

Theoretical study of interactions between electron-deficient arenes and coinage metal anions

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Received: 23 September 2014 / Accepted: 19 January 2015
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Abstract The binding behavior of coinage metal anions with some electron-deficient arenes has been investigated by MP2 calculations, and the character of interactions in these complexes has been examined by NBO analysis. The results indicate that coinage metal anions can interact with electron-deficient arenes to form anion- π , strong σ -type and hydrogen-bonding complexes. The σ -type structure is the global minimum for triazine, trifluorotriazine, hexafluorobenzene and tricyanobenzene, and the hydrogen-bonding structure is the global minimum for trifluorobenzene. There exist some differences in the stability of anion- π complexes for coinage metal anions: the anion- π complexes of Au^- are minima expect for triazine complex; the anion- π complexes of Ag^- are minima expect for tricyanobenzene complex; and the anion- π complexes of Cu^- are not minima expect for trifluorobenzene complex. The binding strength of anion- π and hydrogen-bonding complexes for Au^- is larger than that for Ag^- and Cu^- , but the binding strength of σ complex displays a different sequence: $\text{Cu}^- > \text{Au}^- > \text{Ag}^-$. The binding behavior of coinage metal anions is more similar to that of F^- than that of Cl^- and Br^- . The relaxed potential energy surface scans for some selected systems have been performed to help understand the interactions between coinage metal anions with electron-deficient arenes.

Keywords Anion- π interaction · Coinage metal anions · Electron-deficient arenes · Hydrogen-bonding interaction · Potential energy surface

Electronic supplementary material The online version of this article (doi:10.1007/s00894-015-2584-6) contains supplementary material, which is available to authorized users.

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Introduction

Anion- π interactions are termed as favorable non-covalent contacts between an electron-deficient (π -acidic) aromatic system and an anion. The nature of anion- π interaction has been extensively investigated by theoretical [1–15] and experimental [16–25] studies. Moreover, the interplay between anion- π and other noncovalent interactions has also been examined [26–30]. Besides anion- π interaction, other binding modes have also been established for electron-deficient arenes and anions [31–36]. As shown in Fig. 1, triazine can interact with halide anions (X^-) to form four types of complexes: [31] (1) anion- π interaction complexes; (2) strong σ complexes in which the fluoride anion attacks a partially positive aromatic carbon, changing the hybridization of arene-C to sp^3 ; (3) weak σ complexes, where the anions are located over the periphery of the aromatic ring, which may be formed with less nucleophilic halides ($\text{X} = \text{Cl}, \text{Br}$); and (4) hydrogen-bonding complexes, involving the interaction between the aryl C-H donor and the anion. The electron-withdrawing substituents have a great influence on the binding mode and strength of anion-arene systems. As mentioned above, investigations on less nucleophilic halides, such as Cl^- and Br^- , have indicated that both weak σ and anion- π complexes can be formed with moderately electron-deficient arenes, such as triazine. However, as the electron affinity of the arene is increased, such as in tricyanobenzene, anion- π complexes become unstable for Cl^- and only weak σ complexes can remain. Moreover, when the aryl C-H group is present, it is possible for the hydrogen-bonding complex to be the global minimum. For moderately electron-deficient arenes, hydrogen-bonding interaction is stronger than weak σ and anion- π interactions. In contrast, weak σ interaction is stronger than hydrogen-bonding interaction for strongly electron-deficient arenes.

To the best of our knowledge, the studies of anion- π interactions have focused exclusively on the non-metal anions. Gold is a late transition metal with a filled d shell. It is highly electronegative, somewhat similar to the halogens such as Br and I.

