well as binding energy calculations were employed for the investigation of the $Al_4^{2-}\cdots$H–Y, $Al_4M\cdots$H–Y and $C_6H_6\cdots$H–Y complexes. The calculated results revealed that there exist distinct differences between the hydrogen bonds in all-metal aromatic systems and those in traditional organic aromatic systems in many aspects such as binding energy and interaction distance as well as frequency shift of H–Y. Furthermore, because the aromaticity of all-metal aromatic systems can be changed by interaction with different metal ions, the intensity of hydrogen bonding can also be adjusted and controlled by changing the ions. The natures of hydrogen bonds in all-metal aromatic systems are summarized.

1. Introduction

Recently, the aromaticity concept has been expanded to all-metal complexes by the surprising finding of aluminide clusters Al_4^{2-}.[1] A square Al_4^{2-} unit has two delocalized π electrons in the highest occupied molecular orbital (HOMO). In addition, the $4n + 2$ electron counting rule is satisfied with the two delocalized π electrons ($n = 0$), hence the square Al_4^{2-} was proposed to be aromatic.[1] Since then, the special aromaticity has been continually found in other metallic clusters Ga_4^{2-}, In_4^{2-},[2] XAl_3^- (X = Si, Ge, Sn, Pb),[3] Pn_5^- (Pn = P, As, Sb, Bi),[4] Hg_4^{6-},[5] X_3^- (X = B, Al, Ga)[6] and the concept of metal aromaticity has also been widely used to explain the special stability of many complexes.[2,7–8]

The aromaticity of the all-metal aromatic complex and that of the organic aromatic complex are quite different.[1,9] The energies of the π-MO and σ-MOs are also different for the two types of complex.[4] The predicted magnetic response of Al_4^{2-} is significantly different from that of the conventional carbon-based aromatics.[10] Definitely, the Al_4^{2-} has 3-fold aromaticity whereas benzene has only 1-fold aromaticity. The resonance energy of Al_4^{2-} is at least 2.5 times larger than that of C_6H_6.[11] The aromatic ring-current shielding calculations show that the square-shaped Al_4^{2-} ring sustains a very large diatropic ring current in an external magnetic field.[12] We had reached a conclusion that the ability of an all-metal aromatic complex to adsorb gas molecules is much stronger than that of C_6H_6 based on these differences.[13]

The π–H hydrogen bond is a interesting issue in both chemistry and biology and it plays an important role in maintaining biological structure.[14–19] However, within the concept of organic aromaticity, only organic aromatic hydrogen bonds were proposed and investigated, such as $C_6H_6\cdots CH_4$,[14–15] $C_6H_6\cdots NH_3$,[14,16] $C_6H_6\cdots H_2O$,[14,17] $C_6H_6\cdots HF$[14,18] *etc.* Actually, theoretical studies predicted the existence of the organic aromatic hydrogen bonds, and most of them have already been observed by experiment.[19]

The discovery of metallic aromaticity inspired us to explore whether hydrogen bonding can occur with all-metal aromatic species. In a former study, we found that all-metal aromatic complexes could provide their delocalized π-orbitals to act as proton acceptors by forming hydrogen bonds with HF, and thus a new kind of hydrogen bond, the hydrogen bond in all-metal aromatic systems, was put forward.[20] Without doubt, it is also an interesting question whether there are any similarities or differences between the hydrogen bonds in all-metal aromatic systems and those in traditional organic aromatic systems. Does there still exist an aromatic hydrogen bond when other H–Y molecules such as CH_4, NH_3, H_2O, HCl and HBr act as the hydrogen donor? Does the hydrogen bond in all-metal aromatic systems have any peculiarities? The present work will address these questions by systematic investigations of the interactions between Al_4^{2-}/Al_4M (M = Mg^{2+}, Ca^{2+}, $2Na^+$)/C_6H_6 and H–Y (Y = CH_3, NH_2, OH, F, Cl, Br). Furthermore, deeper understanding of the hydrogen bond in all-metal aromatic systems will help us to explore the nature of the aromaticity of the all-metal system.

2. Computational methods

We optimized the structures of $Al_4^{2-}\cdots$H–Y at the B3LYP/6-311++G**, B3LYP/aug-cc-pVDZ, MP2/6-311++G** and MP2/aug-cc-pVDZ levels of theory, respectively. Energy and frequency calculations as well as zero-point energy (ZPE) corrections have been performed at the same theory level. The calculations of $Al_4M\cdots$H–Y and $C_6H_6\cdots$H–Y were performed at the MP2/6-311++G** level of theory. The computed stationary points have been characterized as minima by diagonalizing the Hessian matrix and analyzing the vibrational

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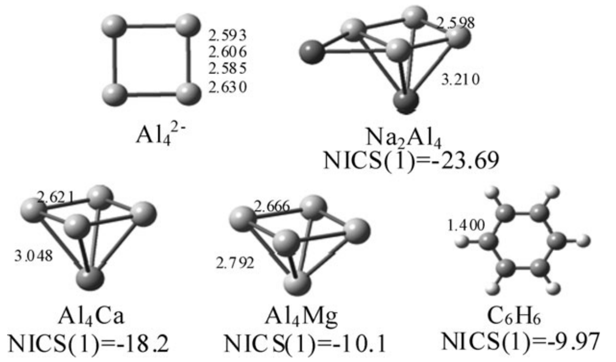

