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ORIGINAL PAPER

Influence of transition metals on halogen-bonded complexes of MCCBr···NCH and HCCBr···NCM' (M, M'=Cu, Ag, and Au)

Qiang Zhao · Dacheng Feng

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Abstract We have performed quantum chemical calculations for the MCCBr···NCH and HCCBr···NCM' (M, M'=Cu, Ag, and Au) halogen-bonded complexes at the MP2 level. The results showed that the transition metals have different influences on the halogen bond donor and the electron donor. The transition metal atom in the former makes the halogen bond weaker, and that in the latter causes it to enhance. Molecular electrostatic potential and natural bond orbital analysis were carried out to reveal the nature of the substitution.

Keywords Electron donor · Halogen bond donor · Molecular electrostatic potential · NBO · Transition metal

Introduction

Halogen bonding Y···Hal (Hal=Cl, Br, or I; Y=N, O, S, or π) is a noncovalent interaction between a halogen atom and an electron-rich partner [1]. Halogen-bonded interaction has been widely investigated both experimentally and theoretically, because it plays a prominent role in supramolecular architectures [2–6], molecular recognition [7, 8], and biological systems [9–12].

The reason why halogen-bonded complexes can be formed has been a confusing question for a long time because covalently-bonded halogens are generally considered to be negative. Recently, Politzer et al. [13–15] studied the electrostatic potentials of halogen-containing molecules and they showed that the halogen atoms bound to carbon often have a region of positive potential along the direction of C—Hal bond directed toward the electron donor. They call this region "σ–hole".

Like hydrogen bonding interaction, electrostatics and polarization are two major driving forces in halogen bonding, and dispersion contributions also play important roles [16]. The strength of the halogen bond is the most concerned topic for the researchers. Except the nature of the halogen atom, the group adjoined it plays a decisive role. Recently, halogen bonds involving metals became a new topic with applications in crystal engineering and allied areas [17–24]. Brammer and co-workers [19] have briefly reviewed the use of C—X···X'—M (X, X' are halogen atoms and M is metal atoms) halogen bonds in forming networks and their utility in investigating the nature of halogen bonds. They found that the strength of the halogen bond can be tuned by changing the inorganic electron donor X'—M. A review by Bertani et al. [25] focused on extended networks based on halogen bond between electron donor groups bound to metals and halo-pyridine and halo-tetrathiafulvalene moieties as electron acceptors. Xu et al. [26] have applied quantum chemical method to investigate the halogen bonding interactions PyCl···X (PyCl=NC_5H_4Cl-4; X=F^-、Cl^-、Br^-) and MPyCl···X (M=Cu^+、Zn^{2+}). This work showed that the Cl···X interactions have been strengthened in the MPyCl···X complexes. We [27] have investigated the MCH_2X···ClF (M=Cu, Ag, and Au;X=F, Cl, and Br) complexes and came to a similar conclusion as Xu. The above findings indicate that the introduction of transition metal atoms have influence on both the halogen bond donor and acceptor.

To understand the nature of the halogen bonds involving metals, we performed theoretical calculations for the MCCBr···NCH and HCCBr···NCM' (M, M'=Cu, Ag, and Au) complexes in this paper. To unveil the mechanism of

Q. Zhao (✉)
Department of Chemical Engineering, Zibo Vocational Institute, Zibo 255314 Shandong Province, People's Republic of China
e-mail: qzhaochem@yahoo.cn

D. Feng
Institute of Theoretical Chemistry, Shandong University, Jinan 250100 Shandong Province, People's Republic of China

Table 1 BSSE-corrected interaction energy ΔE^{CP} (in kcal·mol^{-1}) in the MCCBr···NCH and HCCBr···NCM' (M, M'=Cu, Ag, and Au) complexes calculated at the MP2 level[a]

Complexes	ΔE	BSSE	ΔE^{CP}
HCCBr···NCH	−2.43	0.40	−2.03
HCCBr···NCAg	−4.32	0.93	−3.39
HCCBr···NCCu	−4.12	0.74	−3.38
HCCBr···NCAu	−3.53	0.78	−2.75
AgCCBr···NCH	−1.30	0.45	−0.85
CuCCBr···NCH	−1.48	0.39	−1.09
AuCCBr···NCH	−2.05	0.48	−1.57

[a] BSSE is the basis set superposition error, ΔE is the interaction energy with no BSSE, and ΔE^{CP} is the BSSE-corrected interaction energy. $\Delta E^{CP} = \Delta E + \text{BSSE}$

transition metals, the natural bond orbital (NBO) has been performed for these complexes.

