The Structures of $[X_2Y-N-YX_2]^+$ Cations (X = F, Cl; Y = S, Se). A Comparison of X-ray and ab Initio Studies[1]

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Received July 15, 1994

Key Words: Selenium-nitrogen compounds / Sulfur-nitrogen compounds / Calculations, ab initio

The structures of cationic species of the series $[X_2Y-N-YX_2]^+$ (X = F, Cl; Y = S, Se) have been computed ab initio using all electron treatments for first-row elements and sulfur and quasi-relativistic pseudopotentials for Se and Cl. Split-valence basis sets with polarization and diffuse functions were employed. The MP2 results for the (non-isostructural!) cations $[Cl_2Se-N-SeCl_2]^+$ (**1**: C_s) and $[F_2S-N-SF_2]^+$ (**2**: C_{2v}) are in excellent agreement with the experimental (X-ray) observations. Both structures represent local minima. A deeper minimum for either of the cations is represented by another C_{2v} isomer which for crystal lattice energy reasons is stable in the isolated state only. The geometries of the hitherto unknown species $[Cl_2S-N-SCl_2]^+$ (**3**) and $[F_2Se-N-SeF_2]^+$ (**4**) have been assessed by ab initio HF calculations. In analogy to **2**, cations **3** and **4** are predicted to prefer C_{2v} symmetry. Therefore, **1** exhibits unusual structural features. According to strictly localized natural bond orbital analysis (NBO), the central nitrogen atoms in **1** and **2** possess two lone pairs of electrons (LP: one sp hybrid and one p orbital). The relatively short Se−N and S−N bond distances in **1** (1.741−1.760 Å) and **2** (1.551 Å) can best be attributed to LP(N)→σ*(Y−X) negative hyperconjugation (**1**: Y = Se, X = Cl; **2**: Y = S, X = F).

The preparation and structural characterization (X-ray) of a salt $[Cl_4Se_2N][AsF_6]$ containing the first ternary Se, N,Cl cation, $[Cl_2Se-N-SeCl_2]^+$ (**1**) were achieved recently[1]. Independently and simultaneously Dehnicke et al. reported on the synthesis of the related species $[ClSe-N-SeCl]^+$ in the $[GaCl_4]^-$ salt[2a] (cf. also ref.[2b]). The only known analogue to the seven-atomic **1** is the sulfur, fluorine-containing derivative $[F_2S-N-SF_2]^+$ (**2**)[3]. Only superficially can these two cations be regarded as structurally related species. Whereas **2** exists (as expected) in a C_{2v} symmetry, the nitrogen atom in **1** lies almost in one of the *syn*-Cl−Se−Se−Cl planes (cf. Figure 1). The deviation is 10.5° (X-ray). Therefore, **1** and **2** are obviously examples of an isovalent pair of sterically non-hindered species for which simple VSEPR rules fail. It is worthwhile to mention that there are also some other related compounds and ions for which simple VSEPR considerations are suspect. For example, there are the rather floppy $R_3Si-O-SiR_3$ and $[R_3P-N-PR_3]^+$ species[4,5]. In order to understand the geometries and the electronic structures of the cationic, ternary chalcogen-halogen-nitrogen species more fully, the ground-state structures for the $[X_2Y-N-YX_2]^+$ cations (X = F, Cl; Y = S, Se) were determined in this study by ab initio methods including quasi-relativistic pseudopotentials for Cl and Se.

$[Cl_2Se-N-SeCl_2]^+$ **1** $[F_2S-N-SF_2]^+$ **2**

Results and Discussion

The $[Cl_2Se-N-SeCl_2]^+$ Cation (1)

The solid-state structure of **1** has been determined by low-temperature single-crystal X-ray diffraction (Figure 1, Table 1)[1]. The geometry of the cation can be approximated by C_s symmetry with two significantly different Se−Cl bond lengths [2.169(4) and 2.141(4) Å, Table 1]. The Se−N distances of 1.741(11) and 1.760(11) Å are essentially identical (within 3σ).