Fig. 1 The optimized geometric configurations of Al_4^{2-}, Na_2Al_4 and Al_4M ($M = Mg^{2+}$, Ca^{2+}). For Al_4^{2-}, the bond lengths from the top down were calculated at the B3LYP/6-311++G**, B3LYP/aug-cc-pVDZ, MP2/6-311++G ** and MP2/aug-cc-pVDZ levels of theory, respectively. For Na_2Al_4, Al_4M ($M = Mg^{2+}$, Ca^{2+}) and C_6H_6, the bond lengths were calculated at the MP2/6-311++G** level of theory. The calculation method of NICS is presented in Table 1.

normal modes. In this way, the stationary points can be classified as minima if no imaginary frequency is shown.

The binding energy between an aromatic complex and a hydrogen donor can be obtained by:[21]

$$\Delta E_{BE} = E_{\pi\cdots H\text{–}Y} - E_{\pi} - E_{H\text{–}Y} \qquad (1)$$

A negative value of ΔE_{BE} indicates that the binding between the aromatic complex and the hydrogen donor is energetically favorable.[21] Energies obtained at the equilibrium geometry of the complex for each subsystem are lower than those calculated at the same geometry with the basis functions of the respective subsystem alone. This so-called basis set superposition error (BSSE) should be considered in order to get an accurate binding energy.[22]

We also performed nuclear independent chemical shift (NICS) calculations[23] to predict the aromaticity of the special all-metallic aromatic hydrogen bond systems. The nuclear magnetic resonance (NMR) parameters were calculated for a ghost atom that is placed in the center of the Al_4^{2-} ring, 1 Å below or above the center of the plane. It is well-known that a negative NICS indicates that the corresponding structure is aromatic, and a positive NICS indicates that the corresponding structure is anti-aromatic.[23] Furthermore, some pioneering works have proven that the more negative the NICS is, the more delocalized is the ring.[23b,24]

All calculations were performed with Gaussian 98.[25]

3. Results and discussion

Al_4^{2-} and Na_2Al_4 were considered to be aromatic in pioneering studies.[1–2] Our former study revealed that Al_4M ($M = Mg^{2+}$, Ca^{2+}) is also aromatic.[20] It has been proven that the molecules CH_4, NH_3, H_2O, and HF can all be hydrogen bonded to the organic aromatic benzene.[14–19] Now we tried to address the question whether these H-bond donors H–Y (Y = CH_3, NH_2, OH, F, Cl, Br) could also form H-bonds with the all-metal aromatic complexes Al_4^{2-}/Al_4M ($M = Mg^{2+}$, Ca^{2+}, $2Na^+$) (Fig. 1). As shown in our former paper, for the all-metal aromatic Al_4^{2-}/Al_4M, the all-metal aromatic H-bond is perpendicular to the Al_4 plane, and no all-metal aromatic H-bond is found parallel to the ring.[20] Hence, we mainly focus our investigation on the interaction with H–Y in direction perpendicular to the Al_4 plane.

3.1. Aromatic hydrogen bonds in the Al_4^{2-} system

The optimized geometric configurations and the HOMOs of $Al_4^{2-}\cdots$H–Y complexes are presented in Fig. 2. Al_4^{2-} seems to undergo a small structural variation in forming the $Al_4^{2-}\cdots$H–Y complexes (Fig. 1 and 2). Comparing Al_4^{2-} with $Al_4^{2-}\cdots$H–Y complexes, the Al–Al bond varies only by 0–0.009 Å. It is known that the HOMO of Al_4^{2-} is doubly occupied and is a delocalized π-orbital.[1] A similar delocalized π-orbital can also be found in the HOMO of $Al_4^{2-}\cdots$H–Y complexes. The delocalized π-orbital plays quite an important role in stabilizing the $Al_4^{2-}\cdots$H–Y complexes.

The variation of the aromaticity of Al_4^{2-} in $Al_4^{2-}\cdots$H–Y complexes has been studied by the NICS method which is a magnetic criterion that reflects the ring current. The NICS(0) value, calculated at the center of the ring, is influenced by the σ-bonds and, therefore, calculation of the NICS(1) and NICS(−1) values, 1 Å out of the plane, yields a more reliable result because these values are mainly influenced only by the π system.[23] The NICS calculated results are listed in Table 1. The delocalized HOMO and the negative NICS values indicate that Al_4^{2-} remains aromatic on forming $Al_4^{2-}\cdots$H–Y complexes.