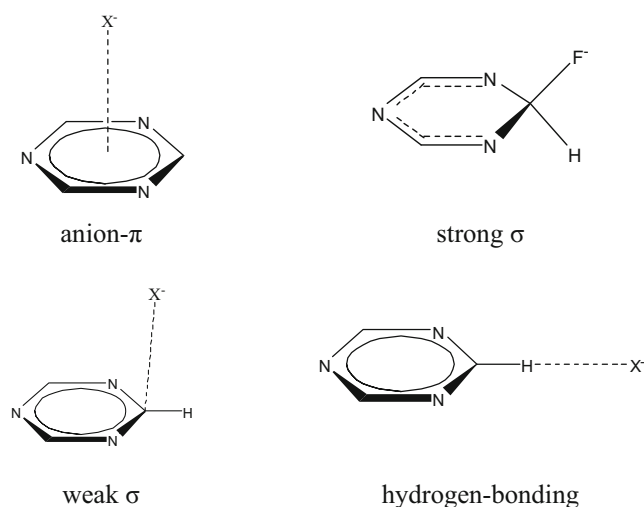


Fig. 1 Binding modes of triazine with halide anions

Therefore, it has been proposed that gold and gold cluster anions are able to participate in the formation of hydrogen bonds. The unusual hydrogen bonding behavior in binary complexes of coinage metal anions (Au^- , Ag^- and Cu^-) with water has been described, and the hydrogen-bond interactions in the complexes of coinage metal and their cluster anions with nucleobase and NH_3 have also been investigated [37–40]. Since the coinage metal anions are somewhat similar to the halide anions, it should be interesting to investigate the interactions between coinage metal anions and electron-deficient arenes, and compare with the results of halide anions. In this work, we perform a theoretical study of binding behavior of coinage metal anions with some selected electron-deficient arenes and expect to get new insight into the anion-arene interactions.

Computational methods

The geometries of all the complexes studied in this work were fully optimized at the MP2 level of theory using the Gaussian 09 programs [41]. The aug-cc-pVDZPP basis set, which uses pseudopotentials to describe the inner core orbitals, was employed for coinage metal atoms [42], whereas aug-cc-pVDZ basis set was applied for other atoms. The vibrational frequencies were calculated for all the optimized geometries. Single-point energy calculations were performed using aug-cc-pVTZ basis set (aug-cc-pVTZPP for coinage metal atoms) to obtain more accurate energies. Basis set superposition error (BSSE) correction was carried out following the counterpoise (CP) method [43]. It should be noted that the benefit of the counterpoise correction in calculating interaction energies is controversial [44, 45]. Natural bond orbital (NBO) analysis [46] was performed via the procedures contained within Gaussian 09. The molecular electrostatic potential (MEP) was calculated at the MP2/aug-cc-pVDZ level, and the MEP surfaces were plotted using GaussView software. [47]

Results and discussion

Binding energies and geometries of Au^- complexes

As shown in Fig. 2, we select five electron-deficient arenes to interact with coinage metal anions, and the molecular electrostatic potential surfaces of arenes are also displayed in Fig. 2. The optimized geometries and the equilibrium distances of

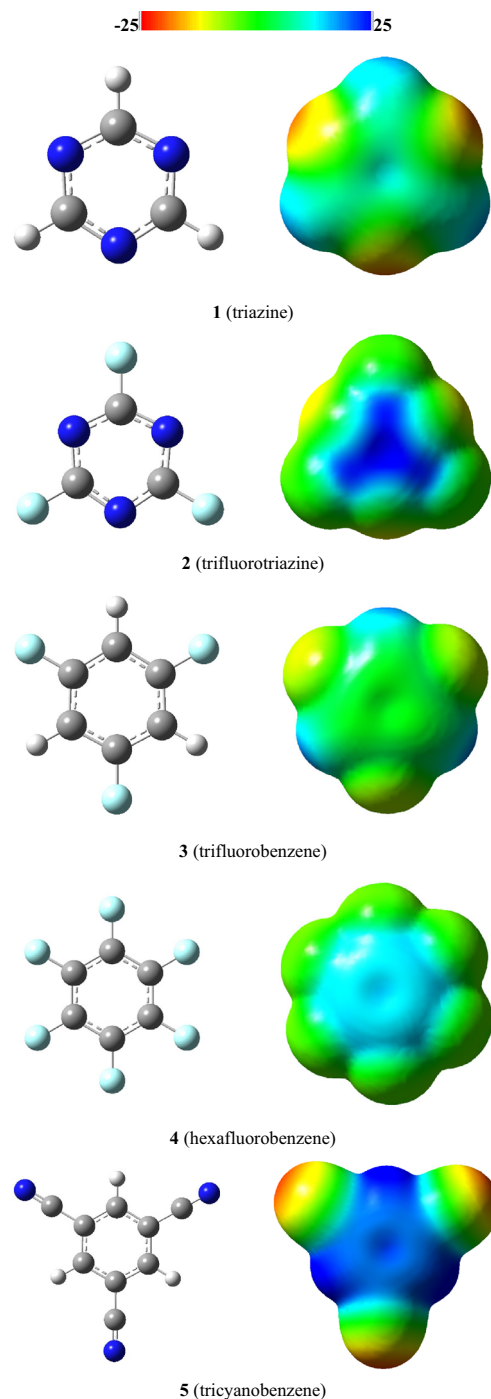


Fig. 2 Structures and MEP maps (ranging from -25 to 25 kcal mol^{-1}) of electron-deficient arenes studied in this paper