The THF calculations located three isomers of **1** in the geometric configuration space which was searched; these isomers were fully optimized (at HF level, Figure 2). Their energies at different theoretical levels (see below) are summarized in Table 1.

In order to differentiate between the two computed C_{2v} isomers we use the structural notation: **1** (d-HF, C_{2v}) for cation **1** with the nitrogen *"down"*; **1** (u-HF, C_{2v}) for the (nitrogen) *"up"*; **1** (d-HF, C_s) designates the experimentally observed C_s isomer with nitrogen down.

For **1**, the nitrogen up-C_{2v} structure is most favoured both at the HF/DZ + P and the correlated MP2 levels (Table 2). Moreover, the experimentally observed d-C_s iso-

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Figure 1. Different views of the structure of the cation **1** in [Cl_2SeN-$SeCl_2$][AsF_6] · CH_3CN as deduced by X-ray diffraction[1]

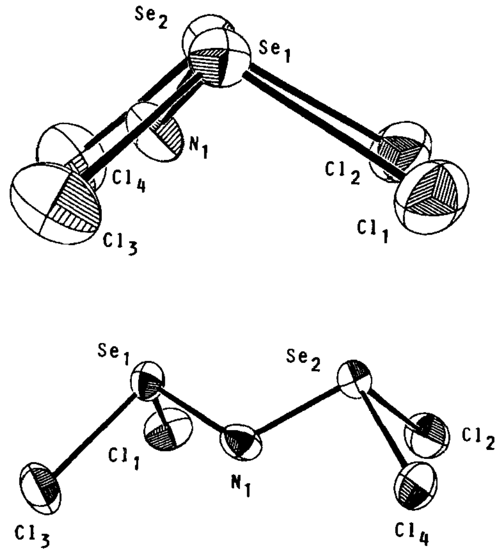

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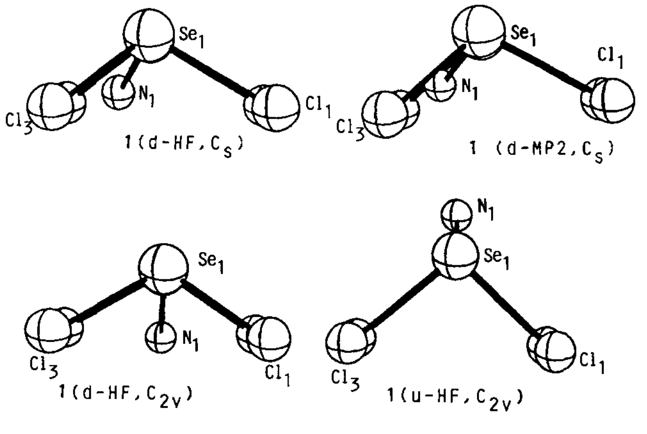
Table 1. Experimental (X-ray) and computed structural parameters for the different isomers of **1** and absolute (−au) and relative (kcal/mol) energies for different isomers of **1** [optimized MP2(FC) geometries]

	1(X-ray) [1]	1(d-HF,C_s)	1(d-MP2,C_s)	1(d-HF,C_{2v})	1(u-HF,C_{2v})
d(Se_1-N_1), Å	1.741(11)	1.800	1.823	1.796	1.760
d(Se_2-N_1), Å	1.760(11)	1.800	1.823	1.796	1.760
d(Cl_1-Se_1), Å	2.169(4)	2.163	2.221	2.150	2.166
d(Cl_2-Se_2), Å	2.169(4)	2.163	2.221	2.150	2.166
d(Cl_3-Se_1), Å	2.141(4)	2.139	2.168	2.150	2.166
d(Cl_4-Se_2), Å	2.141(4)	2.139	2.168	2.150	2.166
<($Se_1N_1Se_2$),°	117.6(2)	115.5	114.5	114.6	135.7
<($N_1Se_1Cl_1$),°	102.9(4)	103.5	104.6	99.6	108.2
<($N_1Se_2Cl_2$),°	103.6(4)	103.5	104.6	99.6	108.2
<($N_1Se_1Cl_3$),°	93.3(4)	95.5	93.2	99.6	108.2
<($N_1Se_2Cl_4$),°	92.8(4)	95.5	93.2	99.6	108.2
<($Cl_1Se_1Cl_3$),°	98.2(2)	99.6	100.1	99.6	98.3
<($Cl_2Se_2Cl_4$),°	98.5(2)	99.6	100.1	99.6	98.3
HF; -au		131.37106		131.37031	131.37924
(rel. kcal/mol)		(5.1)		(5.6)	(0.0)
MP2; -au			132.29690	132.29690	132.30888
(rel. kcal/mol)			(7.5)	(7.5)	(0.0)