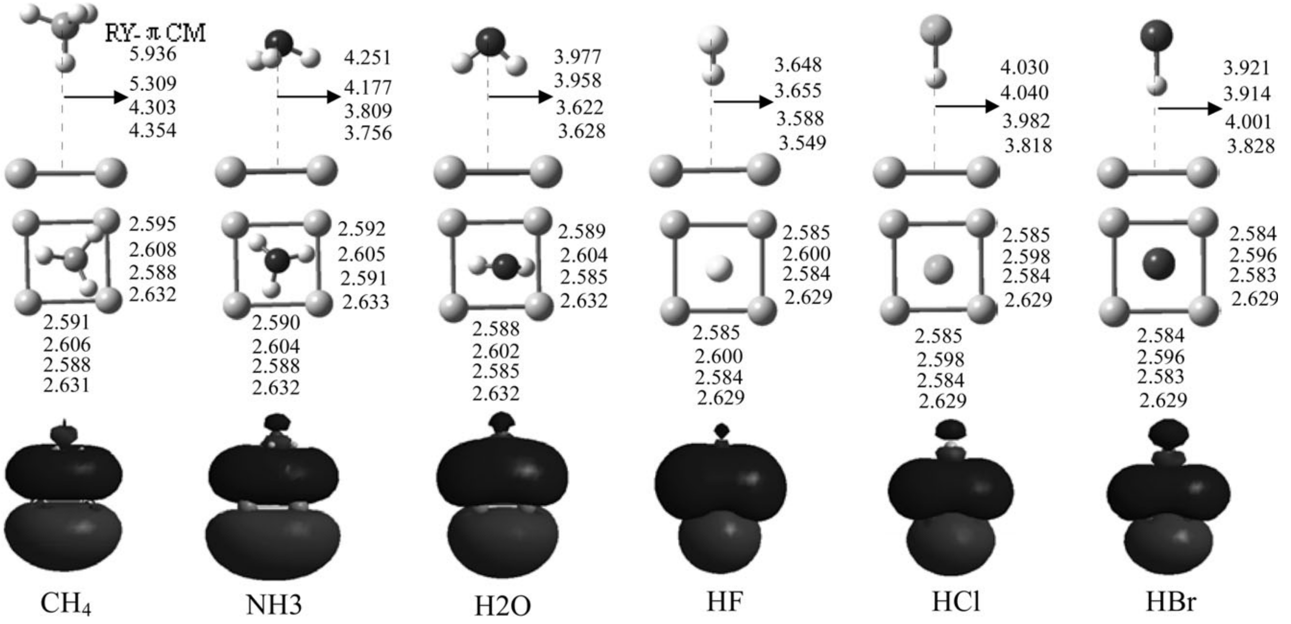

Fig. 2 The optimized geometric configuration and the HOMO of $Al_4^{2-}\cdots$H–Y complex. RY-πCM represents the distance from the Al_4^{2-} plane to the hydrogen donors (C, N, O, F, Cl, Br, respectively). The values shown from the top down were calculated at the B3LYP/6-311++G**, B3LYP/aug-cc-pVDZ, MP2/6-311++G** and MP2/aug-cc-pVDZ levels of theory, respectively.

Table 1 The nuclear independent chemical shifts of the $Al_4^{2-}\cdots H–Y$ complexes[a]

	Al_4^{2-}	$Al_4^{2-}\cdots CH_4$	$Al_4^{2-}\cdots NH_3$	$Al_4^{2-}\cdots H_2O$	$Al_4^{2-}\cdots HF$	$Al_4^{2-}\cdots HCl$	$Al_4^{2-}\cdots HBr$
NICS(1)	−27.32	−27.05	−27.16	−27.69	−29.23	−29.05	−29.72
NICS(0)	−34.28	−33.69	−33.42	−32.90	−32.75	−32.12	−31.15
NICS(−1)	−27.32	−26.95	−26.84	−26.29	−25.46	−24.72	−22.85

[a] Using geometry optimization at the B3LYP/6-311++G** level of theory. Values were calculated with the recommended 6-31+G* basis set at the B3LYP level of theory (ref. 23*a*). NICS(0) is calculated in the center of Al_4^{2-}. NICS(1) and NICS(−1) are calculated at 1 Å out of the plane of Al_4^{2-}. NICS(1) is above the plane and NICS(−1) is below the plane. The NICS values are given in ppm.

As shown in Table 1, the diamagnetic ring currents in the center of the Al_4^{2-} plane and those at 1 Å out of the plane undergo a notable change on forming the $Al_4^{2-}\cdots H–Y$ complexes. Furthermore, it is shown that as the complex progresses from $Al_4^{2-}\cdots CH_4$ to $Al_4^{2-}\cdots HBr$, both NICS(0) and NICS(−1) decrease whereas NICS(1) increases. This implies that, as H–Y varies from CH_4 to HBr, the π-electron cloud moves closer to the H–Y molecules. As a result, the binding energy keeps increasing (Table 2).

