Chalcogen Bond: A Sister Noncovalent Bond to Halogen Bond

Weizhou Wang, Baoming Ji,* and Yu Zhang

College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang 471022, China

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A sister noncovalent bond to halogen bond, termed chalcogen bond, is defined in this article. By selecting the complexes $H_2CS\cdots Cl^-$, $F_2CS\cdots Cl^-$, $OCS\cdots Cl^-$, and $SCS\cdots Cl^-$ as models, the bond-length change, interaction energy, topological property of the electron charge density and its Laplacian, and the charge transfer of the chalcogen bond have been investigated in detail theoretically. It was found that the similar misshaped electron clouds of the chalcogen atom and the halogen atom result in the similar properties of the chalcogen bond and the halogen bond. Experimental results are in good agreement with the theoretical predictions.

Introduction

Unlike the hydrogen bond, the key role of the halogen bond in molecular recognition, crystal engineering, and biomolecular systems has been revealed only in recent years.[1−14] Considering, however, that the halogen atom (Hal) and the halogen bond electron donor (Y) are both negatively charged, the very existence of the halogen bond is surprising. The problem was explained by Politzer et al.,[12,13] who showed the existence of electropositive crown called σ-hole (the region of positive charge) at the outermost region of halogen atom directed to the electron donor (the region of negative charge). At the same time, the three lone electron pairs of Hal produce a belt of negative electrostatic potential around the central part of the halogen atom, leaving the possibility for Hal to act as an electron donor.[10] Similarly, the chalcogen atom (O, S, Se, Te, Po) may also have an electropositive region at its outermost end, as shown in Figure 1, although it has only two lone pairs of electrons. This means that the chalcogen atom (Chal) can also interact with an electron donor to form a noncovalent bond, which is similar to the halogen bond. Borrowing from the definitions of the halogen bond and the hydrogen bond,[7] we call the Chal···Y contact the chalcogen bond.

The well-known chalcogen bond is the noncovalent chalcogen−chalcogen interaction in which one of the chalcogens acts as the acceptor of electron density.[15−19] The chalcogen−chalcogen interaction is very much like the halogen−halogen interaction. Certainly, besides the chalcogen atom, the electron donor can be another atom or group.[20] Previous studies on the chalcogen bond mainly focused on the X−Chal···Y bonding types.[15−20] We know that the chalcogen atom can have a single bond or a double bond with one atom. Then, an interesting question is whether there is the chalcogen bond with the type of X═Chal···Y. In this study, we expanded the concept of chalcogen bond to the X═Chal···Y bonding types and selected $H_2CS\cdots Cl^-$, $F_2CS\cdots Cl^-$, $OCS\cdots Cl^-$, and $SCS\cdots Cl^-$ as model complexes to investigate the X═Chal···Y chalcogen bond in detail. Note that the chalcogen atom donors and acceptors used in this article are simple but representative. For other chalcogen atom donors and acceptors, results should be very similar.

* To whom correspondence should be addressed. Tel: +86-379-65523821. Fax: +86-379-65523821.

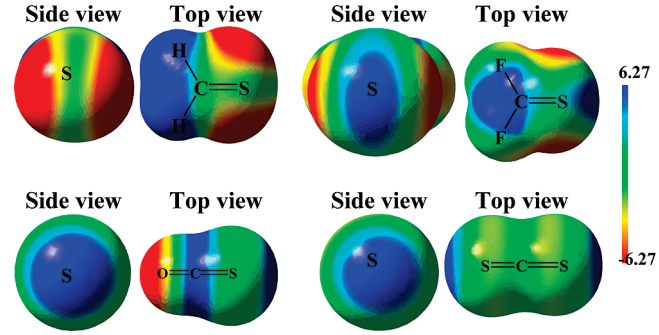

Figure 1. Electrostatic potentials of H_2CS, F_2CS, OCS, and SCS computed at the MP2/aug-cc-pVTZ theory level with a scale of −6.27 (red) to 6.27 kcal/mol.

