

On the Stability and the Bonding Model of $n \rightarrow \sigma^*$ Type Molecular Complexes, R_2Z-X-X : Proposal of 3c-4e Description for $Z-X-X$ in the Adducts

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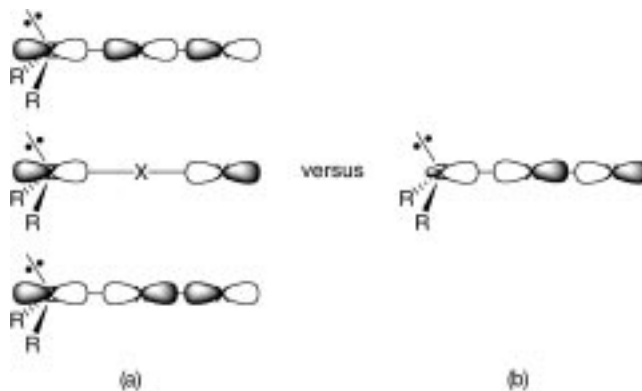
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The stability of the $Z-X-X$ bonds in R_2Z-X-X molecular complexes (MC) was examined for $O(CH_2CH_2)_2Se-I-X$, $PhMeSe-I-X$ ($X = Cl, Br$), and $Se(C_6H_4)_2Se-Br-Br$. The MC adducts were shown to be comparably stable or more stable than the corresponding trigonal bipyramidal adducts (TB) which equilibrate with the MC in some cases. To clarify the reason for the stability of the MC, the model adducts of $H_2Z^1X^2X$ (MC and TB) ($Z = O, S, Se$ and $X = Cl, Br$), together with the related species (H_2Z , X_2 , H_2ZX^+ , and H_2ZX^\bullet), were optimized with the 6-311++G(3df,2pd) basis sets at the MP2 and/or B3LYP levels. Calculations were also performed with different distances between 1Cl and 2Cl ($r(^1Cl, ^2Cl)$) in $H_2S-^1Cl-^2Cl$ (MC) and $r(S, ^2Cl)$ in $H_2S^1Cl^2Cl$ (TB), where $r = r_0 + 0.1m \text{ \AA}$ (r_0 : the optimized distance and $m = -1, 0, 1, 2, \text{ and } 3$). A charge transfer (CT) occurs from S to 2Cl in the $S-^1Cl-^2Cl$ bond of the MC as $r(^1Cl, ^2Cl)$ becomes larger, assuming a singlet multiplicity in the calculations. The situation is equal to that of $^1Cl-S-^2Cl$ in the TB, for which CT occurs from 1Cl to 2Cl . A 3c-4e description of the $Z-X-X$ bond in R_2Z-X-X (MC) is proposed based on the ab initio MO calculations by exhibiting the $10^{-1}X-2$ character, the N-X-L bonding system for hypervalent bonds proposed by Martin, for R_2Z-X-X (MC) practically. Bond orders for typical TB and MC were calculated from literature data according to Pauling's equation. The bond orders agree with the proposed 3c-4e model for the MC.

Introduction

The concept of molecular compounds or molecular complexes (MC) has been developed for a loose reversible association of the original molecules in a well-defined ratio, mostly 1:1. Mulliken has proposed a theory for MC based on quantum mechanics.¹ The driving force for the association is a charge transfer (CT) where electrons move from electron donors to acceptors in the complexes. On the other hand, a theory for complexes with trigonal bipyramidal structure has been proposed by Pimentel and Musher.^{2a} Such trigonal bipyramidal adducts (TB) contain hypervalent three-center-four-electron bonds (3c-4e) composed of linear $\sigma(p)$ orbitals. The 3c-4e description of the $X-Z-X$ bond in TB, such as halogen adducts of chalcogenides (R_2ZX_2 (TB)), was further developed by the preparation and characterization of variety of new compounds with TB structure³ and by

Scheme 1. Bonding Models for R_2ZX_2 (MC): (a) 3c-4e versus (b) $n \rightarrow \sigma^*$ Descriptions



theoretical calculations.² Thus the character of the $X-Z-X$ bond in TB is easily understood by the 3c-4e description of this bond.^{2,3} However, the character of the $Z-X-X$ bond in R_2Z-X-X (MC) cannot be so easily imagined by a weak $n \rightarrow \sigma^*$ CT description in some cases. The 3c-4e model is an attractive description for the $Z-X-X$ bond in R_2Z-X-X (MC) (Scheme 1).

The R_2Z-X-X (MC) are stabilized by CT from $n(Z)$ to $\sigma^*(X-X)$ orbitals of the components. The linear alignment of the three atoms, $Z-X-X$, must be superior to the bent structure for the CT. If the magnitude of the CT is small, the adduct will be an MC with a longer $X-X$ bond. If the magnitude of the CT becomes large enough, the halogen can no longer exist as a halogen molecule, which leads to the formation of a TB with a hypervalent 3c-4e bond.^{3,4} The adduct should be a TB if the electronegativity⁵ of X

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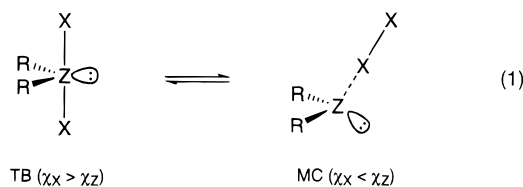
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(χ_X) is larger than that of Z (χ_Z) in R_2ZX_2 , and an MC is not larger than χ_Z (general rule).^{3a,4a,4b} On the basis of this rule, the structure of bromine adducts of selenides is expected to be a TB, but the difference of the electronegativity between Br and Se is small, which in some cases can lead to an equilibrium between TB and MC (eq 1).



Recently, the MC structure became popular in addition to the TB structure and/or ionic ones, since X-ray crystallographic studies increased the number of examples with an MC structure in the solid state, such as Ph_3P-X-X' ($X-X' = Br_2, I_2,$ and IBr).⁶ We encountered the formation of a mixture of a chlorine adduct (TB) and an iodine adduct (MC) of 1-selena-4-oxane when iodine monochloride is allowed to react with the selenide in solutions. The structure of the iodine monochloride adduct of 1-selena-4-oxane has been demonstrated to be $O(CH_2-CH_2)_2Se-I-Cl$ by X-ray crystallographic analysis (see eqs 2 and 3).⁷ The MC structure of selenanthrene with bromine was established in solutions (cf: eq 4).^{4b} An equilibrium between MC and TB was also reported for $ArAr'Se \cdot Br_2$.⁸ These findings show that the stability of MC and TB must be comparable in some cases, which means that the stability of the $Z-X-X$ bond in the MC should be comparable to the stability of the $X-Z-X$ bond in the TB in such a case.

Martin and co-workers redefined the bonding scheme for hypervalent species with a 3c-4e bond based on detailed ab initio MO calculations performed for the trifluoride ion.^{2c} The unique characteristic of all hypervalent molecules is redefined as follows: (1) the presence of at least one occupied high-energy molecular orbital which is *s* rather than *p* in symmetry with respect to a central atom to ligand bond and (2) which has virtually no overlap with the valence orbitals on a central atom.^{2c} The trifluoride ion is a typical TB with the typical 3c-4e bond. However, the definition (2) would be difficult to apply for hypervalent molecules with unsymmetrical 3c-4e bonds, as they appear in an MC.

