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Molecular and Electronic Structure of Selenium and Tellurium Tetrahalides

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ABSTRACT

Molecular and electronic structures of MX_4 *(* $M = Se, Te : X = F, Cl$ *) were studied by the ab initio method with extended basis sets. The study is aimed at supplementing very scarce experimental information about these molecules. The results indicate that all molecules favour distorted disphenoidal geometries (* C_{2v} *point group) in preference to a* C_{4v} *geometry. A possibly interesting phenomenon of energy stabilisation by having bonds of different polarities within the same molecule has been observed in* $SeCl_4$ *and* $TeCl_4$*.*

INTRODUCTION

The compounds where a central atom extends its valence electron octet to a decet (hypervalent compounds) are of considerable interest especially in view of their geometry and chemical bonding. Tetrahalides of sulfur, selenium and tellurium are examples of such systems. The purpose of this work is to describe in greater detail their structures, bonding and possible relationship to chemical and physical properties. A useful summary of scarce available data on chemical and physical properties (including electronic structures) can be found in three review articles [1–3]. Dihalides of S, Se, Te have normal octets but are included in the study in order to provide an "internal reference" for checking the reliability of results on tetrahalides.

CALCULATIONS

The ab initio MO method implemented in the Gaussian 86 package has been used in all calculations; the 6-31G* basis set described halogen atoms, the Binning and Curtiss (6s4p1d) set [4] represented the Se atom and Huzinaga's (4333111/433111/43) set [5] described the Te atom. Both sets included a single d polarisation function. All geometries were fully optimised and correspond to local minima on the potential energy surface as indicated by the absence of imaginary values for harmonic frequencies. The molecular plane was assumed to be an *xz* plane in the dihalides, while in the tetrahalides it was considered to be an axial plane. In order to facilitate a correlation of orbital SCF energies with ionization energies (measured in photoelectron spectra) within Koopmans' approximation, a 92% rule was invoked [6] and eigenvalues scaled accordingly. Possible relativistic effects on the structures of tellurium halides were not considered explicitly but rather *via* comparison with the available experimental data which demonstrated that the expected relativistic bond contractions [7] were masked by basis sets' tendencies to overestimate equilibrium bond lengths at the HF level.

RESULTS AND DISCUSSION

The results obtained from the calculations are presented in Tables 1–3 and Figure 1. Comparison with available experimental data [8–12] reveals that the geometries predicted by the calculations are quite reliable. The electronic structure trends in the MX_4 series are summarised in Figure 1. All SCF orbital energies have been "converted" to ionization energies (E_i) using the 92% rule and represent results of this work. SF_4 is the only exception with ionization energies and assignments obtained from its photoelectron spectrum [13] and high quality calculations [14]. The usual caution should be exercised when using the suggested orbital ordering; that is, the energies that are < 0.5 eV apart cannot be reliably assigned.

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TABLE 1 Molecular geometries of MX_2 and MX_4 (M = Se, Te:X = F, Cl)[a]

Parameter (pm, deg)	*SeF$_2$ Exp.*	*SeF$_2$ SCF*	*SeCl$_2$ Exp.*	*SeCl$_2$ SCF*	*TeF$_2$ Exp.*	*TeF$_2$ SCF*	*TeCl$_2$ Exp.*	*TeCl$_2$ SCF*
M-X	*169*	*170.73*	*215.7(3)*	*215.70*	—	*187.55*	*232.9(3)*	*235.55*
<XMX	*94*	*95.8*	*99.6(5)*	*99.6*	—	*93.3*	*97.0(6)*	*96.5*

Parameter (pm, deg)		SeF_4	$SeCl_4$	TeF_4	$TeCl_4$
M-X_a	exp.	177.134(11)	—	190(2)	—
	SCF	174.49	233.012	188.47	246.08
M-X_e	exp.	168.209(13)	—	179(2)	—
	SCF	166.27	212.251	183.14	231.98
< XMX_a	exp.	169.20(8)	—	—	—
	SCF	166.4	178.0	157.8	173.0
< XMX_e	exp.	100.55(1)	—	—	—
	SCF	101.5	100.5	102.8	101.6

[a] Subscripts a, e refer to axial and equatorial halogen atoms where applicable and numbers in brackets to experimental uncertainties.

The following comments regarding electronic structure trends can be made:

- HOMO in all molecules is partially central atom localised and contains its valence *s* and *p* orbitals. It should not, however, be described as a "lone pair" due to substantial charge transfer to the ligands.
- The other orbitals can be classified into 3 groups in order of increasing ionization energies: halogen lone pairs, *M-X* bonding orbitals and various inner valence *s* orbitals.
- The lone pair levels are clustered in 2 groups of four levels each, the one at lower E_i spanning a wider energy range.
- The usual energy shifts can be discerned, depending on the electronegativities of central and ligand atoms.
- There are "gaps" in the energy level patterns of $SeCl_4$ and $TeCl_4$ in the 18–23 eV range. They can be rationalised through inner valence orbital interactions between central and ligand atoms. Cl 3s, Se 4s and Te 5s atomic ionization energies are: 23.81, 21.19 and 18.6 eV, respectively [15]. Their spherical symmetry would favour strong mutual interactions pushing levels outside this energy region and creating "gaps". Such an explanation appears to be supported by the fact that "gap" is wider in $SeCl_4$ where Se 4s and Cl 3s energies are closer, hence making orbital interactions stronger than in $TeCl_4$.
- The harmonic vibrational frequencies calculated for $SeCl_4$ (Table 3) reflect the fact observed in SeF_4 about relative strengths of equatorial and axial bonds. The latter are weaker with lower values of force constants and hence harmonic frequencies.