Comparing with $C_6H_6\cdots H–Y$ (Fig. 3), the distances of RY-πCM of $Al_4^{2-}\cdots H–Y$ (Fig. 2) are 0.639 Å, 0.337 Å, 0.276 Å, 0.37 Å, 0.398 Å and 0.259 Å larger than those of the corresponding $C_6H_6\cdots H–Y$ complexes at the MP2/6-311++G** level of theory, respectively. It is worth noticing that the differences between the values of RY-πCM for $Al_4^{2-}\cdots H–Y$ and $C_6H_6\cdots H–Y$ (Y = NH_2, OH, F, Cl, Br) are much smaller than that between $Al_4^{2-}\cdots CH_4$ and $C_6H_6\cdots CH_4$, which indicates that the interaction between Al_4^{2-} and CH_4 is quite weak. For the aromatic H-bond forming with benzene, only the configuration with just one H atom pointing toward the π-cloud of C_6H_6 is energetically favorable (Fig. 3), which has also been pointed out by other pioneering studies theoretically or by experiment.[16–19,26] Dissimilarly, we found that for $Al_4^{2-}\cdots H–Y$, the configuration with all H atoms pointing toward the π-electron cloud of Al_4^{2-} is more energetically favorable. The structures of $Al_4^{2-}\cdots NH_3$ and $Al_4^{2-}\cdots H_2O$ with only one hydrogen pointing toward the electron donor are accompanied by a small imaginary frequency. The difference should be ascribed to the differences between Al_4^{2-} and benzene: Al_4^{2-} has a large diatropic ring current[12] and 3-fold aromaticity, whereas benzene has only 1-fold aromaticity.[11] In addition, our calculated results show that the NICS value of Al_4^{2-} is approximately 2.7 times larger than that of benzene (Table 1, Fig. 1), it is known that a larger negative NICS value suggests a higher degree of electron delocalization.[23*b*,24] We can imagine that such a large electron delocalization of Al_4^{2-} is also responsible for the geometric configuration difference between $Al_4^{2-}\cdots H–Y$ and $C_6H_6\cdots H–Y$.

The binding energies of Al_4^{2-} with H–Y are listed in Table 2. It is clear that as H–Y progresses from CH_4 to HF, the interaction energy of Al_4^{2-} and H–Y increases in the same order as that between benzene and H–Y. It is interesting to find that although the values of RY-πCM for $Al_4^{2-}\cdots H–Y$ systems are larger than those for the corresponding $C_6H_6\cdots H–Y$ systems, $Al_4^{2-}\cdots NH_3$, $Al_4^{2-}\cdots H_2O$, $Al_4^{2-}\cdots HF$, $Al_4^{2-}\cdots HCl$ and $Al_4^{2-}\cdots HBr$ all have a stronger interaction compared with the relative $C_6H_6\cdots H–Y$ complexes, respectively. This is reasonable because Al_4^{2-} has the following characteristics compared with C_6H_6: (1) the degree of electron delocalization of Al_4^{2-} is much higher than that of C_6H_6; (2) Al_4^{2-} has 3-fold aromaticity whereas C_6H_6 has only 1-fold aromaticity;[11] (3) the electrostatic contributions from the isolated Al_4^{2-} dianion should be noticeable. However, the binding energy between Al_4^{2-} and CH_4 approximates that between C_6H_6 and CH_4, and thus is a collaborative result of the large values of RY-πCM for $Al_4^{2-}\cdots CH_4$ and the high electron delocalization of Al_4^{2-}.

Cation–π binding can be divided into two parts: electrostatic and non-electrostatic.[26] For hydrogen bonds in all-metal aromatic systems which include dianion Al_4^{2-}, the electrostatic contributions to the binding energies should never be ignored. We adopted the same methods contributed by Mecozzi *et al.*[27] to estimate the electrostatic contribution. As shown in Table 2, the interaction between Al_4^{2-} and CH_4 is almost electrostatic (70.2%). This indicates that the hydrogen bond between the all-metal aromatic complex Al_4^{2-} and CH_4 is quite weak. Although the degree of electron delocalization of Al_4^{2-} is high, the larger value of RY-πCM for the $Al_4^{2-}\cdots CH_4$ complex makes it difficult to form a hydrogen bond between Al_4^{2-} and CH_4. The electrostatic fractions of $Al_4^{2-}\cdots NH_3$, $Al_4^{2-}\cdots H_2O$, $Al_4^{2-}\cdots HF$ and $Al_4^{2-}\cdots HCl$ are 27.5%, 33.9%, 50.9%, 49.0% respectively, exhibiting an upward trend as the electronegativity of Y increases.

As shown in Fig. 2, there exists a big discrepancy between the B3LYP and MP2 geometries, especially for the $Al_4^{2-}\cdots CH_4$, $Al_4^{2-}\cdots NH_3$ and $Al_4^{2-}\cdots H_2O$ complexes. Indeed, a very small imaginary frequency was found in the evaluation of the ZPEs of $Al_4^{2-}\cdots CH_4$, $Al_4^{2-}\cdots NH_3$ and $Al_4^{2-}\cdots H_2O$ calculated at the B3LYP level of theory with the 6-311++G** or aug-cc-pVDZ basis sets. However, no imaginary frequency was found in the evaluation of the ZPEs of $Al_4^{2-}\cdots CH_4$, $Al_4^{2-}\cdots NH_3$ and $Al_4^{2-}\cdots H_2O$ calculated at the MP2 level of theory with 6-311++G** or aug-cc-pVDZ

Table 2 Binding energies (kJ mol^{-1}) of the $Al_4^{2-}\cdots H–Y$ complexes[a]