Au⁻-arene complexes are illustrated in Fig. 3. The binding energy (ΔE) is defined as the energy of complex minus the

sum of energy of the minimum geometry of arene and the corresponding anion. The binding energy has been further

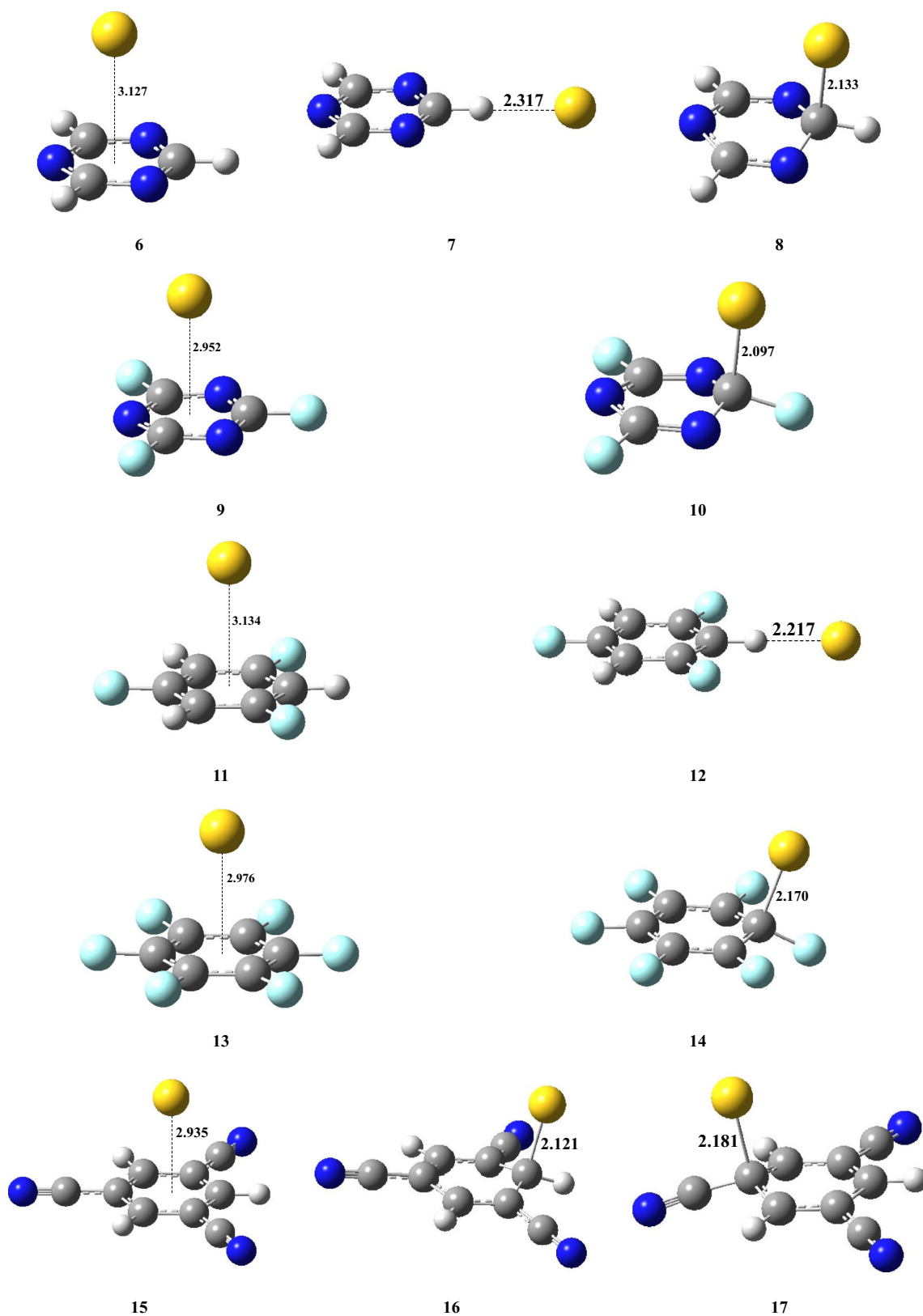


Fig. 3 Optimized geometries of the Au⁻-arene complexes; distances are in Å

corrected for BSSE (ΔE_{BSSE}) and zero point energy ($\Delta E_{\text{BSSE+ZPE}}$) corrections. These energies have been listed in Table 1, and ΔE_{BSSE} will be used in the discussion, which is convenient to compare with our previous study of interactions between triazine and halide anions [36]. The binding energy becomes more negative except for complex **16** when ZPE correction is performed. The geometric parameter and NBO analysis results (charge transfer derived from natural population analysis and Wiberg bond index [48, 49]) are also collected in the table.