mer (computed local minimum) had considerable higher energy [HF: ΔE (u, C_{2v} − d, C_s) = 5.1 kcal/mol; MP2: ΔE (u, C_{2v} − d, C_s) = 7.5 kcal/mol]. Unfavourable crystal lattice effects in the hypothetical **1** (u, C_{2v}) [AsF_6] structure, due to repulsion of the negatively charged nitrogen (see below) in the cation and the AsF_6^- anion, may be responsible. Although this explanation might give the impression that we explain some differences between formally analogous species in terms of orbital interactions and some in terms of crystal interactions (as we do) it is not unreasonable to assume a lattice energy difference between the *up* and the *down* isomer of **1** (AsF_6^- salt) of about 5 kcal/mol. If we only take size effects into account (and one should also consider the electrostatic repulsion, see above) it is likely that the molecular volume of the *up* cation would be one third greater than that of the *down* species (trigonal prism). With the molecular volumes determined by X-ray crystallography[1] of approximately V_M (AsF_6^-) = 105 Å^3 and V_M (*down*-$Cl_4Se_2N^+$) = 158 Å^3 [the molecular volume of CH_3CN was taken to be equal to 87 Å^3, cf. *d*(CH_3CN) = 0.786 g/cm^3] the lattice energy of acetonitrile-free (*down*)[Cl_4Se_2N]$^+$[AsF_6]$^-$ can be estimated to be equal to 113 kcal/mol[6,7]. Assuming a cation volume of (158 + 50) Å^3 the same estimation gives a lattice energy of 108 kcal/mol. We do, however, emphasize that as ab initio the ab initio computations really are, we are so far not able to compute solid-state structures and therefore have to choose some more empirical explanations to rationalize the observed structure.

Figure 2. HF-optimized geometries for **1** (d-HF, C_s), **1** (d-HF, C_{2v}) and **1** (u-HF, C_{2v}) as well as MP2-optimized geometry for **1** (d, C_s)



We also computed (HF/6-31 + G*; effective core potentials for Cl and Se: [5s5p1d]/(3s3p1d)-DZ+P) the rotational barrier of the process moving the nitrogen atom from the d-HF, C_{2v} (0°) via the experimentally observed d-HF, C_s (24°, at HF level!) into the mostly favoured (see above) u-HF, C_{2v} position (180°) (Figure 3).

Only the correlated MP2 calculation (Figure 2) gives a very good agreement with the experiment (deviation angle of N from the Cl_3−Se_1−Se_2−Cl_4 plane, i.e. dihedral angle between the (Se_1−N_1−Se_2) and (Cl_3−Se_1−Se_2−Cl_4) planes: X-ray, 10.5°; ^{1}HF, 24.4°; MP2, 10.7°).

As indicated by NBO analysis[8], the Se−N−Se unit in the **1** (d, C_s) cation has strongly polarized Se−N bonds. The NBO charges at nitrogen and selenium are −1.236 and +1.372 e, resp. (Table 2). The NBO procedure for identifying bonds and lone pairs clearly showed that there are six σ bonds and 16 lone pairs in the cationic species. The two lone pairs at nitrogen are stereochemically active. One has sp character whereas the other is essentially a nearly unhybridized 2p orbital (97% p character). Therefore, Figure 4 (A) shows the best Lewis representation of **1**. Moreover, the calculation finds that 95% of the π electron density is in a hypothetical Se−N π bond localized at the N atom. However, NBO analysis for the [ClSe−N−SeCl]$^+$ cation[2] reveals that the latter can be described by a Lewis structure