A general systematic classification scheme has been proposed, which is practically useful for molecules with electron-rich multicenter (hypervalent) bonding.^{3c,d} The

Table 1. ¹³C NMR Chemical Shifts of $O(^2CH_2^1CH_2)_2Se \cdot XY^a$

XY	$\delta(^1C)$	$\delta(^2C)$	XY	$\delta(^1C)$	$\delta(^2C)$
null ^b	17.2	69.5	null ^b	17.2	69.5
ICl ^c	31.3	-7.1	Cl ₂ ^c	31.2	-7.2
	3.5	-1.7	Br ₂ ^c	28.1	-6.6
IBr ^c	27.9	-6.1	I ₂ ^c	3.1	-1.4
	0.8	-0.9			

^a In CDCl₃. ^b From TMS. ^c From the parent selenide.

$N-X-L$ bonding system starts from a resonance structure that has only single bonds to X, and it designates the bonding around an atom X in terms of the number of valence shell electrons N formally associated directly with X and ligands L directly bonded to it. The R_2ZX_2 (TB) adduct and the trifluoride ion are classified as the 10-Z-4 and 10-F-2 species, respectively. The bonding scheme of $R_2Z^{-1}X^{-2}X$ (MC) is formally represented as 10-¹X-2. The atoms X in R_2ZX_2 (TB), ²X in $R_2Z^{-1}X^{-2}X$ (MC), and Z in R_2ZX_2 (MC) are formally classified as 8-X-1, 8-²X-1, and 8-Z-3, respectively. We would like to represent the situation as follows: $R_2Z^{-1}X^{-2}X$ (MC) is an MC for Z, but the central ¹X is recognized as a TB. Correspondingly, R_2ZX_2 (TB) is a TB for Z, but for X it can be viewed as an MC. This consideration led us to the working hypothesis that the bonding scheme in $R_2Z^{-1}X^{-2}X$ (MC) can be described by the 3c-4e hypervalent model, if the 10-¹X-2 character is proven for $R_2Z^{-1}X^{-2}X$ (MC).

Much attention has been paid to the bonding and the nonbonded interactions between heteroatoms containing 2c-2e,⁹ 2c-3e,⁹ 3c-4e,¹⁰ 4c-6e,¹¹ and other bonds.¹² Ab initio MO calculations were recently performed on $H_2O-X-X'^{13}$ and $H_3N-X-X'^{14}$ ($X-X' = F_2, Cl_2,$ and $Cl-F$), which also encouraged us to further investigate the character of the $Z-X-X$ bond in MC. Here we would like to present the results of our recent investigations, which confirmed our working hypothesis of a 3c-4e description of the bonding in some $n \rightarrow \sigma^*$ type R_2Z-X-X (MC) systems.

Results and Discussion

Stability of MC versus TB in $RR'SeXY$. The ¹³C NMR spectra were measured for 1-selena-4-oxane (**1**) in chloroform-*d* with and without addition of iodine monochloride, iodine monobromide, chlorine, bromine, or iodine (eq 2). Table 1 shows the results. The ¹H, ¹³C, and ⁷⁷Se NMR chemical shifts ($\delta(^1H)$, $\delta(^{13}C)$, and $\delta(^{77}Se)$, respectively) were also measured for selenoanisole (**2**) in the presence or absence of the halogens and interhalogens (eq 3). Table 2 collects the results, which include the half widths ($\nu_{1/2}$) and the integrals of the methyl

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Table 2. ^1H , ^{13}C , and ^{77}Se NMR Chemical Shifts of the MeSe Groups in $2\cdot\text{XY}^a$

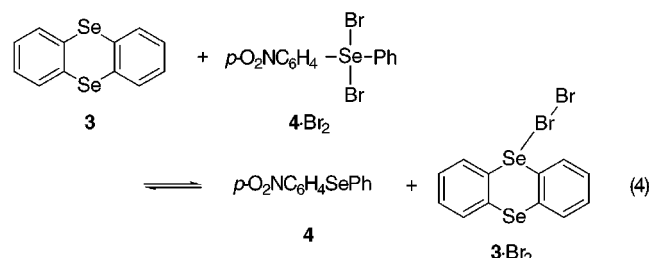
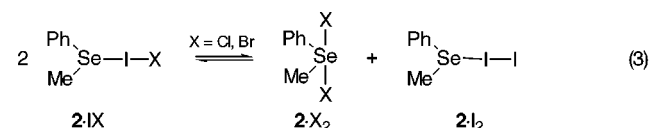
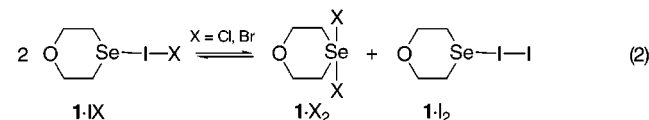
XY	$\delta(^1\text{H})$	$\Delta\nu_{1/2}^b$	content ^c	$\delta(^{13}\text{C})$	$\Delta\nu_{1/2}^b$	$\delta(^{77}\text{Se})$	$\Delta\nu_{1/2}^b$
null ^d	2.35	1.0	1.00	7.2	1.0	206.9	4.0
ICl ^e	1.55	8.8	0.42	39	<i>f</i>	286.0	16.6
	0.38	11.4	0.58	8	<i>f</i>	53.3	25.1
IBr ^e	0.61	2.0	1.00	11.8	5.5	77	<i>f</i>
Cl ₂ ^e	1.56	1.0	1.00	38.7	1.0	285.0	4.9
Br ₂ ^e	1.55	1.0	1.00	36.5	1.0	227.1	4.9
I ₂ ^e	0.33	1.0	1.00	5.6	3.3	44.9	7.7

^a In CDCl₃. ^b In hertz. ^c Relative integrals of the signal(s).^d From TMS for $\delta(^1\text{H})$ and $\delta(^{13}\text{C})$ and from MeSeMe for $\delta(^{77}\text{Se})$.^e From the parent selenide. ^f Very broad.**Table 3.** ^1H NMR Chemical Shifts of **3** and **4** with and without Bromine, Together with Their Mixtures^a

condition	3		4	
	$\delta(^1\text{H}(o))$		$\delta(^1\text{H}(o))$	$\delta(^1\text{H}(2))$
3 ^b	7.700			
3 + Br ₂ ^c	0.124			
4 ^b			7.616	7.337
4 + Br ₂ ^c			0.392	0.788
4 + 2Br ₂ ^c			0.392	0.788
4 + 3Br ₂ ^c			0.393	0.788
3 + 4 + Br ₂ ^c	0.079		0.141	0.283
2 · 3 + 4 + Br ₂ ^c	0.051		0.075	0.150

^a In CDCl₃. ^b From TMS. ^c From the parent selenide.

proton signals. Table 3 exhibits selected $\delta(^1\text{H})$ values of selenanthrene (**3**) and *p*-nitrophenyl phenyl selenide (**4**), together with those of the mixtures with bromine (eq 4).