Relative energies of two possible molecular configurations: disphenoidal (C_{2v}) and square pyramidal (C_{4v}) are also of some interest (Figure 2).

The total energy differences $\Delta E(C_{4v} - C_{2v})$ for SeF_4, $SeCl_4$, TeF_4, and $TeCl_4$ are 30, 87, 12, and 34 $kJmol^{-1}$, respectively. All the molecules favour disphenoidal geometry with axial bonds being longer than equatorial. While the above values of energy differences would be basis set and electron correlation dependent, the favoured geometry is clear. VSEPR model [16] has traditionally explained this structural preference based on the idea of relative sizes of central atom lone pairs and bonding electron pairs. This model, whose foundations have at any rate been questioned [17], provides insufficient insight into the stabilisation mechanisms when applied indiscriminately to all MX_4 halides. Mulliken population analysis can be used only for qualitative guidance, since its results depend on basis set quality and inclusion of electron correlation. Nonetheless, our results (Table 2) seem to indicate that tetrachlorides gain extra stabilisation through changing relative bond polarities of axial and equatorial bonds (making the latter less polar).

TABLE 2 MX_2(M = Se, Te : X = F, Cl) Mulliken Net Atomic Charges

Atom	*SeF$_2$*	*SeCl$_2$*	*TeF$_2$*	*TeCl$_2$*	*SeF$_4$*	*SeCl$_4$*	*TeF$_4$*	*TeCl$_4$*
M	+0.94	+0.20	+1.13	+0.43	+1.84	+0.49	+2.29	+0.93
X(axial)	−0.47	−0.10	−0.57	−0.21	−0.50	−0.31	−0.59	−0.36
X(equat)	-	-	-	-	−0.42	+0.07	−0.56	−0.10

TABLE 3 Harmonic Vibrational Frequencies of $SeCl_4$[a]

ν/cm^{-1}	Symmetry	Mode
427	b_2	asym.stretch.eq
426	a_1	sym.stretch.eq
273	a_1	sym.stretch.ax
267	b_1	asym.stretch.ax
221	b_1	rock
211	a_1	scis.eq
192	a_2	torsion
142	b_2	wag
115	a_1	scis.ax

[a] The calculated harmonic frequencies were scaled by a factor of 0.893.

This problem, which can be classified as "symmetry avoidance" [18], certainly merits further study perhaps by using an ab initio method beyond the HF level.

CONCLUSION

The results presented are relevant to physical and chemical properties of the title compounds in several ways; some are outlined below:

- All the molecules studied should be sufficiently stable in the gas phase so that their basic physical properties (geometry, dipole moments, etc.) can be measured.
- The preferred geometry of a free molecule appears to be disphenoidal (C_{2v} symmetry) but the energy differences between disphenoidal and square pyramidal geometries are fairly small. This observation may explain the tendency towards polymerisation in the solid state which involves some disphenoidal geometry distortion in the process.
- Selenium and tellurium tetrachlorides should be significantly better Lewis bases than the tetrafluorides as indicated by their lower ionization energies.

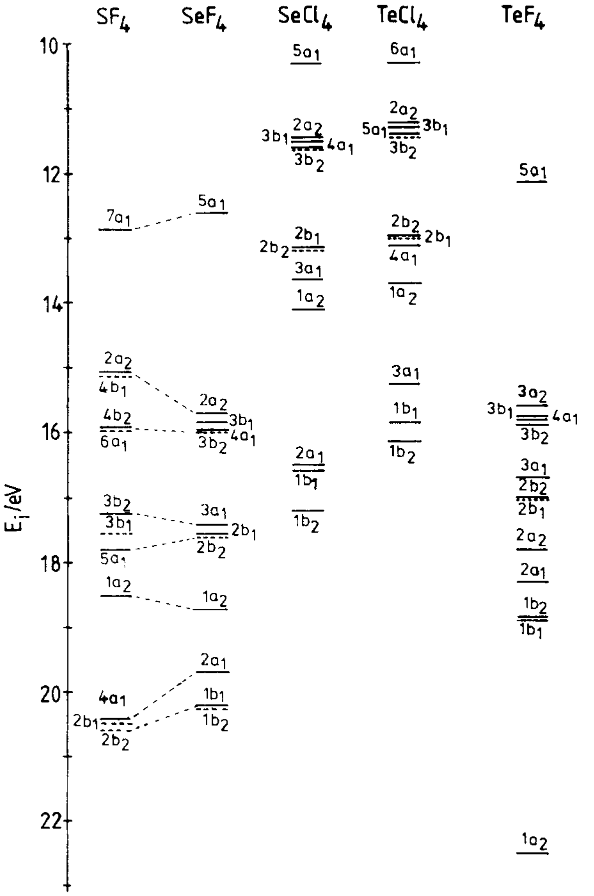

FIGURE 1 Energy level diagram for Group VI tetrahalides.

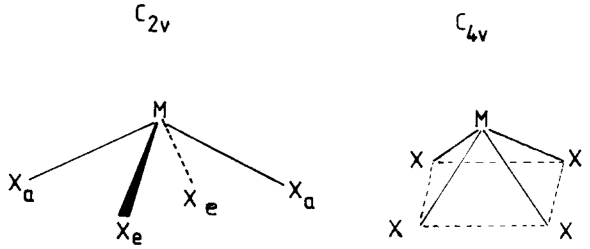

FIGURE 2 Disphenoidal (C_{2v}) and square-pyramidal (C_{4v}) molecular configurations for MX_4.

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