J Mol Model (2014) 20:2133
DOI 10.1007/s00894-014-2133-8

ORIGINAL PAPER

The X···Au interactions in the CF_3X (X = Cl, Br) ···Au_n (n=2, 3, and 4) complexes

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Received: 29 October 2013 / Accepted: 27 December 2013 / Published online: 19 February 2014

Abstract I have performed quantum chemical calculations for the CF_3X (X = Cl, Br) ···Au_n (n=2, 3, and 4) complexes at M05-2X/aug-cc-pVDZ(PP) level. Two types of optimized structures were obtained. Type I complexes are stabilized by the coordination force between the negative electrostatic potential of halogen atom and the gold atom, and type II complexes contain halogen bonds formed between the σ-hole of the halogen atoms and the negative electrostatic potential of Au_n. Results of the interaction energy indicate that type I complexes are more stable than type II complexes. AIM analysis reveals that type II complexes are a closed shell interaction and there is a partially covalent nature for type I complexes.

Keywords Coordination force · Halogen bond · Electron density · Electrostatic potential

Introduction

Intermolecular interactions play a great role in the fields of chemistry, physics, and biology. In recent years, great progress has been made in the research of different types of intermolecular interactions [1–3]. Halogen bonding is a noncovalent interaction between a halogen-containing molecule and a neutral or anionic molecule, which is similar to hydrogen bonding in terms of directionality and strength [4]. Politzer et al. [5–11] reported that a halogen bond is an interaction between a region of positive potential in the axis of the covalent bond of the halogen atom (called the σ-hole) and a region of negative potential on another molecule.

Halogen-bonded interaction plays a prominent role in crystal engineering, molecular recognition, and biological systems [12–22]. Recently, the supramolecular assembly of gold nanoparticles (AuNPs) mediated by the halogen-bonded interactions has been attracted a deal of attention [23–25]. Van der Boom et al. [23, 24] demonstrated for the first time that the assembly of hybrid organic AuNP structures onto planar functionalized surfaces mediated by halogen bonding. Their findings indicate that the formation of structurally well-defined and task-specific nanoparticle-based assemblies based on halogen bond is a realistic possibility. More interestingly, Blakey and co-workers [25] presented the interaction of iodoperfluorobenzene compounds with AuNPs and well defined halogen-bonded assemblies of AuNPs formed. A question was proposed: what is the nature of the interaction between the halogen atom and AuNPs?

In order to solve this problem, I investigated the X···Au interactions in the CF_3X (X = Cl, Br) ···Au_n (n=2, 3, and 4) complexes with quantum chemical calculations. By studying these complexes, the following questions are answered: 1) Is there a X···Au interaction? 2) If this interaction exists, is it a halogen bond or other intermolecular interaction?

Computational details

The geometries of all the complexes were fully optimized by means of the hybrid M05-2X functional [26, 27]. This method has been proven to be reliable for the study of noncovalent complexes [28, 29]. The aug-cc-pVDZ-PP basis set, which uses pseudopotentials to describe the inner core orbitals, was employed for Au, while for other atoms aug-cc-pVDZ was applied. All of the optimized structures were characterized as minima in the potential energy surface by verifying that all the vibrational frequencies are real. The basis set superposition error (BSSE) was eliminated by using the standard counterpoise correction (CP) method of Boys and Bernardi [30]. The above calculations were performed with the Gaussian 09 suite of programs [31].

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The quantum theory of atoms in molecules (QTAIM) analysis [32] was performed with the help of AIMAll [33] using the M05-2X wavefunctions generated by Gaussian 09. The electron density shift was calculated by evaluating the difference between the total electron densities of the $CF_3X\cdots Au_n$ complexes and individual moieties (CF_3X and Au_n), which was fulfilled by the Multiwfn programs [34].