The formation of the 1:1 mixture of **1**·Cl₂ (TB) and **1**·I₂ (MC) from **1**·ICl (MC) in the solution is demonstrated by the $\delta(^{13}\text{C})$ values (Table 1). Such a mixture was not observed in the solid state. In solution, the bonding energy of the hypervalent Cl–Se–Cl bond (and of the $n \rightarrow \sigma^*$ type Se–I–I bond) must be larger than two equivalents of the $n \rightarrow \sigma^*$ type Se–I–Cl bond. On the other hand, an equilibrium between **1**·Br₂ and **1**·I₂ and **1**·IBr is indicated by the $\delta(^{13}\text{C})$ values for the **1**·IBr solution. To clarify this point, the NMR chemical shifts of the adducts with selenoanisole (**2**) were examined.

The $\delta(^1\text{H})$, $\delta(^{13}\text{C})$, and $\delta(^{77}\text{Se})$ values of **2**·ICl shown in Table 2 consist of two sets of chemical shifts similar to the case of **1**·ICl. The chemical shifts for one set were

the same as those of **2**·Cl₂ and those for the second set were slightly different from those of **2**·I₂. The molar fraction of **2**·Cl₂ in the **2**·ICl solution was estimated to be 0.42 based on the integral of the methyl protons, which yields fractions of 0.42 and 0.16 for **2**·I₂ and **2**·ICl, respectively, although the MC adducts were in equilibrium with the components. The larger $\nu_{1/2}$ values for the latter set are consistent with the presence of the equilibrium.

Only one set of signals was observed for **2**·IBr. It must be due to a relatively fast equilibrium between the adducts. The $\delta(^1\text{H})$, $\delta(^{13}\text{C})$, and $\delta(^{77}\text{Se})$ values of MeSe group in **2**·IBr were much smaller than those of the average of **2**·Br₂ and **2**·I₂. The molar fraction of **2**·Br₂ was estimated to be ca. 0.2 assuming that the chemical shifts of **2**·IBr are equal to those of **2**·I₂. The fractions of **2**·I₂ and **2**·IBr were estimated to be about 0.2 and 0.6, respectively. These results show that the stability of **2**·ICl is comparable to that of **2**·Cl₂ and that the two equimolar **2**·IBr are more stable than the mixture of **2**·Br₂ and **2**·I₂. The stability of the $n \rightarrow \sigma^*$ type Se–I–X (X = Cl, Br) bonds suggested to be comparable to that of the hypervalent 3c-4e X–Se–X (X = Cl, Br) bonds.¹⁵

The stability of the MC adduct of **3**·Br₂ relative to that of the TB adduct of **4**·Br₂ was examined by analyzing the $\delta(^1\text{H})$ values of **3**, **4**, their bromine adducts, and the mixtures. Table 3 shows the results.¹⁵ The molar ratios of **3**, **3**·Br₂, **4**, and **4**·Br₂ were calculated to be 0.36, 0.64, 0.64, and 0.36, respectively, when one equimolar amount of **3** was added to a solution of **4**·Br₂ in chloroform-*d*. The *K* value ($K = [\mathbf{3}\cdot\text{Br}_2][\mathbf{4}]/[\mathbf{3}][\mathbf{4}\cdot\text{Br}_2]$) of eq 4 was estimated to be 3.2. The ratios became 1.18, 0.82, 0.81, and 0.19, respectively, when an additional 1 equiv of **3** was added to the solution ($K = 3.0$). These results clearly show that **3**·Br₂ (MC) is more stable than **4**·Br₂ (TB), which in turn exhibits that the $n \rightarrow \sigma^*$ type Se–Br–Br bond in the former must be more stable than the 3c-4e hypervalent Br–Se–Br bond in the latter.

We wondered why some Se–X–Y bonds in the MC were more stable than those expected from the $n \rightarrow \sigma^*$ type CT model. The $n \rightarrow \sigma^*$ type Se–X–X bonds in the MC were therefore examined on the basis of ab initio MO calculations.

Molecular Orbital Calculations for H₂ZX₂. Ab initio MO calculations were performed on the TB and MC adducts (H₂ZX₂) using Gaussian 94 program,¹⁶ together with the related species (H₂Z, X₂, H₂ZX⁺, and H₂ZX^{•17}). The optimized TB and MC structures are indicated by H₂ZX₂ (TB) and H₂ZX₂ (MC) (sometimes H₂ZXX (TB) and H₂Z–X–X (MC)), respectively. Table 4 shows the results of calculations on H₂ZX₂ (TB) and H₂ZX₂ (MC), where (Z, X) = (O, Cl), (S, Cl), and (S, Br), with the 6-311+G(d,p), 6-311+G(2d,p), and 6-311++G(3df,2pd) basis sets at the MP2 and/or DFT (B3LYP) levels.¹⁸ The Z–X–X bonds in MC were calculated to be almost linear, which is in

(15) Further investigations were carried out on the selenides with and without the halogens (and/or interhalogens) in various ratios. Details will be reported elsewhere.

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Table 4. Results of ab Initio MO Calculations for H_2ZX_n with Various Basis Sets at MP2 and/or DFT (B3LYP) Levels

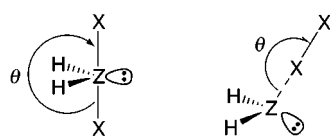
	energy (E) (au)	$r(Z-H)$ (Å)	$r(Z-X)$ (Å)	$r(X-X)$ (Å)	$\angle HZH$ (deg)	$\angle HZX$ (deg)	$\angle ZXX^a$ (deg)
$H_2O-Cl-Cl$ (MC)							
MP2/6-311++G(3df,2pd)	-995.6872	0.9596	2.7380	1.9946	104.31	112.96	180.06
B3LYP/6-311++G(3df,2pd)	-996.8936	0.9619	2.7098	2.0279	105.31	104.70	180.90
$H_2S_2Cl_2$ (TB)							
MP2/6-311+G(d,p)	-1318.0824	1.3308	2.2907		96.14	86.76	170.29
MP2/6-311+G(2d,p)	-1318.1655	1.3305	2.2673		96.17	87.06	171.19
MP2/6-311++G(3df,2pd)	-1318.2683	1.3304	2.2313		96.39	87.00	171.01
B3LYP/6-311++G(3df,2pd)	-1319.8662	1.3382	2.2763		95.65	87.19	171.63
$H_2S-Cl-Cl$ (MC)							
MP2/6-311+G(d,p)	-1318.0925	1.3338	3.3151	2.0333	92.25	110.70	176.80
MP2/6-311+G(2d,p)	-1318.1580	1.3337	3.1304	2.0450	92.88	97.41	179.62
MP2/6-311++G(3df,2pd)	-1318.2623	1.3331	3.1053	2.0011	92.19	93.94	180.69
B3LYP/6-311++G(3df,2pd)	-1319.8593	1.3424	2.9650	2.0551	92.57	93.04	180.47
$H_2S-Br-Br$ (MC)							
MP2/6-311++G(3df,2pd)	-5543.9692	1.3336	3.1456	2.3027	92.27	92.59	181.03
B3LYP/6-311++G(3df,2pd)	-5547.7293	1.3427	3.0332	2.3607	92.61	93.51	180.71

^a $\angle ClS_2Cl$ for TB.**Table 5. Results of ab Initio MO Calculations for H_2SX_n ($X = Cl, Br$) with 6-311++G(3df,2pd) Basis Sets at the MP2 Level**