The MEP map of triazine clearly indicates that an area of positive charge concentrates on the center of the molecule and expands to the hydrogen atoms along the C-H bonds, which implies that triazine can provide binding sites for anion- π , σ -type, and hydrogen-bonding interactions, as illustrated in our previous study [35]. The binding behavior of triazine to halide anions has been investigated in previous studies [31]. The anion- π complex of triazine is not a minimum for F^- with two imaginary frequencies, but is a stable structure for Cl^- and Br^- . Similar to F^- , the anion- π complex of triazine (complex **6** in Fig. 3) is a stationary point for Au^- with one imaginary frequency. Although the Au^- -triazine anion- π complex is not a minimum, the complex possesses a rather large binding energy ($-9.31 \text{ kcal mol}^{-1}$), which is larger than those of stable Cl^- -triazine and Br^- -triazine anion- π complexes. Our previous study at the same level indicates that the binding energies of Cl^- -triazine and Br^- -triazine anion- π complexes are -7.79 and $-6.99 \text{ kcal mol}^{-1}$, respectively. [36] The anion- π complexes of triazine with halide anions can be characterized by the very small amounts of charge transfer from halide anions to triazine, and this is also correct for Au^- : the charge transfer of complex **6** is only 0.0068.

The hydrogen-bonding structure of triazine with Au^- is shown as complex **7** in Fig. 3. The equilibrium distance is 2.317 \AA , and the binding energy is $-9.60 \text{ kcal mol}^{-1}$, which is very close to that ($-9.70 \text{ kcal mol}^{-1}$) of the hydrogen-

bonding complex of triazine with Cl^- [36]. The charge transfer of complex **7** is 0.0599, which is larger than that of the anion- π complex **6**. The bond strength can be estimated with the Wiberg bond index (WBI), and the value of WBI for complex **7** is 0.0790, implying that the hydrogen-bonding interaction is noncovalent.

Triazine can form strong σ complex with F^- and weak σ complexes with Cl^- and Br^- (Fig. 1). The σ complex is also located for triazine with Au^- , as shown in Fig. 3 (complex **8**). The binding energy of **8** is $-19.51 \text{ kcal mol}^{-1}$, which is much larger than those of **6** and **7**. The carbon atom bonded to Au^- in **8** adopts an sp^3 hybridization and the equilibrium distance is rather short (2.133 \AA), which indicates a strongly covalent interaction. This conclusion is also supported by NBO analysis: the charge transfer

is 0.6247 and the value of WBI is 0.6347, suggesting that the interaction is covalent.

The previous study of interactions between triazine and halide anions has shown that the binding strength of F^- -triazine complexes is in the sequence of strong σ complex > hydrogen-bonding complex > anion- π complex; the binding strength of Cl^- -triazine complexes is in the sequence of hydrogen-bonding complex > weak σ complex > anion- π complex; and the binding strength of Br^- -triazine complexes is in the sequence of hydrogen-bonding complex > anion- π complex > weak σ complex [31]. This work shows that the binding strength of Au^- -triazine complexes is in the sequence of strong σ complex > hydrogen-bonding complex > anion- π complex, which is the same as that of F^- -triazine complexes. Therefore, it can be concluded that the binding behavior of Au^- -triazine system is more similar to that of F^- -triazine system than that of Cl^- -triazine and Br^- -triazine systems.