Results and discussion

Geometries and interaction energies

I attempted to search stable structures for the $CF_3X\cdots Au_n$ complexes from different initial configuration. Two types of minimas without imaginary frequencies were obtained. The optimized structures of these complexes are displayed in Fig. 1. For convenience, the left type in Fig. 1 is called type I complex, and the right is type II complex. The most positive MEP, $V_{S,max}$ and the most negative MEP, $V_{S.min}$ in the Br, Cl atoms and the Au_n molecules were calculated at the M05-2X level, which are collected in Table 1. I 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 [5, 8]. The σ-holes in the CF_3Cl and CF_3Br molecules are in the positive outer regions of the halogen atoms, which are accompanied negative lateral sides. $V_{S,max}$ in the Br atom are larger than that in the Cl atom, which is consistent with previous study [8]. It is interesting that there are negative potentials in Au_n, which lies in the plane of the molecules. The molecular surface electrostatic potential of Au_n was shown in Fig. 2. One can see from Fig. 1 and 2 that the gold atom interacted with the negative region of the halogen donor in type I complexes, and for type II complexes, the σ-hole along the C−X bond pointed to the plane of Au_n. Because the halogen bond was defined as the interaction between the σ-hole and the other molecule, type I complexes do not contain halogen-bonded interaction from the geometrical view. Type I complexes are stabilized by the traditional coordination force [35, 36] between the gold atom and the negative potential of the halogen atom, which has been proven to be essential for the transition metal complex. In type II complexes, the interaction is between the σ-hole of the halogen atom and the negative potential of Au_n molecule, which indicates electrostatically-driven halogen-boned interaction.

Table 2 lists the key geometrical parameters and interaction energies for the studied complexes. It is clear that X···Au interactions in type I complexes are far away from linear ($\angle$(C−X···Au)=90°~110°) and the values of $\angle$(C−X···Au) for type II complexes is near to 180°. This again confirms that type I complexes are not halogen bonds because the most essential feature of a halogen bond is the linear interaction between the C−X bond and the negative region of the other molecule. From Table 2 one can see that the distance between halogen and gold atom in type I complexes are smaller than

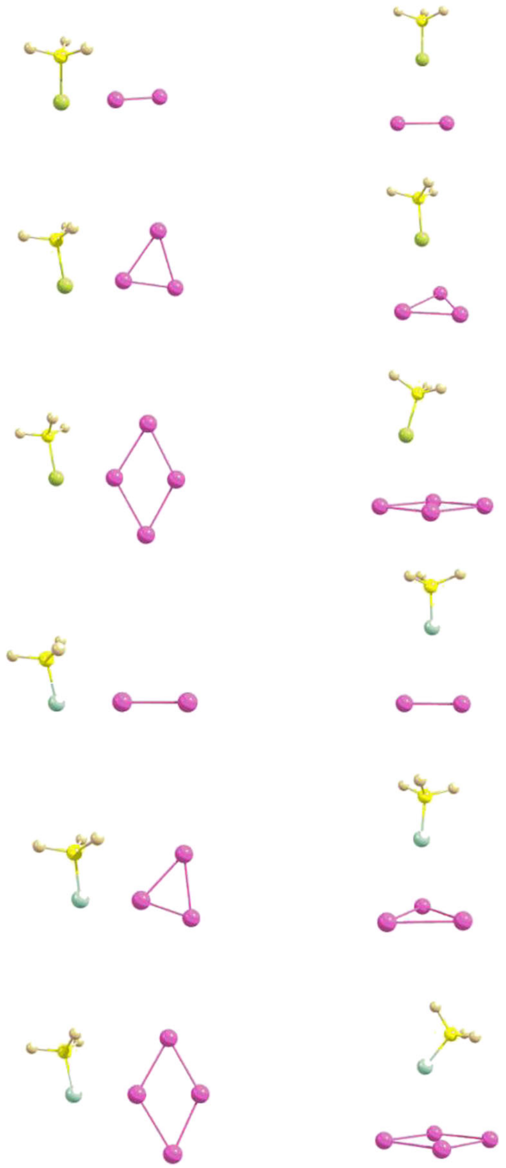

Fig. 1 Optimized geometries of the CF_3X (X=Cl, Br) $\cdots Au_n$ (n=2, 3, and 4) complexes

Table 1 $V_{S,max}$ and $V_{S,min}$ (in kcal mol^{-1}) in the CF_3Br, CF_3Cl, and Au_n molecules (in kcal mol^{-1}) calculated at the M05-2X level

Molecules	$V_{S,max}$(r)	$V_{S.min}$(r)
CF_3Br	22.0	−2.9
CF_3Cl	20.5	−1.9
Au_2	31.4	−12.1
Au_3	32.7	−8.4
Au_4	28.3	−9.73

For the CF_3Br and CF_3Cl molecules, only negative $V_{S.min}$ values on the lateral sides of the halogen are listed