	CH_4	NH_3	H_2O	HF	HCl	HBr
$-\Delta E$a	9.99 (7.11)	32.52 (29.47)	48.17 (44.91)	58.31 (55.09)	56.97 (54.81)	66.50 (40.97)
$-\Delta E$b	8.22 (7.30)	28.41 (24.15)	44.49 (41.31)	54.63 (50.70)	53.55 (49.40)	63.84 (38.42)
$-\Delta E$c	14.82 (9.30)	41.78 (39.35)	54.81 (52.45)	58.47 (54.35)	56.62 (50.64)	59.48 (56.67)
$-\Delta E$d	15.25	42.78	54.73	59.72	61.91	67.05
C_6H_6[b]	8.68 (7.17)	12.46 (10.69)	16.72 (14.58)	20.55 (17.99)	24.26 (21.27)	23.83 (21.61)
C_6H_6[c]	15.50	18.60	21.28	25.54		
$-\Delta E$es[d]	5.77	7.82	15.09	27.80	26.46	11.52

[a] *E*a, *E*b, *E*c and *E*d represent the binding energies calculated at the B3LYP/6-311++G**, B3LYP/aug-cc-pVDZ, MP2/6-311++G** and MP2/aug-cc-pVDZ levels of theory, respectively. Values were corrected with ZPE. Values in parentheses were corrected with BSSE. [b] Binding energy between C_6H_6 and H–Y, calculated at the MP2/6-311++G** level of theory. [c] Values were calculated at the MP2/aug-cc-pVDZ level of theory (ref. 14*a*). [d] ΔEes represents the electrostatic contributions to the binding energies. Electrostatic potential is calculated using the optimized geometry at the B3LYP/aug-cc-pVDZ level of theory.

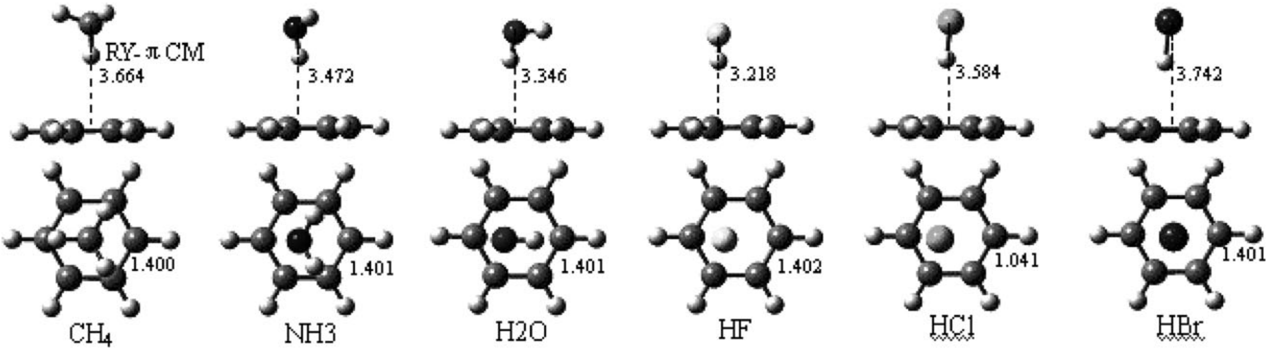

Fig. 3 The optimized geometric configurations of $C_6H_6\cdots H–Y$ complexes. The values shown were calculated at the MP2/6-311++G** level of theory.

basis sets. Though we had tried our best to find out the stable geometries of $Al_4^{2-}\cdots CH_4$, $Al_4^{2-}\cdots NH_3$ and $Al_4^{2-}\cdots H_2O$ at the B3LYP level of theory with 6-311++G** or aug-cc-pVDZ basis sets, unfortunately, we failed.

It is obvious that for Al_4^{2-} complexes (Table 2), the binding energies calculated at the B3LYP level are weaker than those obtained at the MP2 level. Similar results have also been found in the calculations of benzene aromatic hydrogen bonds, and the B3LYP methods also predict a much weaker interaction.[14b] In particular, the result obtained with the B3LYP method on the interaction between all-metal aromatic species and HBr is not satisfying. The variations of the H–Y bonds are 0.001 Å, 0.006 Å, 0.010 Å, 0.019 Å, 0.034 Å and 0.053 Å, for CH_4, NH_3, H_2O, HF, HCl and HBr, respectively at the MP2/6-311++G** level of theory when the hydrogen bond is formed. However, at the B3LYP/6-311++G** level of theory they are 0.001 Å, 0.007 Å, 0.009 Å, 0.029 Å, 0.073 Å and 0.181 Å, respectively. As we can see, bond length calculations for HBr using the latter method are not so good. Furthermore, an extremely big BSSE value was also observed for HBr (Table 2). As pointed out by some pioneering papers, MP2 calculation with a reasonably sized basis set would give more accurate results compared with B3LYP methods for aromatic systems.[14b] Previous studies have indicated that dispersion forces could play an important role in some of these complexes since B3LYP is not good at describing them. Dispersion corrections are needed for the B3LYP level theory to obtain accurate enough results to compare with MP2 calculated results.[28] Hence, we mainly performed calculations using the MP2 method in the following section.

3.2. Aromatic hydrogen bonds in the Al_4M system

We had found that the two negative charges of Al_4^{2-} have a noticeable effect on the hydrogen bond of $Al_4^{2-}\cdots HF$.[20] In order to investigate the effect induced by the two negative charges on the $Al_4^{2-}\cdots H–Y$ complexes, we studied the following neutral all-metal aromatic complexes: Al_4M ($M = Mg^{2+}$, Ca^{2+}), Na_2Al_4.