Compared with triazine, trifluorotriazine (**2**) displays more positive MEP area on the center of molecule (Fig. 2). In contrast with triazine, trifluorotriazine can interact with Au^- to form a stable anion- π complex (**9** in Fig. 3) without imaginary

Table 1 Binding energy (ΔE , ΔE_{BSSE} , and $\Delta E_{\text{BSSE+ZPE}}$, in kcal mol^{-1}), equilibrium distance (R , in \AA), the number of imaginary frequencies is given in parentheses), charge transfer (q_{CT} , in e), and Wiberg bond index (WBI) for the Au^- -arene complexes

Complex	Binding mode	ΔE	ΔE_{BSSE}	$\Delta E_{\text{BSSE+ZPE}}$	R	q_{CT}	WBI
6 (1 + Au^-)	anion- π	-11.45	-9.31	-9.61	3.127 (1)	0.0068	
7 (1 + Au^-)	H-bond	-11.64	-9.60	-9.83	2.317	0.0599	0.0790
8 (1 + Au^-)	σ -type	-24.12	-19.51	-19.53	2.133	0.6247	0.6347
9 (2 + Au^-)	anion- π	-22.24	-19.54	-19.95	2.952	0.0172	
10 (2 + Au^-)	σ -type	-36.64	-31.54	-32.00	2.097	0.7910	0.7367
11 (3 + Au^-)	anion- π	-12.08	-9.63	-10.05	3.134	0.0012	
12 (3 + Au^-)	H-bond	-13.22	-10.78	-11.39	2.217	0.0848	0.1120
13 (4 + Au^-)	anion- π	-21.99	-18.96	-19.23	2.976	0.0079	
14 (4 + Au^-)	σ -type	-25.91	-20.64	-20.88	2.170	0.6070	0.5191
15 (5 + Au^-)	anion- π	-29.47	-25.81	-26.54	2.935	0.0171	
16 (5 + Au^-)	σ -type	-45.27	-39.50	-39.26	2.121	0.8397	0.6985
17 (5 + Au^-)	σ -type	-37.88	-32.03	-32.81	2.181	0.6593	0.4327

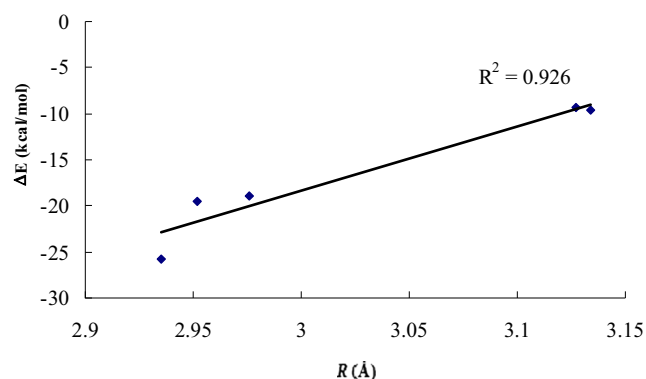


Fig. 4 Correlation between ΔE and R for the anion- π complexes of Au^- with arenes

frequency. The binding energy of **9** is $-19.54 \text{ kcal mol}^{-1}$, which is twice as much as that of **6**. On the other hand, the equilibrium distance of **9** is 2.952 \AA , which is shorter than that of **6**. There exists a linear relationship between binding energies and equilibrium distances for five Au^- -arene anion- π complexes, with correlation coefficient $R^2=0.926$, as shown in Fig. 4. Similar to triazine, trifluorotriazine can form a strong σ complex (**10** in Fig. 3) with Au^- , and the binding energy of **10** ($-31.54 \text{ kcal mol}^{-1}$) is much larger than that of **8**.

The anion- π structure of trifluorobenzene (**3**) with Au^- is shown as complex **11** in Fig. 3. The binding energy ($-9.63 \text{ kcal mol}^{-1}$) and equilibrium distance (3.134 \AA) of **11** are very similar to those of **6**. The binding energy ($-10.78 \text{ kcal mol}^{-1}$) and equilibrium distance (2.217 \AA) of Au^- -trifluorobenzene hydrogen-bonding complex **12** are also similar to those of **7**. Although the binding behavior of anion- π and hydrogen-bonding complexes for Au^- -trifluorobenzene system is similar to that for Au^- -triazine system, the binding behavior of σ complex is another story. Triazine can form strong σ complexes with Au^- , whereas trifluorobenzene cannot form any σ complex with Au^- . The absence of σ complex for trifluorobenzene can be partially explained by the MEP map. As shown in

Fig. 2, there is no obvious positive MEP area on the center of trifluorobenzene molecule. The previous study has shown that the anion- π interaction of trifluorobenzene is dominated by polarization, and the electrostatic contribution is negligible [9].