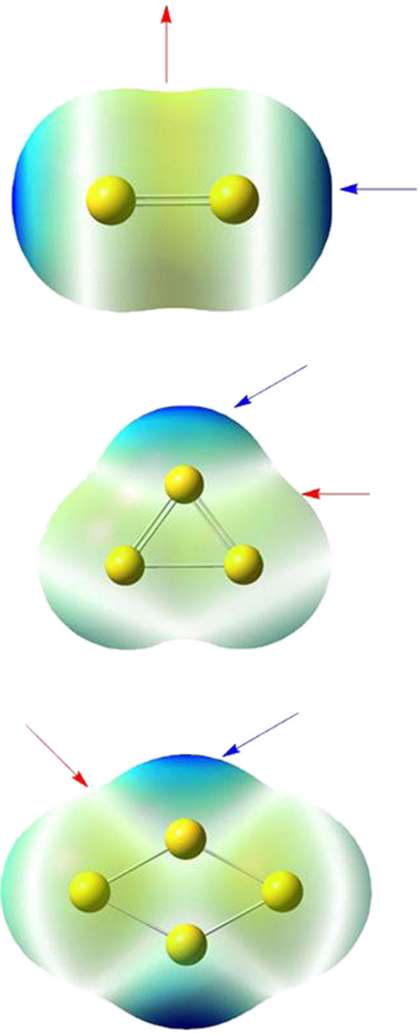

Fig. 2 Molecular surface electrostatic potential of Au_n (n=2, 3, and 4), computed on the 0.001 a.u. contour of the electronic density at M05-2X/aug-cc-pVDZ-PP computational level. The *blue* and *red arrows* are denoted to be the $V_{S,max}$ and $V_{S,min}$ sites respectively

that in type II complexes, which is consistent with the interaction energy. For example, type I complex of $CF_3Br\cdots Au_2$ are more stabilized than type II complex (9.72 vs 2.71 kcal mol^{-1}), and R (X···Au) in the latter is 3.530 Å, larger than the former 2.656 Å. The choice of the gold cluster influences the result slightly. For type I complexes of $CF_3Br\cdots Au_n$, the interaction energy of $CF_3Br\cdots Au_4$ exceeds 1.31 kcal mol^{-1} more than that of $CF_3Br\cdots Au_2$. The interaction energy of $CF_3Cl\cdots Au_3$ and $CF_3Cl\cdots Au_4$ for type I complex is almost the same. In both type I and type II complexes, the Br···Au interactions become much stronger in strength than the Cl···Au interactions. That is to say, the Br···Au coordination force is much stronger than that of Cl···Au. The electrostatic potential in the σ-hole of CF_3Br is more positive than that of CF_3Cl, which decides the stability order of type II complexes. The C−X bonds in all the complexes present a red-shift, which says that the length of the C−X bonds become larger and the vibration frequencies decrease. The degree of the C−X bonds change in type I complexes is larger than that in type II complexes, which is consistent with the previous study [37], indicating that larger interaction energies led to stronger elongation of the C−X bonds.

Electron density shift

In order to obtain a deeper insight into the X···Au interaction, we analyzed the electron density shift that accompanied the formation of the complexes. The shifts of electron densities for the $CF_3Br\cdots Au_n$ complexes are illustrated in Fig. 3. It is clearly seen that the shifts of electron density in type I complexes are greater than that in type II complexes. Figure 3 shows that the electron density lost/gain regions are alternated, and there are differences between these two types of complexes. Gold atoms gained large density and fluorine atoms in the CF_3Br molecules lost a lot of density in type I complexes. For type II complexes, the region of electron density lost is in the backbone of gold clusters and the region of electron density gain is around the fluorine atoms. Type I and II complexes behaved similarly in the interactive regions, which says that the loss and gain of electron density occurs around the outer regions of CF_3Br and Au_n molecules respectively.

AIM analysis

AIM theory is based on a topological analysis of the electron charge density and its Laplacian, which has been successfully applied in characterizing hydrogen bonds and halogen bonds of different strengths in a wide variety of molecular complexes. With this in mind, we performed a topological analysis to gain more insights into the nature of the $CF_3X\cdots Au_n$ complexes. The results show that a bond path exists linking the halogen atom with the gold atom accompanied by a bond critical point (BCP) between the two atoms in type I complexes, and a ring critical point (RCP) formed between one halogen atom and several gold atoms is detected in type II complexes. The electron density at the BCPs and RCPs and their Laplacians are summarized in Table 3. For type I complexes, all the electron densities, ρ, are much larger than those of type II complexes, which is in accordance with the interaction energy. One can see a linear relationship between the electron density and the interaction energy from Fig. 4. The linear correlation coefficient for this dependence amounts to 0.912. The Laplacians, $\nabla^2\rho$, are positive, indicating the typical noncovalent type of interactions in these complexes.