Computational Details

Using the Gaussian 03 program package,[21] structures were fully optimized and characterized by frequency computations at the second-order Møller−Plesset (MP2) theory level with the Dunning's correlation consisted basis sets aug-cc-pVTZ. Interaction energies and electrostatic potentials were also calculated at the MP2/aug-cc-pVTZ level of theory. The basis set superposition error (BSSE) was eliminated by the standard counterpoise (CP) correction method of Boys and Bernardi.[22]

We analyzed the bonding characteristic of the S···Cl contact by using Bader's "atoms in molecules" (AIM) theory.[23] AIM analysis was performed with the AIM2000 software package using the MP2/aug-cc-pVTZ wave functions as input.[24] The analysis went further with the natural bond orbital (NBO) theory of Weinhold and coworkers.[25] NBO analysis used the MP2-optimized structures, the Hartree−Fock (HF) densities, and the built-in subroutines of the Gaussian 03 program.

Results and Discussion

Geometrical Parameters, Interaction Energies and Vibrational Frequencies. Some selected geometrical parameters, vibrational frequencies, and interaction energies of the four chalcogen-bonded complexes were given in Table 1. The structures of the complexes can be seen from Figure 1. For comparison, the C═S bond lengths and the corresponding harmonic vibrational frequencies of the monomers were also listed in Table 1.

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TABLE 1: Optimized Geometries (angstroms and degrees), Frequencies (inverse centimeters), Number of Imaginary Frequencies (N_{img}), and Interaction Energies (kilocalories per mole) of the Four Chalcogen-Bonded Complexes[a]

complex	$r_{(C=S)}$	$d_{(S\cdots Cl^-)}$	∠CSCl$^-$	freq (C=S)	N_{img}	ΔE^{CP}
$H_2CS\cdots Cl^-$	1.6208(**1.6145**)	3.3193	180	1063.0(**1096.9**)	1	−0.81
$F_2CS\cdots Cl^-$	1.5936(**1.5958**)	3.0872	180	symm: 758.7(**801.6**), asy: 1345.4(**1401.5**)	1	**−7.77**
$OCS\cdots Cl^-$	1.5695(**1.5663**)	3.0386	180	symm: 856.6(**888.0**), asy: 2020.8(**2083.8**)	0	−9.88
$SCS\cdots Cl^-$	1.5604(**1.5627**)	3.0072	180	symm: 645.5(**674.4**), asy: 1558.1(**1615.2**)	0	−10.59

[a] Numbers in bold are those of the corresponding monomers.

Table 1 shows that the C=S bonds in $H_2CS\cdots Cl^-$ and $OCS\cdots Cl^-$ are elongated by 0.0063 and 0.0032 Å, respectively, upon the complexes formation, whereas the C=S bonds in $F_2CS\cdots Cl^-$ and $SCS\cdots Cl^-$ are contracted by 0.0022 and 0.0023 Å, respectively, upon the complexes formation. This is similar to the X−Hal bond-length change upon halogen bond formation in which the fluorine substitution always leads to the X−Hal bond contraction.[8,14] The corresponding harmonic vibational frequencies are also shown in Table 1. The frequency analysis reveals the red-shifting character of all C=S$\cdots$Cl$^-$ interactions. For the bond-length change−frequency shift correlation upon molecule complexation, one commonly accepted view is that bond elongation means red shift and bond contraction indicates blue shift. Evidently, the empirical correlation is violated here. McDowell et al. have recently rationalized the correlation between the bond-length change and the sign of the frequency shift upon molecule complexation by employing a model based on perturbation theory.[26] It is also noticed from Table 1 that the structures of $H_2CS\cdots Cl^-$ and $F_2CS\cdots Cl^-$ are transition states (only one imaginary frequency) and the structures of $OCS\cdots Cl^-$ and $SCS\cdots Cl^-$ are true minima (all real frequencies) on their respective potential energy surfaces. As will be shown later, the presence of imaginary frequencies here does not affect the existence of the C=S$\cdots$Cl$^-$ chalcogen bond in real systems because $H_2CS\cdots Cl^-$ and $F_2CS\cdots Cl^-$ are just two model complexes.

It can be seen from Table 1 that the calculated CP-corrected interaction energies of the four complexes are in the −0.8 to −11 kcal/mol range, which are comparable in magnitude to those of the halogen bond.[8] So, from the energy point of view, why not chalcogen bond? Also, similar to the halogen bond, the fluorine substitution causes a considerable enhancement of the chalcogen bond strength.