In contrast with trifluorobenzene, there is an obvious positive MEP area on the center of hexafluorobenzene (**4** in Fig. 2). Both anion- π and strong σ complexes can be located for hexafluorobenzene. The anion- π complex of hexafluorobenzene is shown as complex **13** in Fig. 3, and the binding energy of **13** is $-18.96 \text{ kcal mol}^{-1}$, which is similar to the binding strength of trifluorotriazine anion- π complex **9**. The σ complex of hexafluorobenzene is shown as complex **14** in Fig. 3, and the binding energy of **14** is $-20.64 \text{ kcal mol}^{-1}$, which is similar to the binding strength of triazine σ complex **7**.

The MEP map of tricyanobenzene (**5**) clearly indicates that **5** is a highly deficient-electron arene, as shown in Fig. 2. The binding energy of anion- π complex (**15** in Fig. 3) of **5** with Au^- is $-25.81 \text{ kcal mol}^{-1}$, which is the largest one among all the anion- π complexes studied in this work. Similar to halide anions, Au^- can form two types of σ complexes (**16** and **17** in Fig. 3) with tricyanobenzene. In **16**, Au^- is positioned over a C-H bond, and in **17**, Au^- is positioned over a C-CN bond. The binding energies of **16** and **17** are -39.50 and $-32.03 \text{ kcal mol}^{-1}$, respectively. Tricyanobenzene can form stable hydrogen-bonding complexes with halide anions [31], but to our surprise, tricyanobenzene cannot form stable hydrogen-bonding complex with Au^- .

Binding energies and geometries of Ag^- and Cu^- complexes

The calculation results for Ag^- and Cu^- complexes are listed in Tables 2 and 3, respectively. The binding behavior of Ag^- and Cu^- is generally similar to that of Au^- , but there are still some important differences. First, there are some differences in the

Table 2 Binding energy (ΔE , ΔE_{BSSE} , and $\Delta E_{\text{BSSE}+\text{ZPE}}$, in kcal mol^{-1}), equilibrium distance (R , in \AA), the number of imaginary frequencies is given in parentheses), charge transfer (q_{CT} , in e), and Wiberg bond index (WBI) for the Ag^- -arene complexes

Complex	Binding mode	ΔE	ΔE_{BSSE}	$\Delta E_{\text{BSSE}+\text{ZPE}}$	R	q_{CT}	WBI
18 (1 + Ag^-)	anion- π	-6.19	-5.23	-5.52	3.414	0.0033	
19 (1 + Ag^-)	H-bond	-6.42	-5.47	-5.46	2.458	0.0459	0.0608
20 (1 + Ag^-)	σ -type	-16.58	-14.30	-14.60	2.171	0.7418	0.6365
21 (2 + Ag^-)	anion- π	-14.93	-13.61	-14.23	3.136	0.0084	
22 (2 + Ag^-)	σ -type	-28.78	-26.42	-27.10	2.246	0.8914	0.6994
23 (3 + Ag^-)	anion- π	-7.12	-5.93	-6.31	3.339	0.0022	
24 (3 + Ag^-)	H-bond	-7.44	-6.58	-6.72	2.699	0.0366	0.0509
25 (4 + Ag^-)	anion- π	-16.71	-14.99	-15.66	3.012	0.0176	
26 (4 + Ag^-)	σ -type	-21.21	-18.67	-19.33	2.295	0.7502	0.4979
27 (5 + Ag^-)	anion- π	-21.54	-19.96	-21.18	3.161(2)	0.0083	
28 (5 + Ag^-)	σ -type	-39.02	-36.47	-36.52	2.209	1.0476	0.6402
29 (5 + Ag^-)	σ -type	-30.51	-28.60	-29.39	2.384	0.8445	0.3617

Table 3 Binding energy (ΔE , ΔE_{BSSE} , and $\Delta E_{\text{BSSE+ZPE}}$, in kcal mol⁻¹), equilibrium distance (R , in Å, the number of imaginary frequencies is given in parentheses), charge transfer (q_{CT} , in e), and Wiberg bond index (WBI) for the Cu⁻-arene complexes