The electronic energy density can also provide another insight into the nature of noncovalent interactions. The electronic energy density H, local one-electron kinetic energy density G, and local potential energy density V are also given in Table 3. The sum of G and V is H. G is positive and V is negative. The positive or negative sign of H depends on the

Table 2 Geometric and energetic data calculated with M05-2X for the CF_3X (X = Cl, Br) $\cdot Au_n$ (n=2, 3, and 4) complexes

Complexes	R (X···Au)	∠(C−X···Au)	Δr (C−X)	Δυ (C−X)	ΔE	ΔE_{BSSE}
$CF_3Br\cdots Au_2$(I)	2.656	95.6	0.031	−10.24	−10.45	−9.72
$CF_3Br\cdots Au_3$(I)	2.607	97.4	0.041	−22.98	−11.65	−10.88
$CF_3Br\cdots Au_4$(I)	2.605	101.4	0.037	−13.88	−11.81	−11.03
$CF_3Br\cdots Au_2$(II)	3.296	179.6	0.006	−7.55	−3.11	−2.71
$CF_3Br\cdots Au_3$(II)	3.328	166.3	0.004	−7.32	−3.43	−2.93
$CF_3Br\cdots Au_4$(II)	3.436	144.0	0.008	−6.76	−3.84	−3.24
$CF_3Cl\cdots Au_2$(I)	2.586	100.8	0.030	−7.39	−7.61	−6.99
$CF_3Cl\cdots Au_3$(I)	2.560	101.5	0.037	−13.63	−8.13	−7.51
$CF_3Cl\cdots Au_4$(I)	2.576	102.9	0.231	−11.55	−8.03	−7.51
$CF_3Cl\cdots Au_2$(II)	3.398	178.7	0.003	−5.10	−1.97	−1.73
$CF_3Cl\cdots Au_3$(II)	3.334	171.6	0.001	−0.41	−2.26	−1.93
$CF_3Cl\cdots Au_4$(II)	3.361	131.7	0.001	−0.37	−2.62	−2.30

Energies are given in kcal mol^{-1} and distances in Å. R (X···Au) is the distance between the halogen and gold atom in type I complexes. For type II complexes, R (X···Au) denotes the distance between the halogen atom and the centroid of Au_n. Δr(C−X) represents the variation of C−X bond distance and Δυ(C−X) is the C−X vibrational frequence change. ΔE and ΔE_{BSSE} is the interaction energy of the complexes without and with BSSE correction respectively

relative magnitude of G and V. If the G value is larger than the absolute value of V, the H value is positive, thus a purely closed shell interaction is expected. Otherwise, the negative H indicates that the interactions correspond to some degree of covalent character. From Table 3 one can see that the negative H value is found for type I complexes and the positive H value is obtained for type II complexes. This indicates that type II complexes are a closed shell interaction and there is a partially covalent nature for type I complexes [38].

Conclusions

In summary, I have investigated the noncovalent complexes between CF_3X (X = Cl, Br) and Au_n (n=2, 3, and 4) using ab initio calculations. It was found that there were two different

Table 3 AIM properties (in a.u.) for the systems under study

Complexes	ρ	$\nabla^2\rho$	G	V	H
$CF_3Br\cdots Au_2$(I)	0.0524	0.159	0.0474	−0.0552	−0.0078
$CF_3Br\cdots Au_3$(I)	0.0588	0.171	0.0534	−0.0640	−0.0106
$CF_3Br\cdots Au_4$(I)	0.0591	0.173	0.0538	−0.0644	−0.0106
$CF_3Br\cdots Au_2$(II)	0.0093	0.024	0.0051	−0.0041	0.0010
$CF_3Br\cdots Au_3$(II)	0.0068	0.017	0.0036	−0.0029	0.0007
$CF_3Br\cdots Au_4$(II)	0.0088	0.023	0.0049	−0.0041	0.0008
$CF_3Cl\cdots Au_2$(I)	0.0504	0.185	0.0517	−0.0570	−0.0053
$CF_3Cl\cdots Au_3$(I)	0.0543	0.195	0.0554	−0.0622	−0.0068
$CF_3Cl\cdots Au_4$(I)	0.0526	0.189	0.0532	−0.0593	−0.0061
$CF_3Cl\cdots Au_2$(II)	0.0068	0.018	0.0037	−0.0028	0.0009
$CF_3Cl\cdots Au_3$(II)	0.0062	0.017	0.0035	−0.0026	0.0009
$CF_3Cl\cdots Au_4$(II)	0.0084	0.025	0.0054	−0.0046	0.0008