Figure 3. Rotation of the N atom from the (a) d-HF, C_{2v} (0°) via the (b) d-HF, C_s (24°, HF level) into the (c) u-HF, C_{2v} position (180°) and rotational barrier

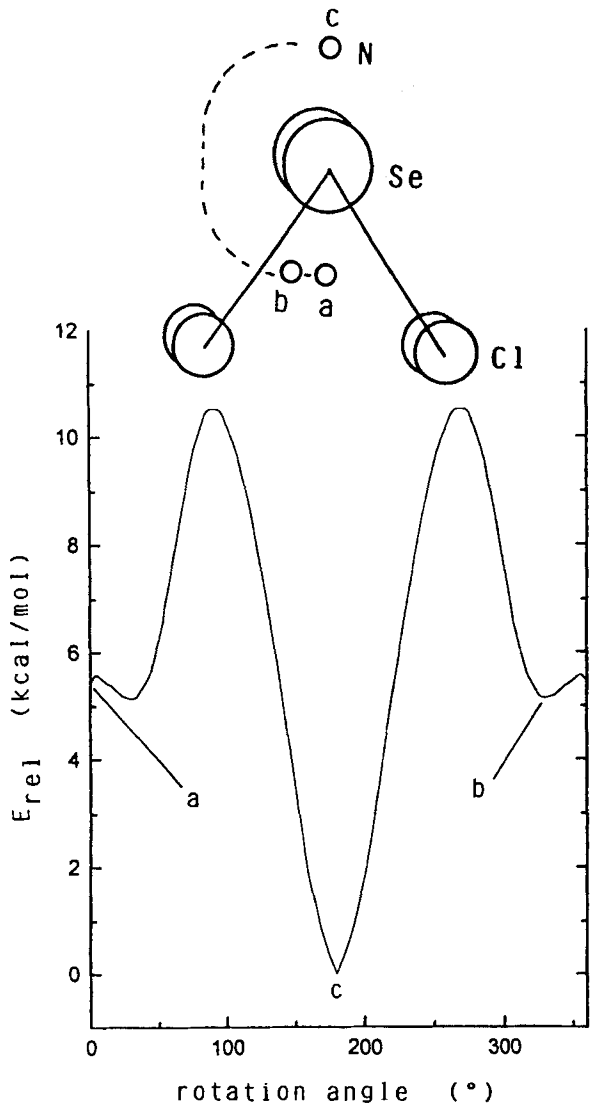
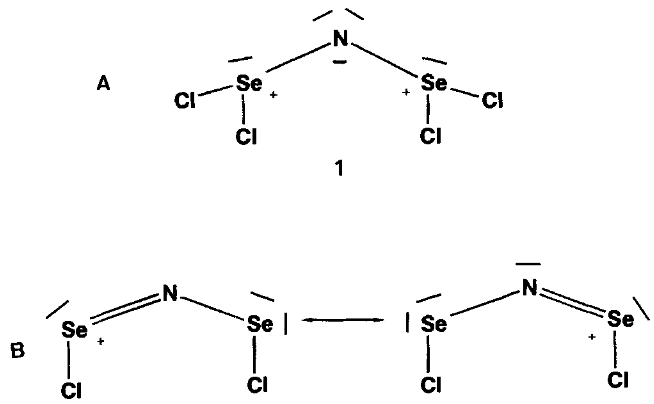


Table 2. Calculated NBO charges for **1**, [ClSe−N−SeCl]$^+$, and **2** (Y = S, Se; X = F, Cl) (HF level)

	N_1	Y_1	Y_2	X_1	X_2	X_3	X_4
1, q (e)	-1.236	+1.372	+1.372	-0.159	-0.159	-0.095	-0.095
$[Cl_1Se_1\text{-}N\text{-}Se_2Cl_2]^+$, q(e)	-0.903	+1.121	+1.121	-0.169	-0.169		
2, q(e)	-1.244	+2.057	2.057	-0.467	-0.467	-0.467	-0.467

Figure 4. Lewis representations of the cations **1** (A) and [ClSe−N−SeCl]$^+$ (B)



(and the mesomeric resonance structure) containing one π bond (π bond electron density: N, 62%; Se, 38%; Figure 4).