It has been found that the order of the NICS values is: Al_4^{2-} (−27.32) > Na_2Al_4 (−23.69) > Al_4Ca (−18.26) > Al_4Mg (−10.14) and for the binding energy is: $Al_4^{2-}\cdots HF$ > $Na_2Al_4\cdots HF$ > $Al_4Ca\cdots HF$ > $Al_4Mg\cdots HF$.[20] This suggested that the higher the degree of the delocalization of the π-cloud is, the larger is the binding energy with HF. In the present work, the above conclusion was testified by more examples with different hydrogen donors. The relative order of the binding energy of $Al_4M/Na_2Al_4\cdots H–Y$ complexes is: $Al_4^{2-}\cdots H–Y$ > $Na_2Al_4\cdots H–Y$ > $Al_4Ca\cdots H–Y$ > $Al_4Mg\cdots H–Y$ (Tables 2 and 3), which further confirmed that the interaction between the all-metal aromatic systems and the hydrogen donors is related to the delocalized π-electron cloud.

The binding energies of Al_4M ($M = Mg^{2+}$, Ca^{2+}) and Na_2Al_4 are quite different; why? It is mainly because Mg^{2+} and Ca^{2+} can induce a high perturbation of the Al_4^{2-} anion (Fig. 1), inducing a large reduction of the aromaticity of Al_4^{2-}. Specifically, the NICS values were decreased by 9.06 and 17.18 ppm for Al_4Ca and Al_4Mg, respectively. Hence, the binding for complexes containing Al_4Ca and Al_4Mg is rather weak (Table 3). However, in the process of forming Na_2Al_4, the Al_4^{2-} anion undergoes only a small change (Fig. 6) and Na_2Al_4 retains considerable aromaticity (NICS = −23.69 ppm). As a result, the binding energy of $Na_2Al_4\cdots H–Y$ is large. This indicates a method to control the intensity of the hydrogen bond in all-metal aromatic systems. Because the aromaticity of an all-metal aromatic system can be changed by interaction with different metal ions, the intensity of the hydrogen bond can also be adjusted and controlled by changing the ions.

As with the Al_4^{2-} complexes, the RY-πCM values for the neutral all-metal aromatic complexes $Al_4M\cdots H–Y$ (Fig. 4, 5 and 6) are larger than those of the relative $C_6H_6\cdots H–Y$ (Fig. 3). As we can see, though Al_4M possesses a much higher degree of electron delocalization compared with C_6H_6, the binding energies between Al_4M and H–Y are much weaker than those of C_6H_6 and H–Y. This is reasonable because, although larger delocalization may strengthen the binding, longer distances will simultaneously weaken the interaction anyway. The final result is an integrated result of the two incompatible effects. As a result, for the Al_4Mg system, it is almost not favorable to bind CH_4 and NH_3. The binding between Al_4Ca and CH_4 is also not favorable.

3.3. Frequency shifts of H–Y in complexes with all-metal aromatic systems

The frequency shifts of the H–Y stretching modes of $Al_4^{2-}\cdots H–Y$ and $Al_4M\cdots H–Y$ systems calculated at the MP2/

Table 3 Binding energies (kJ mol^{-1}) of the $Al_4M\cdots H–Y$ complexes[a]

$-\Delta E$	CH_4	NH_3	H_2O	HF	HCl	HBr
Al_4Mg	4.05 (0.91)	3.48 (0.42)	7.68[b] (4.62)	5.51 (2.92)	8.78 (4.49)	9.98 (6.42)
Al_4Ca	3.81 (−0.11)	6.41 (2.46)	8.08 (4.12)	10.68 (6.94)	12.58 (7.49)	13.33 (9.16)
Al_4Na_2	3.60 (2.20)	13.65 (11.66)	14.58 (9.87)	23.63 (21.68)	22.10 (18.72)	21.75 (19.81)

[a] Values were calculated at the MP2/6-311++G** level of theory and corrected with ZPE. Values in parentheses were corrected with BSSE. [b] A very small imaginary frequency was found in the evaluation of ZPE.