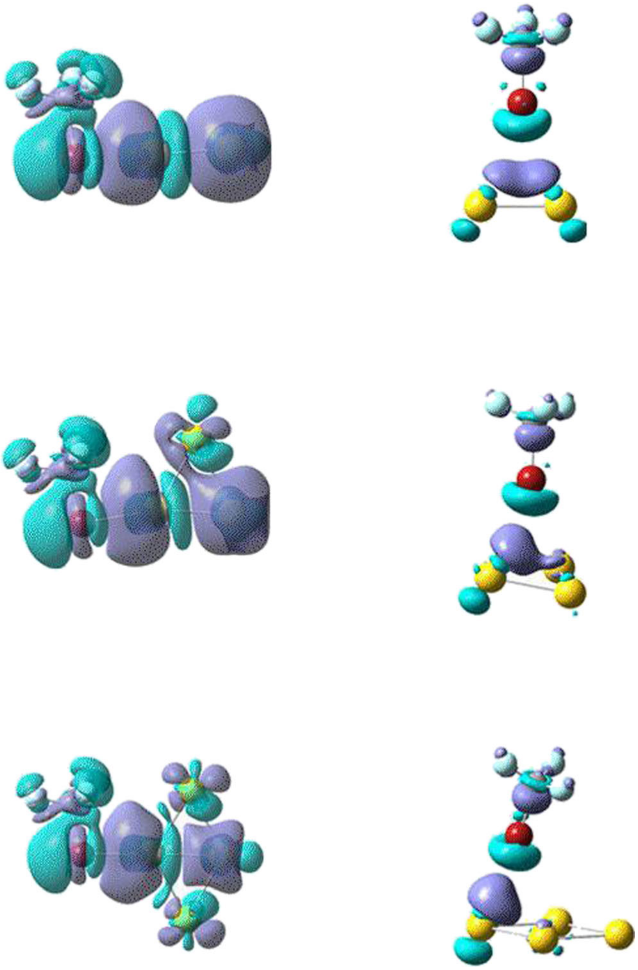

Fig. 3 Shifts of electron density, in a.u., as a result of the $CF_3Br\cdots Au_n$ complexes. The plots are computed in the 0.001 electrons/bohr^3 contours of the molecular electronic densities. *Purple* regions denote electron gain, and *turquoise* regions represent electron lost

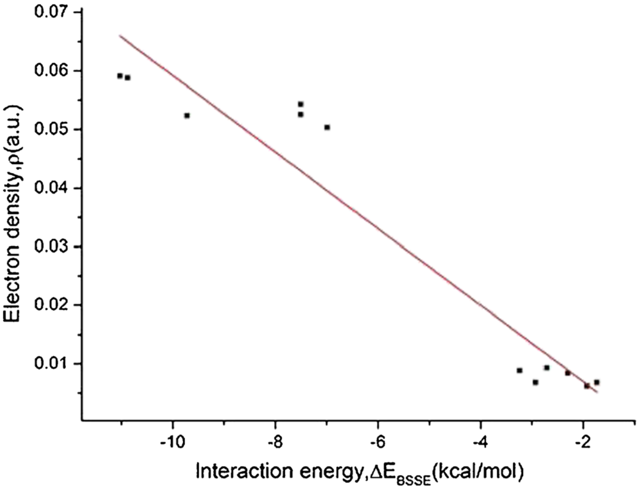

Fig. 4 Relationship between the interaction energy and electron density

optimized structures. One is stabilized by the coordination force between the negative region of halogen atom and the gold atom, and the other contains a halogen bond formed between the σ-hole of the halogen atom and the negative electrostatic potential of Au_n. Type I complexes are more stable than type II complexes, which is confirmed by geometric and energetic parameters. The result of electron density shift is consistent with the interaction energy. By means of AIM analysis, BCPs and RCPs were detected in type I and type II complexes respectively. The electron density of BCP in type I complexes is larger than that in type II complexes. The electronic energy density for these two types of complexes has different plus or minus, indicating different natures for the two noncovalent interactions.

Acknowledgments The author is grateful for the help of the high performance computing centre in Shandong University and reasonable advice of Prof. Feng in Shandong University.

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