Although the σ-bound form of **1** (no localized p_π-p_π bonds) agrees well with the results of NBO analysis, how can one explain (within the NBO formalism) the relatively strong Se−N bonds in **1**, which are substantially shorter (1.741, 1.760 Å) than the expected value for the bond order of one (cf. sum of covalent radii of N and Se: 1.870 Å)[9]? The quantum mechanical computation (subjecting the HF density matrix as represented in the localized NBOs to a second-order perturbative analysis) indicates two fairly strong interactions of the p lone pair (p-LP) at nitrogen with the unoccupied, antibonding σ* orbitals of the Se−Cl bond: p-LP(N)→σ*(Se_1-Cl_1), 22.6 kcal/mol; p-LP(N)→σ*(Se_2-Cl_2), 22.6 kcal/mol.

The energy was computed according to

$$E^{(2)}_{\varphi\varphi^*} = -2\,\frac{\langle\varphi \mid h^F \mid \varphi^*\rangle^2}{E\varphi^* - E\varphi}$$

with h^F being the Fock operator[10].

This "p-LP(N)→σ*(Se−Cl) (negative) hyperconjugation"[10] is illustrated in Figure 5. Obviously, the interaction with the two antibonding σ*(Se_1-Cl_3) and σ*(Se_2-Cl_4) orbitals is rather weak (2.9 kcal/mol) due to geometrical reasons (Figure 7). This also explains the two different sets of Se−Cl bond distances in **1**. The electron density contour map in Figure 6 illustrates interaction of the two antibonding σ*(Se_1-Cl_1) and σ*(Se_2-Cl_2) orbitals with the nitrogen lone pair.

Figure 5. Negative p-LP(N)→σ*(Se−Cl) hyperconjugation in **1**

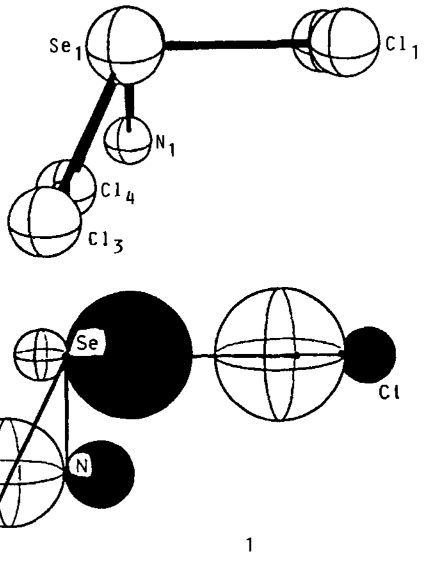
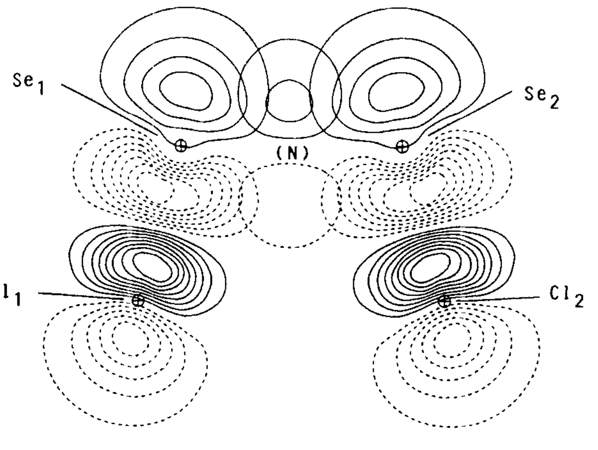


Figure 6. Electron density contour map for the interaction of two antibonding $\sigma^*(Se_1-Cl_1)$ and $\sigma^*(Se_2-Cl_2)$ orbitals with the nitrogen lone pair in **1** (diagram in $Cl_1-Se_1-Se_2-Cl_2$ plane)