	H_2S	$H_2S^1Cl^{*a}$	$H_2S^1Cl^+$	$H_2S_2Cl_2$ (TB)	$H_2S^1Cl^2Cl$ (MC)	$H_2S^1Br^{*b}$	$H_2S^1Br^+$	H_2SBr_2 (TB)	$H_2S^1Br^2Br$ (MC)
E (au)	-398.8986	-858.5500	-858.2595	-1318.2683	-1318.2623	-2971.4031	-2971.1101	-5543.9556	-5543.9692
$r(S-H)$ (Å)	1.3324	1.3332	1.3496	1.3304	1.3331	1.3339	1.3487	1.3320	1.3336
$r(S-X)$ (Å)		2.5540	1.9719	2.2313	3.1053	2.7991	2.1522	2.4232	3.1456
$r(X-X)$ (Å)					2.0011				2.3027
$\angle HSH$ (deg)	92.15	92.66	93.37	96.39	92.19	92.42	93.35	95.23	92.27
$\angle HS^1X$ (deg)		88.48	100.03	87.00	93.94	89.38	99.66	87.19	92.59
$\angle S^1X^2X$ (deg)				171.01 ^c	180.69			171.66 ^c	181.03
$Qn(S)$	-0.2158	0.0336	0.6110	0.6296	-0.1988	-0.0645	0.4687	0.5055	-0.1881
$Qn(H)$	0.1079	0.1240	0.1798	0.1494	0.1136	0.1226	0.1852	0.1577	0.1162
$Qn(H_2S)$		0.2815	0.9706	0.9283	0.0284	0.1807	0.8390	0.8208	0.0443
$Qn(X)$		-0.2815	0.0294	-0.4642	0.0080	-0.1807	0.1610	-0.4104	0.0110
$Qn(X^2)$				-0.4642	-0.0364			-0.4104	-0.0553

^a Spin densities: S(S) 0.3174, S(H) -0.0142, S(Cl) 0.7110. ^b Spin densities: S(S) 0.2035, S(H) -0.0102, S(Br) 0.8168. ^c $\angle X^2S^1X$ for TB.

accordance with the observations. The TB adduct of $H_2S_2Cl_2$ was found to be more stable than the MC when 6-311+G(2d,p) and 6-311++G(3df,2pd) basis sets at the MP2 level and 6-311++G(3df,2pd) basis sets at the B3LYP level were applied. However, the application of the 6-311+G(d,p) basis sets at the MP2 level lead to the prediction that the TB is less stable than the MC, which is not in accordance with the experimental findings on diorganyl sulfide dichlorides.^{3a,d}



TB MC
Z = O, S, Se and X = Cl, Br

The optimized $r(O-Cl)$ and $r(Cl-Cl)$ values in $H_2O-Cl-Cl$ (MC) were 2.738 and 1.995 Å, respectively, with the 6-311++G(3df,2pd) basis sets at the MP2 level and 2.710 and 2.028 Å, respectively, with the same basis sets at the B3LYP level.¹³ The calculated values reproduce

(17) Calculations for radical species see, (a) Kobayashi, T.; Matsuzawa, H.; Iwata, S. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 3172. (b) Takane, S.; Fueno, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3633.

(18) Ab initio MO calculations, that take into account electron correlation by using MP2 and DFT (B3LYP) methods, predicted much shorter distances between S and Cl ($r(S-Cl)$) for $H_2S-Cl-Cl$ (MC), relative to the HF level, which reflects the complex interaction between S and Cl atoms in the MC. The $r(S-Cl)$ for $H_2S-Cl-Cl$ (MC) with the 6-311++G(3df, 2pd) basis sets at the HF level was predicted to be 3.7538 Å, for example.

the bond lengths observed for $O(CH_2CH_2)_2OCl_2$ (2.67 and 2.02 Å, respectively),¹⁹ fairly well. The ($r(S-Br)$, $r(Br-Br)$) distances in $H_2S-Br-Br$ (MC) were calculated to be (3.146, 2.303 Å) and (3.033, 2.361 Å) at the MP2 and the B3LYP levels, respectively, applying the 6-311++G(3df,2pd) basis sets. The observed values for a 1:2 adduct of 1,2,4,5-tetrakis(ethylthio)benzene with bromine are (2.81, 2.41 Å).²⁰ The calculated $r(S-Br)$ and $r(Br-Br)$ distances are 0.22–0.34 Å longer and 0.11–0.05 Å shorter than the observed ones, respectively. The observed values for $(CH_2)_4S-Br-Br$ are (2.321, 2.724 Å).²¹ The differences between the observed and calculated values are very large in this case. This discrepancy must be due to the ionic nature of $(CH_2)_4S-Br-Br$ (such as $(CH_2)_4S^+-Br^-$ in the solid state). The calculated $r(S, Br)$ in $H_2S^1Br^+$ is 2.152 Å (see Table 5), which is slightly shorter than the observed value in $(CH_2)_4S-Br-Br$.

After the comparison of the observed structure of some MC with that calculated for some models, calculations on H_2ZX_2 (TB) and H_2ZX_2 (MC) were performed in more detail for Z = S, Se and X = Cl, Br, together with the related species (H_2Z , X_2 , H_2ZX^+ , and H_2ZX^\bullet), applying the 6-311++G(3df,2pd) basis sets at the MP2 level. Tables 5 and 6 exhibit the energies (E), optimized structures, and natural charges (Qn), obtained from a natural population analysis,²² for the sulfur and the selenium

(19) Hassel, O.; Stroffmme, K. O. *Acta Chem. Scand.* **1959**, *13*, 1775.
(20) Bock, H.; Havlas, Z.; Rauschenbach, A.; Näther, C.; Kleine, M. *Chem. Commun.* **1996**, 1529.

(21) Allegra, G.; Wilson, G. E., Jr.; Benedetti, E.; Pedone, C.; Allbert, R. *J. Am. Chem. Soc.* **1970**, *92*, 4002.

(22) NBO Ver. 3.1, Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F.

Table 6. Results of ab Initio MO Calculations for H₂SeX_n (X = Cl, Br) with 6-311++G(3df,2pd) Basis Sets at the MP2 Level

	H ₂ Se	H ₂ Se ¹ Cl ^a	H ₂ Se ¹ Cl ⁺	H ₂ SeCl ₂ (TB)	H ₂ Se ¹ Cl ² Cl (MC)	H ₂ Se ¹ Br ^b	H ₂ Se ¹ Br ⁺	H ₂ SeBr ₂ (TB)	H ₂ Se ¹ Br ² Br (MC)
<i>E</i> (au)	-2401.1385	-2860.7964	-2860.5145	-3320.5261	-3320.5023	-4973.6472	-4973.3643	-7546.2113	-7546.2094
<i>r</i> (Se-H) (Å)	1.4591	1.4595	1.4758	1.4580	1.4598	1.4601	1.4749	1.4592	1.4603
<i>r</i> (Se- ¹ X) (Å)		2.5956	2.1049	2.3337	3.1784	2.8139	2.2744	2.5159	3.1908
<i>r</i> (¹ X- ² X) (Å)					2.0052				2.3102
∠HSeH (deg)	91.27	91.91	92.10	95.16	91.30	91.63	92.02	94.24	91.36
∠HSe ¹ X (deg)		88.01	97.65	86.51	92.10	89.21	97.52	86.79	92.56
∠Se ¹ X ² X (deg)				169.65 ^c	180.80			170.56 ^c	180.65
<i>Qn</i> (Se)	-0.1072	0.2366	0.8296	0.8483	-0.0843	0.1280	0.6849	0.7185	-0.0666
<i>Qn</i> (H)	0.0536	0.0691	0.1219	0.0927	0.0594	0.0693	0.1271	0.1008	0.0627
<i>Qn</i> (H ₂ Se)		0.3748	1.0733	1.0338	0.0588	0.2666	0.9390	0.9200	0.0587
<i>Qn</i> (¹ X)		-0.3748	-0.0733	-0.5169	0.0042	-0.2666	0.0610	-0.4600	0.0048
<i>Qn</i> (² X)				-0.5169	-0.0388			-0.4600	-0.0635