Atoms in Molecules Analysis. Bader's AIM theory,[23] which is based on a topological analysis of the electron charge density and its Laplacian, has been widely applied in the study of the noncovalent bonds.[23,27] Employing AIM theory, Popelier developed a set of criteria for the assessment of the existence of hydrogen bond.[27] The most important evidence of hydrogen bonding is the existence of a bond path, an interatomic surface (IAS), and a bond critical point (BCP) between the donor hydrogen nucleus and the acceptor. At the same time, the electron density (ρ_b) at this BCP should range from 0.002 to 0.035 au, and the Laplacian of the electron density ($\Delta^2\rho_b$) should range from 0.024 to 0.139 au. In our previous study,[8] we found that the three criteria for hydrogen bond are all echoed in halogen bond. In the present study, the topological properties of the chalcogen bond were examined.

Figure 2 clearly shows the existence of a BCP in each S$\cdots$Cl$^-$ chalcogen bond. The bond paths associated with the chalcogen bond BCPs can also be seen in Figure 2. The electron density (ρ_b) of the BCP of the chalcogen bond is listed in Table 2. Again, the values for the chalcogen bonds fall within the proposed range of 0.002 to 0.035 au for the hydrogen bond. It has been proven that ρ_b is related to the bond order and thus to the bond strength.[23] As a result, the value of ρ_b is much lower for the S$\cdots$Cl$^-$ chalcogen bond in complex $H_2CS\cdots Cl^-$ compared with those of the S$\cdots$Cl$^-$ chalcogen bonds in the other three complexes. The two negative eigenvalues of the Hessian matrix of electron density, λ_1 and λ_2, measure the degree of contraction of ρ_b perpendicular to the bond toward the critical point, and the positive eigenvalue (λ_3) measures the degree of contraction parallel to the bond and from the BCP toward each of the neighboring nuclei. The Laplacian $\Delta^2\rho_b$ is the sum of eigenvalues λ_1, λ_2, and λ_3. Bader pointed out that for closed-shell interactions (ionic bonds, hydrogen bonds, and van der Waals interactions), the value $\Delta^2\rho_b$ is positive.[23] According to Table 2, the S$\cdots$Cl$^-$ chalcogen bonds are all typical closed-shell interactions. Moreover, the positive values of $\Delta^2\rho_b$ all lie in the proposed range of 0.024 to 0.139 au for hydrogen bond. Evidently, the topological properties of the chalcogen bonds studied here also meet the three criteria for the existence of the hydrogen bond and the halogen bond. The ellipticity, ε, is defined as $\lambda_1/\lambda_2 - 1$ and measures the extent to which charge is preferentially accumulated. The ellipticity provides a measure of not only the π character of a bond but also the bond stability. A large value of bond ellipticity reflects the bond instability; that is, the bond can be easily ruptured. In Table 2, the ε(S$\cdots$Cl$^-$) value of complex $H_2CS\cdots Cl^-$ is much larger than the ε(S$\cdots$Cl$^-$) values of the other three complexes, which means that the former chalcogen bond is weaker. This is consistent with the order of interaction energies.

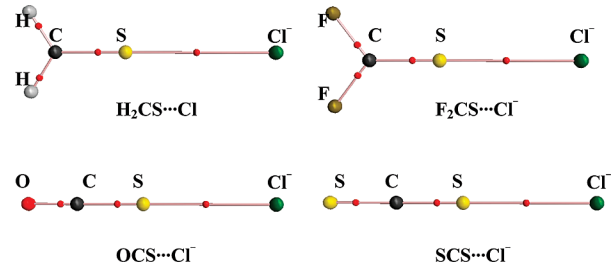

Figure 2. Structures and molecular graphs for the four studied chalcogen-bonded complexes. Small red dots represent the critical points.

Natural Bond Orbital Analysis. To better understand the nature of the chalcogen bond, NBO analysis has been carried out at the HF/aug-cc-pVTZ level of theory using MP2/aug-cc-pVTZ geometry. Some significant donor−acceptor orbital interactions and their second-order perturbation stabilization energies are collected in Table 3. Note that the second-order perturbation stabilization energy, ΔE^2, will allow us to quantitatively evaluate the charge transfer involving the formation of the chalcogen bond.