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In order to establish that all three computed isomers of **1** represent (local) true minima (no imaginary frequencies) we calculated the normal vibrations for all isomers. Table 3 shows the ab initio-computed frequencies for the cation **1** and those obtained experimentally for $\mathbf{1}[AsF_6]$ by IR and Raman spectroscopy. Calculated and observed wavenumbers compare nicely. Moreover, although harmonic ab initio-computed vibration frequencies are usually too large compared to experiment, it has been established that for these types of molecules the applied pseudopotentials predict the experimental (anharmonic) frequencies remarcably well. No scaling factor had to be applied. The assignments were made on the basis of the computed normal vibrations (Table 3).

Table 3. IR and Raman frequencies obtained for the $(SeCl_2)_2N^+$ cation in $\mathbf{1}[AsF_6]$ and those computed[a] ab initio for **1** (d-HF, C_s). $\tilde{\nu}$ in cm^{-1}, n.o. not observed, o.o.s. out of scale

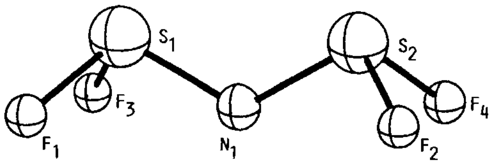
IR (KBr disc, 25°C)	Raman (647nm, 20mW,20°C)	HF [b]	assignment
956 m			?
826 m	n.o.	833	ν_{as}(SeNSe)
565 w	572 (3)	550	ν_s(SeNSe)
n.o.	n.o.	468 and 462	ν(SeCl)
432 m	435 (10)	449	ν_s(SeCl)
n.o.	403 (3)	437	ν_{as}(SeCl)
330 w	322 (5)	293	γ(SeNSe)
281 m	273 (1)	224	δ(SeCl)
o.o.s.	183 (1)	212	δ(SeCl)
o.o.s.	173 (8)	175	δ(SeCl)

[a] Numerical second derivatives. – [b] Effective core potentials for Cl and Se: [5s5p1d]/(3s3p1d)-DZ+P.

The $[F_2S-N-SF_2]^+$ Cation (2)

The structure of cation **2** (in the AsF_6^- salt) has been determined by single-crystal X-ray diffraction[3]. In the crystalline state, **2** possessess C_{2v} symmetry. At HF and correlated MP2 levels, a minimum for the observed C_{2v} structure was found (Figure 7). The MP2 distances and angles compare well with the experimental data, the deviations are less than 0.06 Å and 2.5° (Table 4). NBO analysis (see also Table 3) also reveals a species bound by six σ bonds and two lone pairs at nitrogen. Due to $p\text{-}LP(N)\rightarrow\sigma^*(S-F)$ negative hyperconjugation[10] (4 · 21 = 84 kcal/mol; due to symmetry C_{2v}-identical interaction to all four Se–F bonds) the S–N bond distances are rather short and have bond orders of greater than unity [$d(SN)_{exp.}$ = 1.551 Å; sum of covalent radii, 1.740 Å][9]. For the same reasons as for cation **1**, the **2** (u, C_{2v}) structure favoured in the isolated state [ΔE (d, C_{2v} – u,C_{2v}) = 5.4 kcal/mol] is not found in the crystal because of cation-anion interactions.

Figure 7. MP2-optimized geometry for **2** (d-C_{2v})



2

Table 4. Experimental (X-ray) and computed structural parameters for **2**

	2(X-ray)[3]	2(d-HF,C_{2v})	2(d-MP2,C_{2v})
abs. energy, -au		1246.76898	1247.91144
d(S-F), Å	1.523(8)	1.527	1.577
d(S-N), Å	1.551(10)	1.551	1.582
<(FSF), °	94.0(5)	96.2	96.2
<(FSN), °	100.2(6)	101.4	100.5
<(SNS), °	121.1(6)	126.5	123.5