^a Spin densities: S(Se) 0.4563, S(H) -0.0268, S(¹Cl) 0.5973. ^b Spin densities: S(Se) 0.3219, S(H) -0.0241, S(¹Br) 0.7263. ^c ∠¹ClSe²Cl for TB.

compounds. The TB adducts were found to be more stable than the corresponding MC for H₂SCl₂, H₂SeCl₂, and H₂SeBr₂, whereas H₂SBr₂ (TB) was calculated to be less stable than H₂SBr₂ (MC), which was in accordance with the observations. The energy difference between H₂SeBr₂ (TB) and H₂SeBr₂ (MC) was only 0.0019 au (5.0 kJ mol⁻¹), which indicated the possible existence of an equilibrium between TB and MC in ArAr⁺Se⁻Br₂.

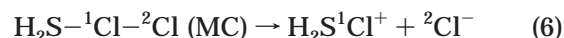
Large positive and negative charges were predicted on the central and the terminal atoms of the TB adducts, which are well explained by the 3c-4e model for the bond.³ On the other hand, the predicted *Qn* values on Z (and H₂Z), ¹X, and ²X in H₂Z-¹X-²X (MC) were negative, positive, and negative, respectively. The development of a positive charge on the central atom ¹X in the MC, as well as the negative charge predicted on the terminal atom ²X, are in agreement with the 3c-4e model of the Z-¹X-²X bond. The development of negative charge on the terminal atom, Z, also seems to agree with that model. But one has to be careful. The charge on Z of H₂Z-X-X (MC) has to be compared with that of free H₂Z, since the MC is formed by the reaction of H₂Z with X₂. The *Qn* values on Z in H₂Z-X-X (MC) (Z = S, Se and X = Cl, Br) were predicted to be slightly more positive than those on the corresponding atoms of H₂Z. The magnitude of the positive charge at the Z atoms as well as the H₂Z components were larger for X = Br than for X = Cl in the MC,²³ irrespective of the electronegativity⁵ of the elements.

Let us compare the charges on Z in H₂ZX₂ (MC) with those of the atoms in H₂ZX⁺, which corresponds to the charge transfer in the reaction of H₂ZX⁺ with X⁻ to form H₂Z-X-X (MC). The most typical example is found for (Z,X) = (Se,Cl). The charges at Se and ¹Cl in H₂Se¹Cl⁺ were 0.830 and -0.073, respectively. They became -0.084 and 0.004 in H₂Se-¹Cl-²Cl (MC), after reaction with ²Cl⁻. The positive charge development at ¹Cl in the MC is interesting. The negative charge at ²Cl⁻ decreases to -0.039 in H₂Se-¹Cl-²Cl (MC): the negative charge does not accumulate on ¹Cl, but is transferred to Se in H₂Se-¹Cl-²Cl (MC). A negative charge of ca. 0.96 passes through ¹Cl to Se or H₂Se. Some negative charge also moves from ¹Cl to Se or H₂Se during this process. Similar amounts of CT are also predicted for other MC adducts where the charge at ¹X in H₂Z¹X⁺ is determined by the relative electronegativity of X and Z. A similar picture

for the character of the CT is obtained if one considers the formation of H₂Z-X-X (MC) from H₂Z¹X[•] and ²X[•] (see Tables 5 and 6).

The above results are well explained by assuming that the Z-¹X-²X bonds in H₂Z-¹X-²X (MC) (Z = S, Se and X = Cl, Br) can be discussed by a 3c-4e model. The slightly less negative charge predicted on Z of H₂Z-X-X (MC), relative to that of H₂Z, is also explained by the 3c-4e hypervalent character of the Z-¹X-²X bonds, since the formation of the bonds is connected with an unavoidable CT from H₂Z to X₂ in the initial stage of the MC formation. The two electrons in one of the lone pair orbitals of Z extend over the σ*(¹X-²X) orbital of the newly formed 3c-4e Z-¹X-²X bond. The expected development of negative charge on Z in the formation of H₂Z-X-X (MC) is canceled by the CT from Z to X₂ in the initial stage of the interaction. The 3c-4e character of the Z-X-X bond in the MC was further examined through the investigation of some distance dependences.

Characters of CT in the Formation of H₂SCl₂ (TB and MC). Ab initio MO calculations were performed on H₂S¹Cl²Cl (TB) and H₂S-¹Cl-²Cl (MC) with different *r*(S-²Cl) and *r*(¹Cl-²Cl) values: *r*(S-²Cl) = *r*₀(S-²Cl) + 0.1*m* Å and *r*(¹Cl-²Cl) = *r*₀(¹Cl-²Cl) + 0.1*m* Å, where *r*₀(S-²Cl) and *r*₀(¹Cl-²Cl) are the optimized values for the TB and MC and *m* = -1, (0), 1, 2, 3.



From these calculations we obtain the character of the CT for the initial stage of the dissociation processes for the TB and MC, which corresponds to eqs 5 and 6, respectively. The process will produce H₂S¹Cl⁺ and ²Cl⁻, if it is assumed that the singlet multiplicity is conserved during the reaction. Figures 1 and 2 show the plots of *Qn* versus the bond lengths in the TB and MC, together with those for H₂S¹Cl⁺ and ²Cl⁻ (A). As seen from Figure 1, the *Qn* values of ¹Cl and ²Cl in H₂S¹Cl²Cl (TB) are increased and decreased, respectively, whereas the values for S, H, and H₂S change only little with increasing *r*(S-²Cl). The main result in the case of the TB is a CT from ¹Cl to ²Cl.²⁴

In the case of the MC (Figure 2), the *Qn* values of S and H₂S in H₂S-¹Cl-²Cl (MC) increase with increasing *r*(¹Cl-²Cl). The *Qn* value of ²Cl decreases and that of ¹Cl is almost unchanged. The ionic species, H₂S¹Cl⁺ and ²Cl⁻, are again produced at the end of this process if it is

(23) The reason must be very complex. The character of CT in the 3c-4e bond seems to be more typical for X = Cl than for X = Br. Further investigations are necessary as the predicted charges also depend on the optimized structures (see also Figure 2).