Computational methods

The systems have been optimized at the MP2 computational level. The small-core Los Alamos ("LANL2TZ(f)") pseudopotentials and basis sets that include the Dunning-Huzinaga full TZ and Los Alamos ECPs plus TZ have been employed for the Au atom with an extra f polarization function [28], while for the Ag atom we have used the cc-PVDZ-pp basis set [29], which is a correlation consistent-type basis set with valence-only correlation and based on a small-core relativistic pseudopotential (pp). The standard all-electron Pople-type 6-311++G(d,p) basis set has been utilized for Cu atom and all remaining nonmetal atoms. The basis set superposition error (BSSE) was eliminated by using the standard counterpoise (CP) correction method of Boys and Bernardi [30]. All optimized structures were characterized as minima in the potential energy surface by verifying that all the vibrational frequencies are real. NBO method [31] has been used to calculate the orbital energy, the atom charge and to analyze the interaction of occupied and empty orbitals. The above calculations were performed by using the Gaussian 03 program suite [32].

Table 2 Geometrical parameters in the MCCBr···NCH and HCCBr···NCM' (M, M'=Cu, Ag, and Au) complexes calculated at the MP2 level[a]

Complexes	R(Br···N)	θ(C—Br—N)
HCCBr···NCH	3.155	179.5
HCCBr···NCAg	3.029	179.9
HCCBr···NCCu	3.036	179.9
HCCBr···NCAu	3.077	179.9
AgCCBr···NCH	3.230	179.8
CuCCBr···NCH	3.232	179.4
AuCCBr···NCH	3.171	179.5

[a] R(Br···N) is binding distance (in Å), and θ(C—Br—N) is the angle of ∠C—Br—N (in degree)

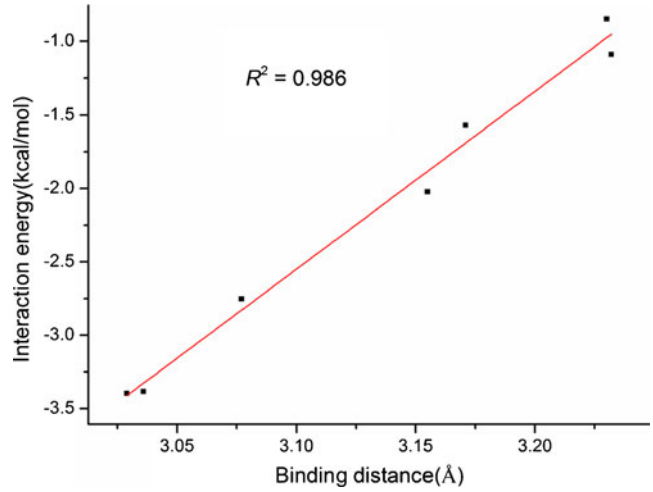

Fig. 1 The relationship between the interaction energy and the binding distance

Results and discussion

Interaction energies and geometries

Table 1 lists the BSSE-corrected interaction energies in the MCCBr···NCH and HCCBr···NCM' (M, M'=Cu, Ag, and Au) complexes. The interaction energy is calculated to be −2.03 kcal·mol^{-1} in the HCCBr···NCH complex. When the H atom in the electron donor NCH is substituted with a Au atom, the interaction energy is increased to be −2.75 kcal·mol^{-1}. The corresponding

Table 3 $V_{S,max}$(r) and $V_{S.min}$(r) in the MCCBr and NCM' (M, M'=Cu, Ag, and Au) molecules (in kcal·mol^{-1})

Molecules	$V_{S,max}$(r)	$V_{S.min}$(r)
NCH	–	−33.9
HCCBr	30.8	–
NCAg	–	−55.9
NCCu	–	−55.3
NCAu	–	−48.4
AgCCBr	14.4	–
CuCCBr	16.3	–
AuCCBr	20.7	–

Table 4 Orbital energy (in ev) of the n(N) and σ*(C—Br) orbitals, and NPA charge (in e) of the N and Br atoms in the MCCBr and NCM' molecules

Molecules	$E\{n(N)\}$	$E\{\sigma^*(C—Br)\}$	$q(N)$	$q(Br)$
NCH	−0.754	–	−0.348	–
HCCBr	–	0.349	–	0.208
NCAg	−0.655	–	−0.483	–
NCCu	−0.667	–	−0.471	–
NCAu	−0.683	–	−0.439	–
AgCCBr	–	0.379	–	0.161
CuCCBr	–	0.376	–	0.164
AuCCBr	–	0.365	–	0.185

interaction energies in the HCCBr···NCAg and HCCBr···NCCu complexes are more negative compared to the HCCBr···NCAu complex, and the HCCBr···NCAg complex is most stable (−3.39 kcal·mol^{-1}). The result shows that the transition metals in the electron donor enhance the Br···N halogen bonding interaction. When the H atom in the halogen donor HCCBr is replaced by a transition metal atom, the result is different. The interaction strength has a decrease in the MCCBr···NCH complex compared to the HCCBr···NCH complex. The interaction energy in the AuCCBr···NCH and CuCCBr···NCH complex is −1.57 kcal·mol^{-1} and −1.09 kcal·mol^{-1} respectively, and is greatly weakened when the H atom is replaced by the Ag atom (−0.85 kcal·mol^{-1}). The above results show that transition metal atoms have different influences on the halogen bonding for the halogen donors and electron donors, and different types of metal atoms produce different intermolecular strengths.