Comparison of the Structures of 1 and 2

Both, the HF and MP2 geometries of both cations $[Cl_2Se-N-SeCl_2]^+$ [**1** (d, C_s)] and $[F_2S-N-SF_2]^+$ [**2** (d-C_{2v})], fit the experimentally determined (X-ray) structural parameters satisfactorily. However, only the correlated MP2 result gives good agreement for **1** (d, C_s) with the nitrogen plane deviation angle from the $Cl_3-Se_1-Se_2-Cl_4$ plane (cf. Figure 2). Whereas the calculations indicate that the u, C_{2v} isomers of both **1** and **2** should be slightly more favourable, the experimentally observed down structure (d) for both species can be rationalized since the cation-anion interactions in the solid state should be unfavourable for the crystalline up (u) isomers. Why does **1** prefer the d, C_s structure while **2** exists in the d, C_{2v} geometry? The optimizations of **2** begun in C_s symmetry led to the C_{2v} geometry. In contrast, cation **1** possesses (in agreement with experimental X-ray results) a d, C_s minimum lower in energy than the d, C_{2v} structure (MP2, 1.4 kcal/mol). Thus, the computations reflect the observed structural features for **1** and **2**. But how can one explain this behaviour in terms of simple chemistry? The distorted but roughly trigonal prismatic S_2F_4 and Se_2Cl_4 moieties are significantly different in size. Apparently the unsymmetrical d, C_s geometry provides a better net positive overlap for the LP(N)→σ*(Y−X) negative hyperconjugation (Y = S, Se; X = F, Cl). Thus, nitrogen prefers to occupy the d, C_s position, but this is not possible in the relatively small S_2F_4 derivative for electrostatic reasons. Hence, the stability, strength (and shortness) of the Se−N bonds in **1** and the S−N bonds in **2** can be ascribed to the good positive net overlap for the negative hyperconjugation. This is due to (i) a favourable geometrical arrangement of the atoms involved (**1**) and (ii) a sulfur-orbital contraction because of the highly electronegative fluorine substituents (see below).

The $[Cl_2S-N-SCl_2]^+$ (3) and $[F_2Se-N-SeF_2]^+$ (4) Cations

The successful preparation of salts of the cations **1** and **2** led naturally to the exploration of the analogous cations **3** and **4**. Unfortunately, all our attempts to prepare AsF_6^- or $SbCl_6^-$ salts containing **3** have been unsuccessful. We could not even prepare a stable solid containing **3** or **4**. Perhaps this is not possible, as **3** might decompose to the thermodynamically more stable $[ClS-N-SCl]^+$ salt and chlorine (eq. 1). (Note that $[ClY-N-YCl]^+$ salts have been reported for both Y = S and Se)[2,11,12,13]. It is interesting to mention that the isovalently related decomposition of the unknown $[Cl-O-Cl-O-Cl]^+$ ion into ClO_2^+ and Cl_2 explains the formation of chloryl salts from Cl_2O and Lewis acids[14].

$$[Cl_2S-N-SCl_2]^+[AsF_6]^- \rightarrow [ClS-N-SCl]^+[AsF_6]^- + Cl_2 \quad (1)$$

3

$[F_2Se-N-SeF_2]^+$ **4**

Notwithstanding all the experimental synthetic difficulties, three possible structures are envisaged for each of the cations **3** and **4**: (d, C_s), (d, C_{2v}), and (u, C_{2v}) were computed. However, no local minimum could be found for them in C_s symmetry. The HF-optimized geometries for the up (u) and down (d) C_{2v} structures of **3** and **4** are given in Figure 8 and Table 5. So far, for these still hypothetical compounds we have not performed correlated computations since MP2 calculations are very expensive for these type of large molecules.