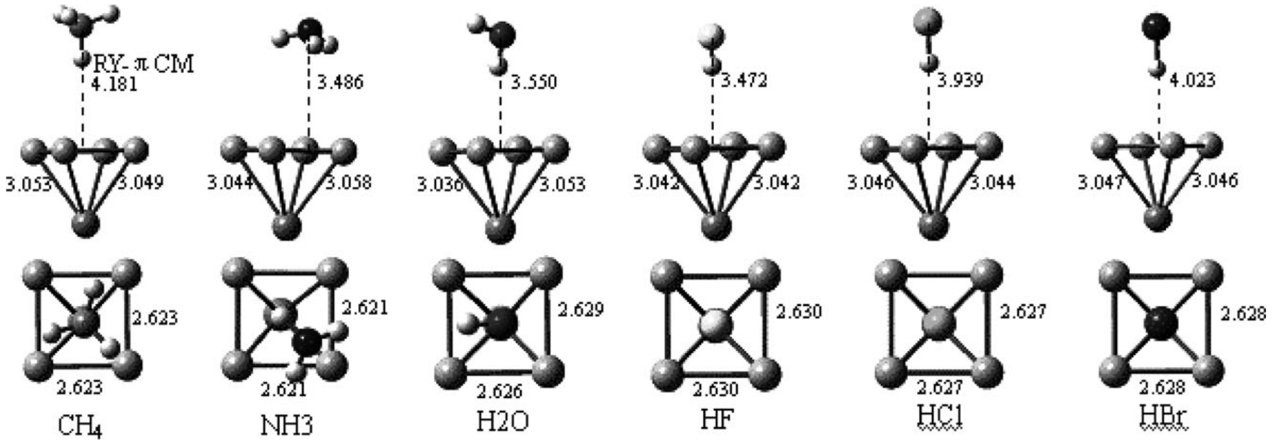

Fig. 4 The optimized geometric configurations of $Al_4Ca\cdots H–Y$ complexes. The values shown were calculated at the MP2/6-311++G** level of theory.

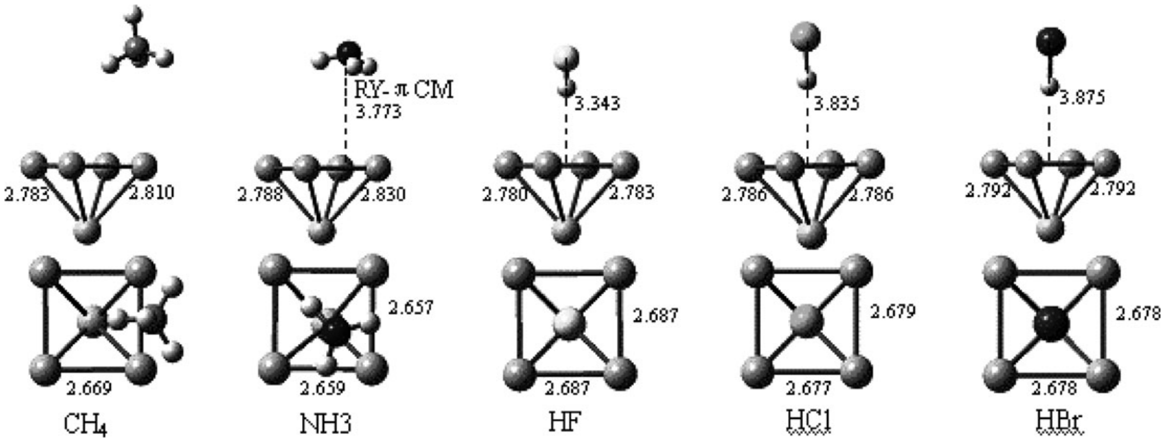

Fig. 5 The optimized geometric configurations of $Al_4Mg\cdots H–Y$ complexes. The values shown were calculated at the MP2/6-311++G** level of theory.

6-311++G** level of theory are listed in Table 4. In order to compare the frequencies of all-metal aromatic systems and organic aromatic systems, the H–Y stretching modes of $C_6H_6\cdots H–Y$ were also calculated at the same level of theory and are presented in Table 4. These frequency shifts were calculated using the harmonic frequencies of $Al_4^{2-}/Al_4M/C_6H_6\cdots H–Y$ systems minus the relative frequency of H–Y.

Generally speaking, for traditional $C–H\cdots X$ hydrogen bonds, a blue-shift was observed.[29] For the $C_6H_6\cdots H–CH_3$ complex, one C–H stretching mode was found to be blue-shifted and the other three C–H modes were red shifted. However, for the all-metal aromatic systems, all the C–H stretching modes were observed to be red shifted. For other complexes with hydrogen donors H–Y (Y = NH_2, OH, F, Cl,

Table 4 Frequency shifts of the H–Y stretching modes[a]

	H–Y	$C_6H_6\cdots H–Y$	$C_6H_6\cdots H–Y$[b]	$Al_4^{2-}\cdots H–Y$	$Al_4Mg\cdots H–Y$	$Al_4Ca\cdots H–Y$
CH_4	3213.8	8.4	16.0	−16.7	−11.9	−7.1
	3213.8	−12.8	−9.0	−33.6	−13.2	−11.7
	3213.8	−12.8	−9.0	−34.3	−14.4	−11.8
	3076.4	−6.9	−2.8	−35.2	−13.8	−11.9
NH_3	3682.8	−14.0	−8.4	−88.3	−11.0	−19.7
	3682.0	−14.7	−10.8	−92.0	−14.5	−20.8
	3530.9	−11.2	−7.5	−55.1	−16.5	−18
H_2O	4002.2	−24.4	−29.1	−169.5	−34.9	−45.5
	3884.1	−19.4	−30.6	−122.8	−34.0	−53.7
HF	4195.1	−90.1	−166.0	−415.3	−161.6	−150.2
HCl	3087.1	−51.6		−469.4	−125.8	−117.9
HBr	2738.4	−39.1		−657.7	−161.4	−132.9

[a] Frequency shifts were calculated at the MP2/6-311++G** level of theory. All frequencies are in cm^{-1}. [b] Values were calculated at the MP2/aug-cc-pVDZ level of theory (ref. 14*a*).