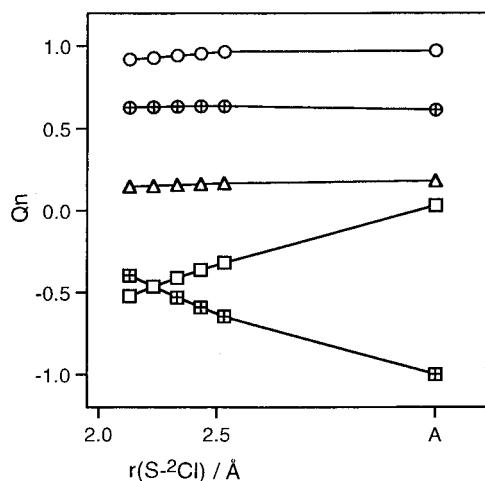


Figure 1. Plots of Q_n in $\text{H}_2\text{S}^1\text{Cl}^2\text{Cl}$ (TB) against $r(\text{S}-^2\text{Cl})$, together with those for $\text{H}_2\text{S}^1\text{Cl}^+$ and $^2\text{Cl}^-$ (A); $r_0(\text{S}-^2\text{Cl}) = 2.231 \text{ \AA}$; \oplus stands for $Q_n(\text{S})$, \circ for $Q_n(\text{H}_2\text{S})$, \triangle for $Q_n(\text{H})$, \square for $Q_n(^1\text{Cl})$, and \boxplus for $Q_n(^2\text{Cl})$.

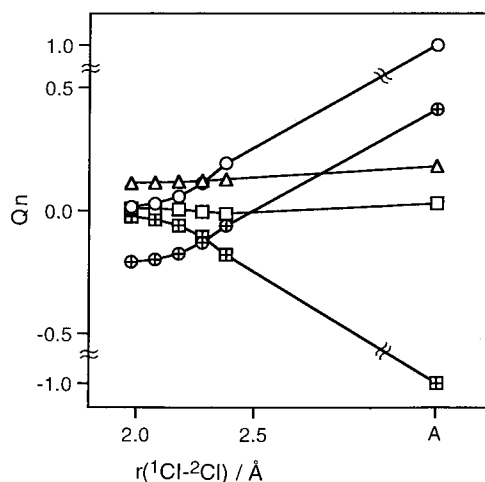


Figure 2. Plots of Q_n in $\text{H}_2\text{S}-^1\text{Cl}-^2\text{Cl}$ (MC) against $r(^1\text{Cl}-^2\text{Cl})$, together with those for $\text{H}_2\text{S}^1\text{Cl}^+$ and $^2\text{Cl}^-$ (A); $r_0(^1\text{Cl}-^2\text{Cl}) = 2.001 \text{ \AA}$; \oplus stands for $Q_n(\text{S})$, \circ for $Q_n(\text{H}_2\text{S})$, \triangle for $Q_n(\text{H})$, \square for $Q_n(^1\text{Cl})$, and \boxplus for $Q_n(^2\text{Cl})$.

assumed that the singlet multiplicity is conserved during the reaction. The results demonstrate that the $\text{S}-^1\text{Cl}-^2\text{Cl}$ bond in $\text{H}_2\text{S}-^1\text{Cl}-^2\text{Cl}$ (MC) can be indeed analyzed by the 3c-4e model. The CT must be examined not by the nature of elements but by their positions (Scheme 2). The character of the CT in $\text{H}_2\text{Se}-^1\text{Br}-^2\text{Br}$ (MC) was found to be essentially the same as the one discussed for $\text{H}_2\text{S}-^1\text{Cl}-^2\text{Cl}$ (MC).

Molecular Orbitals Constructing the 3c-4e Bond of Z-X-X in MC. Molecular orbitals were calculated for H_2SeBr_2 (MC) with the 3-21G^(*) basis sets of the Mac Spartan program,²⁵ using the structure optimized with the 6-311++G(3df,2pd) basis sets at the B3LYP level. The

(24) The ($Q_n(\text{C})$, $Q_n(\text{H})$, $Q_n(\text{Cl})$) values for CH_3Cl and CH_2Cl_2 were calculated to be (-0.4538, 0.1816, -0.0910) and (-0.3093, 0.1890, -0.0344), respectively, with the MP2/6-311++G(3df, 2pd) method. The values for CH_3^+ and CH_2Cl^+ were calculated to be (0.4205, 0.1932, no Cl atom) and (0.1644, 0.2283, 0.3792), respectively, based on the same method. The ($Q_n(\text{C})$, $Q_n(\text{H})$, $Q_n(^1\text{Cl})$, $Q_n(^2\text{Cl})$) values were found to be (-0.2747, 0.1901, -0.0207, -0.0846) for $\text{CH}_2^1\text{Cl}^2\text{Cl}$, if the calculations were performed with a C-²Cl bond length 0.1 \AA longer than the optimized value. The calculated CT mainly occurs from C to Cl, if the dissociation proceeds from CH_2XCl to CH_2X^+ (X = H or Cl) and Cl^- . In this case the character of CT corresponds to the 2c-2e model.

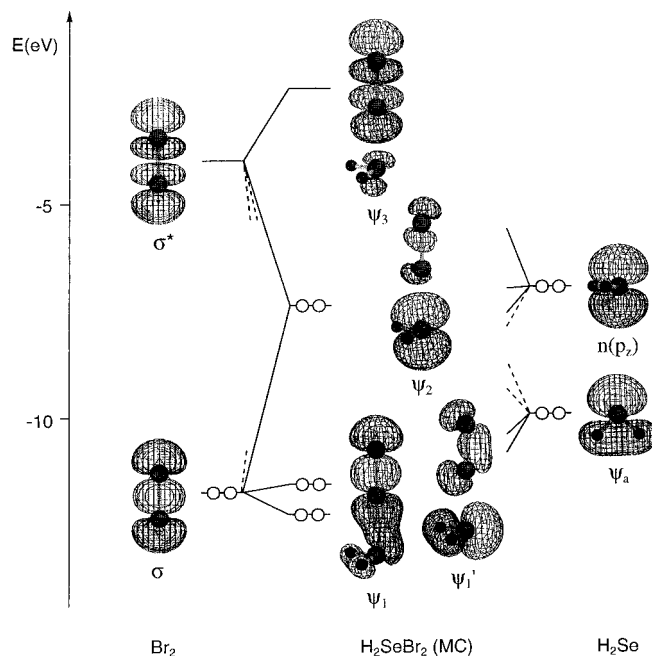
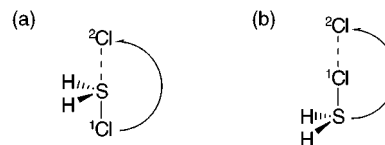


Figure 3. Energy diagram in the formation of the 3c-4e bond (ψ_1 , ψ_1' , ψ_2 , and ψ_3) in H_2SeBr_2 (MC) from the $n(p_z)$ and ψ_a of H_2Se and the σ and σ^* of Br_2 .