Complex	Binding mode	ΔE	ΔE_{BSSE}	$\Delta E_{\text{BSSE+ZPE}}$	R	q_{CT}	WBI
30 (1+Cu ⁻)	anion- π	-5.19	-4.14	-4.61	3.213(1)	0.0056	
31 (1+Cu ⁻)	H-bond	-6.71	-5.93	-5.95	2.583	0.0378	0.0505
32 (1+Cu ⁻)	σ -type	-28.83	-26.24	-26.65	1.927	0.9371	0.7064
33 (2+Cu ⁻)	anion- π	-13.81	-12.32	-13.51	2.893(2)	0.0145	
34 (2+Cu ⁻)	σ -type	-42.23	-39.44	-40.29	1.913	1.1554	0.7503
35 (3+Cu ⁻)	anion- π	-5.94	-4.68	-5.24	3.168	0.0060	
36 (3+Cu ⁻)	H-bond	-7.30	-6.42	-6.56	2.571	0.0457	0.0625
37 (4+Cu ⁻)	anion- π	-14.82	-12.83	-14.83	2.716(1)	0.0345	
38 (4+Cu ⁻)	σ -type	-32.42	-29.40	-30.32	1.941	1.0971	0.6009
39 (5+Cu ⁻)	anion- π	-20.84	-19.37	-20.60	3.155(2)	0.0144	
40 (5+Cu ⁻)	σ -type	-50.96	-48.06	-48.21	1.919	1.3030	0.6494
41 (5+Cu ⁻)	σ -type	-39.44	-36.46	-37.24	1.987	1.1561	0.4555

stability of anion- π complexes: the anion- π complexes of Au⁻ are minima expect for triazine complex **6**; the anion- π complexes of Ag⁻ are minima expect for tricyanobenzene complex **27**; and the anion- π complexes of Cu⁻ are not minima expect for trifluorobenzene complex **35**. Moreover, there are also some differences in the binding strength of complexes. The binding strength of anion- π complexes for Au⁻ is larger than that for Ag⁻ and Cu⁻. For example, the binding energy of **6** is -9.31 kcal mol⁻¹, which is larger than those of **18** (-5.23 kcal mol⁻¹) and **30** (-4.14 kcal mol⁻¹). A similar trend can be found for the binding strength of hydrogen-bonding complexes. For example, the binding energy of **7** is -9.60 kcal mol⁻¹, which is larger than that of **19** (-5.47 kcal mol⁻¹) and **31** (-5.93 kcal mol⁻¹). In contrast with anion- π and hydrogen-bonding complexes, the binding strength of σ complex displays a sequence: Cu⁻ > Au⁻ > Ag⁻. For example, the binding energy of **8** is -19.51 kcal mol⁻¹, which is larger than that of **20** (-14.30 kcal mol⁻¹), but smaller than that of **32** (-26.24 kcal mol⁻¹).

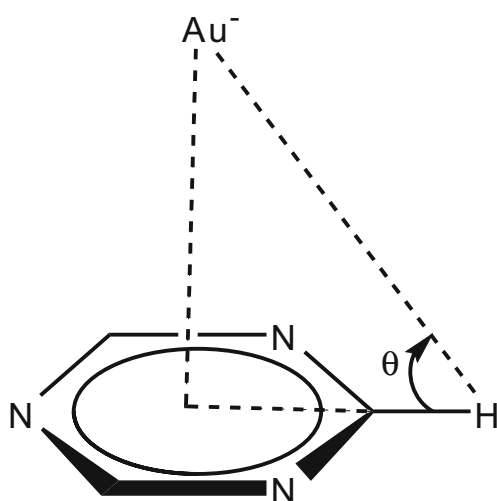


Fig. 5 Illustration of θ in Au⁻-arene system

Potential energy surfaces

In order to examine the local details of potential energy surfaces around the binding sites, we have performed the relaxed potential energy surface scans for some selected systems (Au⁻-triazine, Au⁻-trifluorobenzene and Au⁻-tricyanobenzene) at the MP2/aug-cc-pVDZ level. The scan begins from the anion- π interaction structure, and the angle variable θ is incremented step by step. The complex changes to the hydrogen-bonding structure via σ -type interaction structure with the increase in