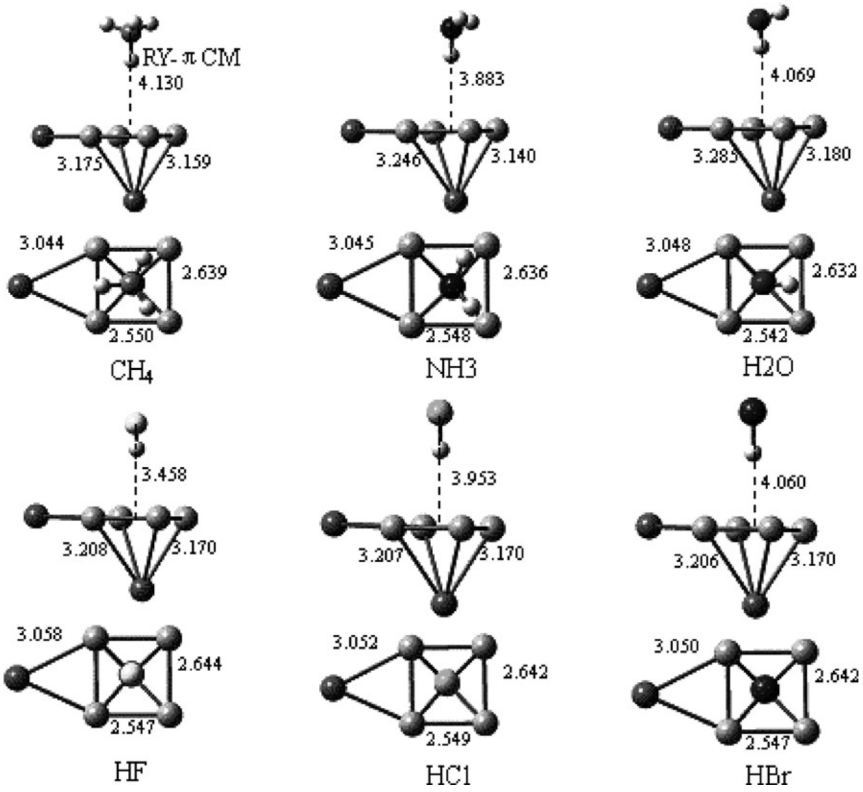

Fig. 6 The optimized geometric configurations of $Na_2Al_4\cdots H–Y$ complexes. The values shown were calculated at the MP2/6-311++G** level of theory.

Br), the stretching modes of both C_6H_6 and all-metal aromatic systems were all red shifted.

Similar to what is observed in C_6H_6 aromatic hydrogen bond systems, for Al_4^{2-} and Al_4M systems, the extent of the frequency shifts increased as one progressed from CH_4 to HF. This suggests that the red shifts are correlated to the electronegativity of the Y atom. However, as the hydrogen donor progresses from HF to HBr, the degree of frequency shift is not very regular. For C_6H_6 aromatic systems, the order of the degree of frequency shift is: HF > HCl > HBr. For Al_4^{2-}, the order is: HF < HCl < HBr. For Al_4M, the order is: HCl < HBr < HF.

It is shown that the extents of the frequency shifts of the all-metal systems are much severer than those of the C_6H_6 system and that the Al_4^{2-} complexes possess the largest values. This indicates that the red shifts of aromatic hydrogen bonds are correlated to not only the electronegativity of the Y atom, but also to the degree of electron delocalization of the aromatic systems.

4. Conclusion

Based on the recent advance of the aromaticity concept into all-metal species, we revealed that there does exist a hydrogen bond in $Al_4M\cdots H–F$.[20] In the present work, we found that the all-metal species can also provide delocalized π-orbitals to act as the proton acceptor by forming a hydrogen bond with NH_3, H_2O, HF, HCl as well as HBr. However, the binding between the all-metal aromatic system and CH_4 is not as favorable as that between C_6H_6 and CH_4. Though the values of RY-πCM for $Al_4^{2-}\cdots H–Y$ (Y = NH_2, OH, F, Cl, Br) systems are larger than those of the corresponding $C_6H_6\cdots H–Y$ systems, the binding energy between Al_4^{2-} and H–Y is comparatively stronger. However, the hydrogen bonds in Al_4M (M = Ca^{2+}, Mg^{2+}) systems are rather weak, even weaker than those of C_6H_6. It was also found that the larger the binding energy is, the shorter the distance is between the π-electron cloud and the hydrogen donor.

All these results revealed that the following factors can influence the strength of the hydrogen bond in all-metal aromatic systems: (1) the degree of delocalization of the π-electron cloud; (2) the electronegativity of the hydrogen donor; (3) the distance from the center of the Al_4^{2-} plane to the hydrogen donor.

The degree of the frequency shift of the H–Y stretching mode can be influenced by the following factors: (1) the degree of delocalization of the π-cloud; (2) the electronegativity of the hydrogen donor.

Above all, the present work could give a deeper understanding of not only the hydrogen bond in all-metal aromatic systems but also of the nature of the aromaticity in the all-metal systems. Such special hydrogen bonding is very important for the contributions to the unusual stabilities of the complexes containing Al_4^{2-}. Furthermore, this idea to test hydrogen bond complexes between Al_4^{2-} and H–Y goes the first step towards making the dianion Al_4^{2-} in solution. We believe that such hydrogen bonding should exist widely in other all-metal aromatic systems.

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