Scheme 2. Characters of CT in the Heterolytic Dissociation of $\text{H}_2\text{S}^1\text{Cl}_2$ (a) for TB and (b) for MC



overlap between the $\sigma^*(\text{Br}-\text{Br})$ and the $n(p_z)$ of H_2Se decreases dramatically as $r(\text{Se},\text{Br})$ becomes larger, which affects significantly the shapes of ψ_2 and ψ_3 . Since the shortest $r(\text{Se},\text{Br})$ value was predicted at the B3LYP level (Table 4), this structure was employed to depict the orbitals, although the real value might be even shorter than the predicted one. Figure 3 shows the energy diagram for the formation of H_2SeBr_2 (MC), together with the molecular orbitals ψ_1 , ψ_1' , ψ_2 , and ψ_3 in H_2SeBr_2 (MC), the $n(p_z)$ and ψ_a of H_2Se , and the σ and σ^* of Br_2 . The orbitals ψ_1 , ψ_2 , and ψ_3 , result mainly from the $n(p_z)$ of H_2Se and the σ and σ^* of Br_2 while the contribution from ψ_a is large in ψ_1' . The orbitals ψ_2 and ψ_3 of H_2SeBr_2 (MC) are HOMO and LUMO which again supports the 3c-4e interpretation of the Se-Br-Br bond, according to the redefinition proposed by Martin et al.^{2c}

Bond Orders for Z-X-X in MC and for X-Z-X in TB. The 3c-4e character of the bonding in the investigated MC was further examined by calculating bond orders from observed bond lengths of TB and MC adducts using Pauling's equation²⁶ (eq 7). $D(n)$ and $D(1)$ represent the bond distances where the bond orders are n (<1) and 1, respectively. Table 7 shows the results. The bond orders between the adjacent atoms in the 3c-4e bond are expected to be in the order of 0.5 because the ψ_2 orbital is usually nonbonding. The Z-X-X bond is well

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(26) (a) Pauling, L. *J. Am. Chem. Soc.* **1947**, *69*, 542. (b) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, New York, 1960; Chapter 7.

Table 7. Bond Lengths and Bond Orders in Some TB and MC^a

compound	TB/MC	$\angle XZX$ (deg)/ $\angle ZXX'$ (deg)	$r(Z-X)$ (Å)/ $r(X-X')$ (Å)	$\sum r_{co}$ (Å)/ $\sum r'_{co}$ (Å)	$r_{obs} - \sum r_{co}$ (Å)/ $r_{obs} - \sum r'_{co}$ (Å)	n	ref
F ₂ SF ₂	TB	186.9	1.646	1.68	-0.034	1.14	<i>b</i>
(CF ₃) ₂ SF ₂	TB	186.1	1.681	1.68	0.001	1.00	<i>c</i>
(Me ₂ N) ₂ SF ₂	TB	174.7	1.770	1.68	0.09	0.71	<i>d</i>
(4-ClC ₆ H ₄) ₂ SCl ₂	TB	174.5	2.259	2.03	0.229	0.42	<i>e</i>
			2.323	2.03	0.293	0.32 (av 0.37)	
Ph ₂ SeCl ₂	TB	180	2.30	2.16	0.14	0.58	<i>f</i>
(4-MeC ₆ H ₄) ₂ SeCl ₂	TB	177.5	2.38	2.16	0.22	0.43	<i>g</i>
S(CH ₂ CH ₂) ₂ SeBr ₂	TB	184.9	2.547	2.31	0.237	0.40	<i>h</i>
Ph ₂ SeBr ₂	TB	180	2.52	2.31	0.21	0.45	<i>f</i>
(4-MeC ₆ H ₄) ₂ SeBr ₂	TB	177	2.55	2.31	0.24	0.40	<i>g</i>
Me ₂ TeCl ₂	TB	172.44	2.488	2.36	0.128	0.61	<i>i</i>
			2.541	2.36	0.181	0.50 (av 0.56)	
Ph ₂ TeBr ₂	TB	178	2.682	2.51	0.172	0.52	<i>j</i>
(4-ClC ₆ H ₄) ₂ TeI ₂	TB	173.5	2.922	2.70	0.222	0.43	<i>k</i>
			2.947	2.70	0.247	0.39 (av 0.41)	
1,2-C ₆ H ₄ (CH ₂) ₂ TeI ₂	TB	176.53	2.900	2.70	0.200	0.46	<i>k</i>
			2.928	2.70	0.228	0.42 (av 0.44)	
C ₄ H ₈ O ₂ Cl ₂	MC		2.67	1.65	1.02	0.02	<i>l</i>
			<i>178</i>	<i>2.02</i>	<i>1.98</i>	<i>0.04</i>	<i>0.86</i>
C ₄ H ₄ O ₂ Br ₂	MC		2.71	1.80	0.91	0.03	<i>m</i>
			<i>180</i>	<i>2.31</i>	<i>2.28</i>	<i>0.03</i>	<i>0.89</i>
ArEtSBr ₂	MC		2.81	2.18	0.63	0.09	<i>n</i>
			<i>m</i>	<i>2.41</i>	<i>2.28</i>	<i>0.13</i>	<i>0.61</i>
(CH ₂) ₄ SBr ₂	MC		2.321	2.18	0.141	0.58	<i>o</i>
			<i>182</i>	<i>2.724</i>	<i>2.28</i>	<i>0.444</i>	<i>0.18</i>
I ₂ S(CH ₂ CH ₂) ₂ SI ₂	MC		2.867	2.37	0.497	0.15	<i>p</i>
			<i>177.9</i>	<i>2.787</i>	<i>2.66</i>	<i>0.127</i>	<i>0.61</i>
(PhCH ₂) ₂ SI ₂	MC		2.78	2.37	0.41	0.21	<i>q</i>
			<i>179</i>	<i>2.819</i>	<i>2.66</i>	<i>0.159</i>	<i>0.54</i>
BrIS(CH ₂ CH ₂) ₂ SIBr	MC		2.687	2.37	0.317	0.30	<i>r</i>
			<i>178.2</i>	<i>2.646</i>	<i>2.47</i>	<i>0.176</i>	<i>0.51</i>
(CH ₂) ₄ SeI ₂	MC		2.762	2.50	0.262	0.37	<i>s</i>
			<i>180.6</i>	<i>2.914</i>	<i>2.66</i>	<i>0.254</i>	<i>0.38</i>
O(CH ₂ CH ₂) ₂ SeI ₂	MC		2.755	2.50	0.255	0.38	<i>t</i>
			<i>185.2</i>	<i>2.956</i>	<i>2.66</i>	<i>0.296</i>	<i>0.32</i>
I ₂ Se(CH ₂ CH ₂) ₂ SeI ₂	MC		2.829	2.50	0.329	0.28	<i>u</i>
			<i>180.0</i>	<i>2.870</i>	<i>2.66</i>	<i>0.21</i>	<i>0.45</i>
O(CH ₂ CH ₂) ₂ SeICl	MC		2.63	2.50	0.13	0.61	<i>v</i>
			<i>184.2</i>	<i>2.73</i>	<i>2.32</i>	<i>0.41</i>	<i>0.21</i>
Me ₃ NI ₂	MC		2.27	2.03	0.24	0.40	<i>w</i>
			<i>179</i>	<i>2.83</i>	<i>2.66</i>	<i>0.17</i>	<i>0.52</i>
Me ₃ NICl	MC		2.30	2.03	0.27	0.35	<i>x</i>
			<i>180</i>	<i>2.52</i>	<i>2.32</i>	<i>0.20</i>	<i>0.46</i>
Ph ₃ PI ₂	MC		2.481	2.43	0.051	0.82	<i>y</i>
			<i>178.22</i>	<i>3.161</i>	<i>2.66</i>	<i>0.501</i>	<i>0.15</i>