For the halogen bond, the charge transfer from the lone electron pairs of the halogen atom acceptor is mainly directed to the X−Hal antibonding orbital of the halogen atom donor.[8] Gleiter and coworkers systematically explored the nature of the chalcogen−chalcogen interactions.[17−19] They also found that the charge transfer occurs mainly between the lone pair of the donor

TABLE 2: Density (ρ_b), Density Laplacian ($\Delta^2\rho_b$), Eigenvalues of the Hessian Matrix (λ_1, λ_2, λ_3), and Ellipticity (ε) at the Bond Critical Points between S and Cl$^-$ of the Four Chalcogen-Bonded Complexes[a]

complex	interaction	ρ_b	$\nabla^2\rho_b$	λ_1	λ_2	λ_3	ε
$H_2CS\cdots Cl^-$	S$\cdots$Cl$^-$	0.0109	0.0356	−0.0071	−0.0061	0.0487	0.1583
$F_2CS\cdots Cl^-$	S$\cdots$Cl$^-$	0.0171	0.0518	−0.0119	−0.0112	0.0749	0.0686
$OCS\cdots Cl^-$	S$\cdots$Cl$^-$	0.0188	0.0557	−0.0130	−0.0130	0.0818	0.0000
$SCS\cdots Cl^-$	S$\cdots$Cl$^-$	0.0202	0.0598	−0.0143	−0.0143	0.0883	0.0000

[a] All units are atomic units.

TABLE 3: Some Significant Donor−Acceptor Orbital Interactions and Their Second-Order Perturbation Stabilization Energies (ΔE^2, kilocalories per mole) of the Four Chalcogen-Bonded Complexes[a]

complex	donor	acceptor	interaction	ΔE^2
$H_2CS\cdots Cl^-$	LP(1) Cl$^-$	BD*(2) C=S	$n\rightarrow\sigma^*$	0.24
	LP(3) Cl$^-$	BD*(1) C=S	$n\rightarrow\pi^*$	0.40
	LP(4) Cl$^-$	BD*(2) C=S	$n\rightarrow\sigma^*$	3.39
$F_2CS\cdots Cl^-$	LP(1) Cl$^-$	BD*(1) C=S	$n\rightarrow\sigma^*$	0.56
	LP(3) Cl$^-$	BD*(2) C=S	$n\rightarrow\pi^*$	0.72
	LP(4) Cl$^-$	BD*(1) C=S	$n\rightarrow\sigma^*$	6.76
$OCS\cdots Cl^-$	LP(1) Cl$^-$	BD*(1) C=S	$n\rightarrow\sigma^*$	0.68
	LP(2) Cl$^-$	BD*(3) C=S	$n\rightarrow\pi^*$	0.48
	LP(3) Cl$^-$	BD*(2) C=S	$n\rightarrow\pi^*$	0.48
	LP(4) Cl$^-$	BD*(1) C=S	$n\rightarrow\sigma^*$	8.56
$SCS\cdots Cl^-$	LP(1) Cl$^-$	BD*(1) C=S	$n\rightarrow\sigma^*$	0.59
	LP(2) Cl$^-$	BD*(3) C=S	$n\rightarrow\pi^*$	0.69
	LP(3) Cl$^-$	BD*(2) C=S	$n\rightarrow\pi^*$	0.69
	LP(4) Cl$^-$	BD*(1) C=S	$n\rightarrow\sigma^*$	7.91

[a] BD* denotes the formally empty antibonding orbital, and LP denotes the occupied lone pair.

chalcogen atom and the chalcogen−carbon antibonding σ^* orbital. For the chalcogen bond with the type of X=Chal$\cdots$Y, it can be seen from Table 3 that the largest charge transfer occurs also between the lone electron pairs of Cl$^-$ and the C=S antibonding σ^* orbital. Let us add here that the energy of the C=S antibonding σ^* orbital is higher than that of the C=S antibonding π^* orbital. It is the orbital directionality that determines the overlap of the lone electron pair of Cl$^-$ and the C=S antibonding σ^* orbital. In comparing the stabilization energy terms in Table 3 with the corresponding interaction energy terms in Table 1, it is found that they do not correlate. This indicates that the consideration of only the charge-transfer interaction is sufficient in describing the ground-state stabilization of the chalcogen bond, and the electrostatic effect, polarization, charge-transfer, and dispersion contributions all play an important role. This is also true for the halogen bond and the chalcogen−chalcogen interaction.[5,17−19] In the complex $F_2CS\cdots Cl^-$ or $SCS\cdots Cl^-$, if there is such a large amount of charge being transferred to the C=S antibonding σ^* orbital, then why does not this bond grow consistently longer? This can be explained by employing the electrostatic attractive interaction: it is the electrostatic attractive interaction that causes the C=S bond in these complexes to be contracted.[14]