The geometrical parameters of the MCCBr···NCH and HCCBr···NCM' (M, M'=Cu, Ag, and Au) complexes are present in Table 2. All of θ(C—Br—N) are close to 180º, indicating that these halogen bonding interactions have good directivity and substitution of the transition metals only change the angle faintly. The binding distance R (Br···N) is in a range of 3.1—3.2 Å, which is smaller than the sum of van der Waals radii of N and Br [33]. The binding distance of HCCBr···NCH complex is 3.155 Å, which is larger than the HCCBr···NCM' complexes and smaller than the MCCBr···NCH complexes. A good consistency between the binding distance and the interaction energy is found in the HCCBr···NCM' complexes. The HCCBr···NCAg complex has the shortest binding distance, and the largest one is that of the HCCBr···NCAu complex. For the MCCBr···NCH complexes, there is a difference. The interaction energy of the CuCCBr···NCH complex is more negative than that of the AgCCBr···NCH complex, but the sequence of the binding distance is opposite. A good linear relationship is present between the binding distance and the interaction energy with a regression coefficient of 0.986, which has been displayed in Fig. 1.

Table 5 Second-order stabilization energies (E^2, in kcal·mol^{-1}) and amount of charge transfer (Q_{CT}, in e) in MCCBr···NCH and HCCBr···NCM' (M, M'=Cu, Ag, and Au) complexes

Complexes	E^2	Q_{CT}
HCCBr···NCH	1.64	0.00182
HCCBr···NCAg	2.91	0.00439
HCCBr···NCCu	2.71	0.00432
HCCBr···NCAu	2.26	0.00293
AgCCBr···NCH	1.27	0.00045
CuCCBr···NCH	1.27	0.00053
AuCCBr···NCH	1.57	0.00088

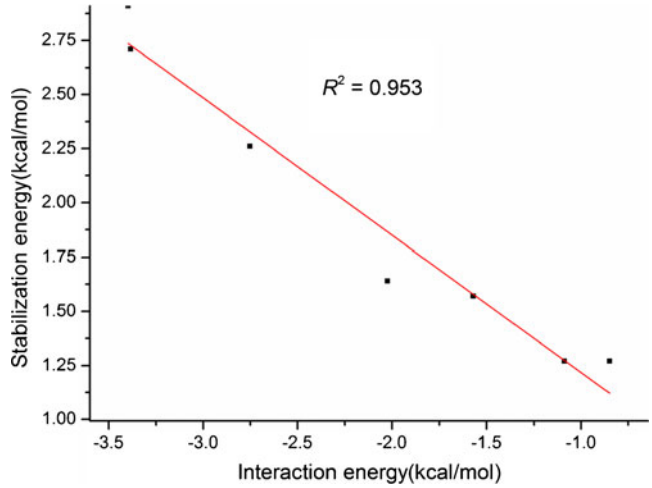

Fig. 2 The relationship between the interaction energy and the stabilization energy