^a Italic number shows data around the X-X' bond in MC. ^b Reference 28. ^c Reference 29. ^d Reference 30. ^e Reference 3a. ^f Reference 31. ^g Reference 32. ^h Reference 33. ⁱ Reference 34. ^j Reference 35. ^k Reference 36. ^l Reference 19. ^m Reference 37. ⁿ Reference 20: $\angle SBrBr$ being not given. ^o Reference 21. ^p Reference 38. ^q Reference 39. ^r Reference 40. ^s Reference 41. ^t Reference 42. ^u Reference 43. ^v Reference 7. ^w Reference 44. ^x Reference 45. ^y Reference 6b.

described by the 3c-4e model if the two bond orders in Z-X-X are close to each other.

$$D(n) = D(1) - 0.60 \log n \quad (7)$$

Before we discuss the bond orders of Z-X-X in the MC, we first deal with those in the TB. The bond orders between S and F ($n(S,F)$)²⁷ in R₂SF₂ (TB)²⁸⁻³⁰ were found to be 1.14-0.71, depending on the electronegativity of the equatorial ligands. The value of $n(S,Cl)$ for (4-ClC₆H₄)₂SCl₂^{3a} is 0.37 on the average. The $n(Se,X)$ values for R₂SeX₂ (X = Cl, Br)³¹⁻³³ are in the range 0.58-0.40 and $n(Te,X)$ for R₂TeX₂ (X = Cl, Br, I)³⁴⁻³⁶ lie between

0.61 and 0.39. The two bond orders for the essentially symmetric X-Z-X group differ up to 0.1, which is attributed to the crystal packing effect.

The $n(O,X)$ and $n(X,X)$ values in O(CH₂CH₂)₂OX₂ (X = Cl,¹⁹ Br³⁷) are in the ranges 0.02-0.03 and 0.86-0.89, respectively. The $n(S,I)$ values of sulfide diiodides^{38,39} lie between 0.15 and 0.21, and their $n(I,I)$ values between 0.54 and 0.61 and the ($n(S,I)$, $n(I,Br)$) for BrIS(CH₂CH₂)₂-SIBr⁴⁰ is (0.30, 0.51). The values for $n(Se,I)$ and $n(I,I)$ of

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selenide diiodides^{41–43} are in the ranges 0.28–0.38 and 0.37–0.45, respectively. The bond orders for the selenide diiodides are in the same range as for other TB adducts of selenides and tellurides, and the $n(\text{Se}, \text{I})$ and $n(\text{I}, \text{I})$ values are close with each other. Therefore, the selenide diiodides are well described by the 3c-4e model. The bonds in sulfide diiodides have to be described by a somewhat unsymmetric 3c-4e model, due to the substantially smaller $n(\text{S}, \text{I})$ values compared to those of $n(\text{I}, \text{I})$. The S–I–Br bond in $\text{BrIS}(\text{CH}_2\text{CH}_2)_2\text{SIBr}$ is understood in a similar way. The chlorine and bromine adducts of the ether are but described by the weak $n \rightarrow \sigma^*$ CT model. Nevertheless, we prefer to describe the O–X–X bonds by the unsymmetrical 3c-4e model, too.

The S–Br–Br bonds in 1,2,4,5-tetrakis(ethylthio)benzene tetrabromide²⁰ and in $(\text{CH}_2)_4\text{SBr}_2$ ²¹ are also described as the unsymmetrical 3c-4e model, with an ionic character of $\text{S}^+-\text{Br}-\text{Br}^-$ for the latter. The Se–I–Cl bonds in $\text{O}(\text{CH}_2\text{CH}_2)_2\text{SeICl}$ ⁷ and the P–I–I bond in Ph_3PI_2 ^{6b} can also be viewed the unsymmetrical 3c-4e bonds with a stronger Z–X bond. The N–I–I bond in Me_3NI_2 ⁴⁴ and the N–I–Cl bond in Me_3NICl ⁴⁵ are typical 3c-4e bonds judging from the calculated bond orders.

Conclusion

It is proposed that the Z–X–X bond in $\text{R}_2\text{Z}-\text{X}-\text{X}$ (MC), such as halogen adducts of selenides or sulfides, can be described by the 3c-4e model. The 3c-4e description of the Z–X–X bonds in MC makes it easier to understand the character of the bonding in these systems by comparison with the X–Z–X bonds in TB, which are extensively investigated and well characterized so far. The comparison is achieved by changing the central atom Z in X–Z–X with the terminal atom X in Z–X–X, although the electronegativity of Z and X must be carefully taken into account.

Experimental Section

Chemicals were used without further purification unless otherwise noted. Solvents were purified by standard methods.

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Boiling points were uncorrected. ¹H, ¹³C, and ⁷⁷Se NMR spectra were measured at 400, 100, and 76 MHz, respectively. The ¹H, ¹³C, and ⁷⁷Se chemical shifts are given in ppm relative to those of internal CHCl_3 slightly contaminated in the solution (or TMS), CDCl_3 as the solvent, and external MeSeMe , respectively. Column chromatography was performed on silica gel (Fujidebison BW-300). Acidic alumina and basic alumina (E. Merck) were also used on silica gel, if necessary.

1-Selena-4-oxane (1) was prepared according to the literature.^{7,46} The crude product after usual workup was distilled to give **1** in 55% yield as a colorless oil, bp 167.5–168.0 °C. lit.⁴⁶ bp 167.5–168.5 °C. ¹H NMR (CDCl_3 , 400 MHz) 2.55–2.80 (m, 4H), 3.92–4.17 (m, 4H); ¹³C NMR (CDCl_3 , 100 MHz) 17.18, 69.54.

Iodine monochloride was prepared by distillation under reduced pressure after stirring the mixture of iodine and chlorine. It gave 72% yield as a black oil, bp 98.0–99.5 °C. lit.⁴⁷ bp 94.7–102 °C. Iodine monobromide was used as the equimolar mixture of bromine and iodine in carbon tetrachloride.

MO Calculations. Ab initio MO calculations were performed on a Power Challenge L computer with the Gaussian 94 program.¹⁶ The 6-311++G(3df,2pd) basis sets at the MP2 level were mainly applied on the TB and MC structures of H_2ZX_2 , H_2Z , and H_2ZX^+ (Z = S, Se and X = Cl, Br) and the UMP2 formalism with the 6-311++G(3df,2pd) basis sets was used for the corresponding radicals, $\text{H}_2\text{ZX}^\bullet$,¹⁷ supposing doublet spin multiplicity. Calculations were also carried out for $\text{H}_2\text{O}-\text{Cl}-\text{Cl}$ (MC), $\text{H}_2\text{S}-\text{Cl}_2$ (TB and MC), and $\text{H}_2\text{S}-\text{Br}-\text{Br}$ (MC) using various basis sets with or without application of MP2 and/or DFT (B3LYP) methods. The molecular orbitals shown in Figure 3 were obtained with the MacSpartan program²⁵ and the 3-21G^(*) basis sets using the optimized geometry from the B3LYP/6-311++G(3df,2pd) calculations.

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Supporting Information Available: The character of CT in $\text{H}_2\text{S}^1\text{Cl}^2\text{Cl}$ (TB and MC) in the dissociation to $\text{H}_2\text{S}^1\text{Cl}^\bullet$ and $^2\text{Cl}^\bullet$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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