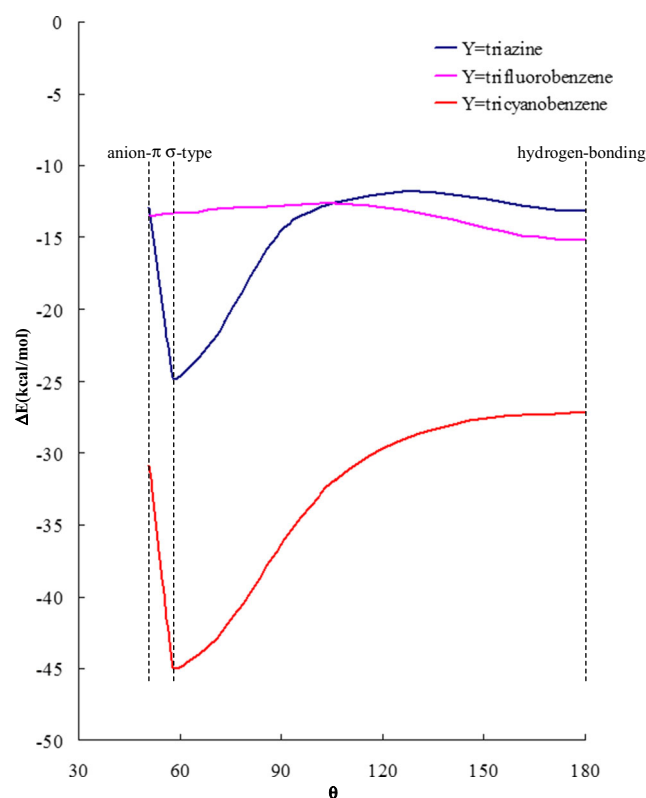


Fig. 6 The relaxed potential energy surface scans for Au⁻-Y systems

θ . As an example, the illustration of θ for Au⁻-triazine system is shown in Fig. 5.

The results of potential energy surface scans for three Au⁻-arene systems are displayed in Fig. 6, and the approximate locations of binding sites are also illustrated in the figure: anion- π interaction (θ is about 50), σ -type interaction (θ is about 60), and hydrogen-bonding interaction (θ is about 180). Figure 6 shows that the binding strength of Au⁻-tricyanobenzene system is obviously larger than that of Au⁻-triazine and Au⁻-trifluorobenzene systems. The global minima are strong σ complexes for Au⁻-triazine and Au⁻-tricyanobenzene systems, and the potential energy surfaces of these two systems are rather steep. In contrast with Au⁻-triazine and Au⁻-tricyanobenzene systems, the potential energy surface of Au⁻-trifluorobenzene system is very flat, and there is no stable σ complex on it. The global minimum for Au⁻-trifluorobenzene system is the hydrogen-bonding complex, which is separated from the stable anion- π complex by an energy barrier. Although the anion- π complex for Au⁻-tricyanobenzene system is also a stable structure, the energy barrier separating σ complex from anion- π complex for Au⁻-tricyanobenzene system is so small that the energy barrier cannot be reflected in Fig. 6. The shape of potential energy surface for Au⁻-triazine system is similar to that for Au⁻-tricyanobenzene system, but their binding behavior in hydrogen-bonding area is different: the hydrogen-bonding complex is a stable structure for Au⁻-triazine system, but not for Au⁻-tricyanobenzene system. Although the hydrogen-bonding complex for Au⁻-tricyanobenzene system is not a stable structure, it should be noted that the binding energy around hydrogen-bonding area for Au⁻-tricyanobenzene system is still rather large because the MEP (Fig. 2) around hydrogen atoms in tricyanobenzene molecule is highly positive.

Conclusions

In this study, the binding behavior of coinage metal anions with some electron-deficient arenes has been investigated. Coinage metal anions can interact with electron-deficient arenes to form anion- π , strong σ -type, and hydrogen-bonding complexes. The binding behavior of Ag⁻ and Cu⁻ is generally similar to that of Au⁻, but there are still some important differences. First, there are some differences in the stability of anion- π complexes: the anion- π complexes of Au⁻ are minima expect for triazine complex; the anion- π complexes of Ag⁻ are minima expect for tricyanobenzene complex; and the anion- π complexes of Cu⁻ are not minima expect for trifluorobenzene complex. Moreover, there are some differences in the binding strength of complexes. The binding strength of anion- π and hydrogen-bonding complexes for Au⁻ is larger than that for Ag⁻ and Cu⁻, but the binding strength of σ complex displays a different sequence: Cu⁻ > Au⁻ > Ag⁻.

The σ -type structure is the global minimum for triazine, trifluorotriazine, hexafluorobenzene, and tricyanobenzene, and the hydrogen-bonding structure is the global minimum for trifluorobenzene. We have compared the binding behavior of coinage metal anions with halide anions, which indicates that the binding behavior of coinage metal anions is more similar to that of F⁻ than that of Cl⁻ and Br⁻. A surprising discovery is that tricyanobenzene cannot form a stable hydrogen-bonding complex with coinage metal anions, which is totally different from the binding behavior of halide anions with tricyanobenzene. The relaxed potential energy surface scans for some selected systems are helpful to understand the interactions between coinage metal anions with electron-deficient arenes.

Acknowledgments Supported by the HPC Center, Kunming Institute of Botany, CAS, China.

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