Experimental Evidences

In fact, the chalcogen bonds with the type of X=Chal$\cdots$Y exist in a large number of crystal structures, although no one give special emphasis on their roles in crystal growth and design. Table 4 collects some typical chalcogen bonds with the type of X=Chal$\cdots$Y in the crystal structures. Among the crystal structures listed in Table 4, the crystal structure of HIDVOF [bis(4,6-dimethyl-2-thiopyrimidinium)tetrachlorozincatum(II) monohydrate][31] is very interesting. As shown in Figure 3, in the crystal structure of HIDVOF, there are two kinds of C=S bonds: one is involved in the formation of the C=S$\cdots$Cl$^-$ chalcogen bond, and the C=S bond length is 1.650 Å; the other is intact, and the C=S bond length is 1.654 Å. The C=S bond is contracted about 0.004 Å upon the chalcogen bond formation. Selecting 4,6-dimethyl-2-thiopyrimidinium$\cdots$Cl$^-$ as the model complex and keeping the O$\cdots$Cl$^-$ distance constant at the experimental value 3.548 Å, we also computed the C=S bond-length change at the MP2/aug-cc-pVTZ theory level. The computation shows that the C=S bond is contracted about 0.011 Å, which agrees very well with the experimental observation.

TABLE 4: Selected Typical Chalcogen Bonds in the Crystal Structures

recode	contact	$R_{(C=S)}$ (Å)	$R_{(S\cdots X)}$ (Å)	∠CSX (deg)	ref
BXIMAM	C=S$\cdots$O	1.642	3.040	170.50	28
THHYDT	C=S$\cdots$S	1.642	3.432	162.81	29
WOSLEV	C=S$\cdots$N	1.633	3.320	166.17	30
HIDVOF	C=S$\cdots$Cl$^-$	1.650	3.548	167.18	31

Conclusions

From this study, the following conclusions can be drawn: (i) The chalcogen bonds are defined as those in which chalcogens behave as acceptors of electron density. Besides the X−Chal$\cdots$Y bonding types, the X=Chal$\cdots$Y bonding types are also of the chalcogen bond. (ii) The bond-length change, interaction energy, topological property of the electron charge density and its Laplacian, and the charge transfer of the chalcogen bond are very much like those of the halogen bond because of the similar misshaped electron clouds of the chalcogen atom and the halogen atom. (iii) In agreement with the theoretical results, the existence of the chalcogen bond with the type of X=Chal$\cdots$Y and the contraction of the X=Chal bond upon complex formation have been verified clearly by the crystal structure experiments.

Both oxygen and sulfur are indispensable elements of life, so the chalcogen bond should also exist in the biological

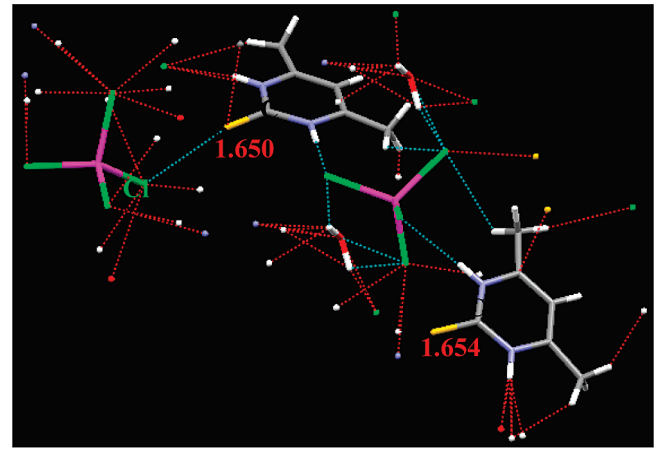

Figure 3. Crystal structure of the bis(4,6-dimethyl-2-thiopyrimidinium)tetrachlorozincatum(II) monohydrate.

systems. We believe that the key role of the chalcogen bond in molecular recognition, crystal engineering, and biomolecular systems will be rediscovered in the near future.

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