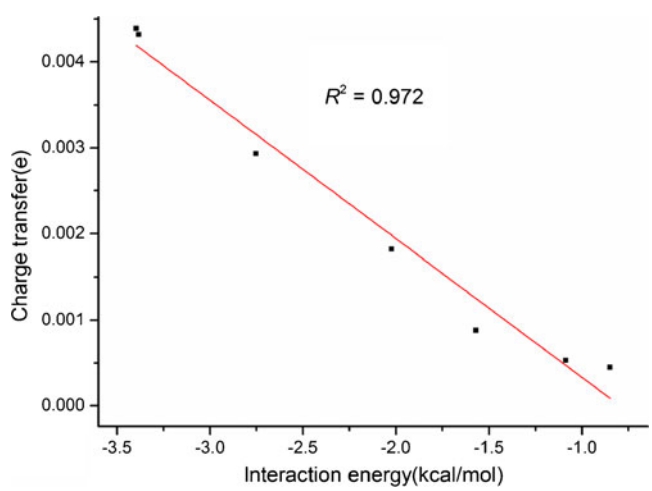

Fig. 3 The relationship between the interaction energy and the charge transfer

Molecular electrostatic potential analysis

Molecular electrostatic potential (MEP) has been confirmed to be an effective tool for analyzing and predicting noncovalent interactions [13–15]. The values of MEP are denoted as $V_S(r)$. Politzer et al. have taken that halogen bonding interaction is an electrostatically-driven noncovalent interaction and the halogen bond donating and accepting tendencies can be related quantitatively to most positive MEP, $V_{S,max}(r)$ and most negative MEP, $V_{S.min}(r)$. We calculated $V_{S,max}(r)$ of the Br atom in the MCCBr molecules and $V_{S.min}(r)$ of the N atom in the NCM' molecules. We take the surfaces to be the 0.001 electrons/bohr^3 contours of the molecular electronic densities, which have been verified to be sufficient to compute MEP by Politzer [13–15]. The results are summarized in Table 3. The MEP values have a very good consistency with the interaction energy. That is to say, $V_{S,max}(r)$ of the Br atom in the MCCBr molecules decreases in the order of HCCBr> AuCCBr>CuCCBr>AgCCBr, and $V_{S.min}(r)$ of the N atom in the NCM' molecules increases in the order of NCH< NCAu<NCCu<NCAg. The above analysis shows that the inclusion of transition metal atoms did not change the nature of the Br···N halogen bond, which is driven by electrostatic interaction.

NBO analysis

To evaluate the origin of halogen bonding in the MCCBr···NCH and HCCBr···NCM' systems, the NBO analysis has been carried out. In the MCCBr···NCH and HCCBr···NCM' complexes, the donor orbital is the lone pair electrons orbital, n(N), in the N atom, and the accepting orbital is the antibonding orbital of the C—Br bond, σ^*(C—Br). We computed the orbital energy of the n(N) and σ^*(C—Br) orbitals in the MCCBr and NCM' molecules, which is present in Table 4. Both $E\{n(N)\}$ and $E\{\sigma^*(C—Br)\}$ increase when the H atoms in the NCH and HCCBr molecules are replaced by Ag, Cu, or Au atom. The order of $E\{n(N)\}$ is NCAg> NCCu>NCAu, and $E\{\sigma^*(C—Br)\}$ has the same order. This indicates that the electron donating ability strengthened and the halogen donating ability weakened. We also computed the NPA charge of the N and Br atoms in the MCCBr and NCM' molecules. The result shows that q(N) becomes more negative and q(Br) becomes more positive when the H atoms in the NCH and HCCBr molecules are replaced by Ag, Cu, or Au atom. The order of q(N) is NCAg>NCCu>NCAu, and the order of q(Br) is NCAg<NCCu<NCAu. The above analysis indicates that the results of orbital energy and NPA charge have the same trend with the interaction energy and molecular electrostatic potential.

To measure the orbital interaction [$n(N)\rightarrow\sigma^*(C—Br)$] quantificationally, the second-order stabilization energies (E^2) and amount of charge transfer (Q_{CT}) are summarized in Table 5. The stabilization energy of the $n(N)\rightarrow\sigma^*(C—Br)$ orbital interaction in the HCCBr···NCH complex is 1.64 kcal·mol^{-1}. This value increases in the HCCBr···NCM' complexes and decreases in the MCCBr···NCH complexes, which is consistent with the interaction energy. The order of E^2 is the same as the interaction energy in most of the complexes, except for the AgCCBr···NCH and CuCCBr···NCH complexes, which have the same E^2 values (1.27 kcal·mol^{-1}). Charge transfer occurs between the electron donors and halogen donors. Q_{CT} is very small, indicating that the charge transfer has a small contribution in the complex formation. When the H atoms are replaced by Ag, Cu, or Au atom, Q_{CT} increases for the HCCBr···NCM' complexes and decreases in the MCCBr···NCH complexes, which is in accordance with the interaction energy and the stabilization energy. Figure 2 shows the relationship between the stabilization energy and the interaction, and a plot of the charge transfer with the interaction energy is displayed in Fig. 3.

Conclusions

The MCCBr···NCH and HCCBr···NCM' (M, M'=Cu, Ag, and Au) halogen-bonded complexes have been investigated at the MP2 level using different basis sets. The transition metal atoms in the halogen bond donors result in a weakening of the halogen bonds, whereas those in the electron donors lead to an enhancement of the halogen bonds. The binding distance presents a good linear relationship with the interaction energy. MEP analysis reveals that the $V_{s,max}$ values on the Br atoms decreases and the $V_{s,min}$ values on the N atoms become more negative as the H atoms are replaced by Cu, Ag, or Au atom. The results of the stabilization energy and the charge transfer are in accordance with the interaction energy.

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