Figure 8. HF-optimized structures for **3** and **4** in C_{2v} symmetry

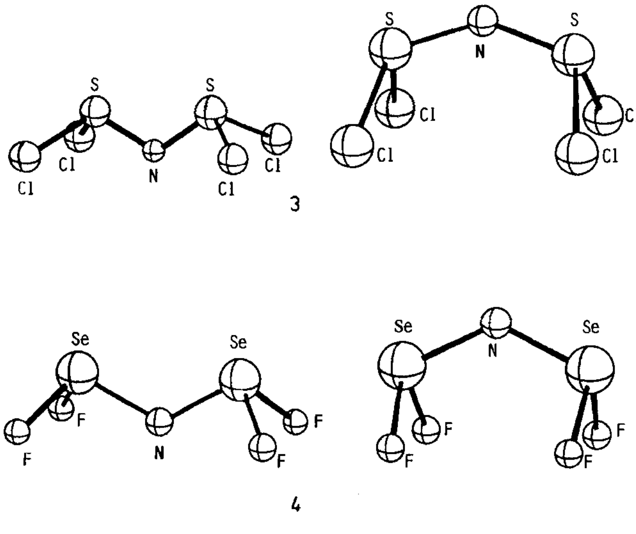


Table 5. HF-optimized structural parameters and energies for **3** and **4** in C_{2v} symmetry (**3**: X = Cl, Y = S; **4**: X = F, Y = Se)

	3(HF-d,C_{2v})	3(HF-u,C_{2v})	4(HF-d,C_{2v})	4(HF-u,C_{2v})
abs. energy, -au	908.11226	908.11705	469.92998	469.95106
rel. energy, kcal/mol	3.0	0.0	13.2	0.0
d(Y-N), Å	1.598	1.568	1.732	1.729
d(Y-X), Å	1.998	2.019	1.706	1.717
<(YNY), °	116.7	142.2	124.4	129.7
<(NYX), °	103.5	109.5	97.5	103.7
<(XYX), °	101.1	100.3	93.7	92.7

As expected, the u, C_{2v} isomers are slightly more favourable for both **3** (3.0 kcal/mol) and **4** (13.2 kcal/mol) in the isolated state. However, for reasons discussed above, we expect the hitherto unknown species to possess d, C_{2v} geometry in the solid state. In the series of $[X_2Y-N-YX_2]^+$ cations (X = F, Cl; Y = S, Se), the fluorine-bound species **2** and **4** show stronger Y−N bond stabilization due to negative hyperconjugation[10] than the chlorine-coordinated derivatives **1** and **3**. The calculated Y−N bond distances at the HF level are: *d*(SN) **2** = 1.551, *d*(SN) **3** = 1.598, *d*(SeN) **4** = 1.732, and *d*(SeN) **1** = 1.800 Å as fluorine is more electronegative than chlorine. The enhanced positive charge at the chalcogen atoms leads to Y orbital contraction and therefore better overlap with the comparatively small p lone pair at nitrogen.

Conclusions

The structures of a series of ternary cations of the $[X_2Y-N-YX_2]^+$ (X = F, Cl; Y = S, Se) type have been computed ab initio and, for the known species, compared with the experimental data. Both ab initio and X-ray data indicate strong Y−N chalcogen-nitrogen bonds with bond orders greater than one. The relatively short Y−N bond distances are ascribed to lone pair (N) → σ*(Y−X) (negative) hyperconjugation (Y = S, Se; X = F, Cl). Apparently the negative hyperconjugation (one strong and one weak bond) in unsymmetrical C_s **1** is stronger than those in the symmetrical (two medium strong bonds) species in **2**. Moreover, for $[Cl_2Se-N-SeCl_2]^+$ in C_s symmetry hyperconjugation not only explains the short Se−N bond lengths but also the two different sets of Se−Cl bond distances.

This work was supported by the *Deutsche Forschungsgemeinschaft* (Erlangen and Berlin) as well as by the *Fonds der Chemischen Industrie* (Erlangen and Berlin), the *North Atlantic Treaty Organization* (Berlin and Chapel Hill, CRG 920034), the *Convex Computer Corporation*, the *LRZ München* and the *HLRZ Jülich*. The research fellowship from the *Bundesminister für Bildung und Wissenschaft* (Graduiertenkolleg) to A.S. is gratefully acknowledged.

Experimental

Computational Methods: The computations were carried out with the Gaussian 92 program using the 6-31+G* basis set for nitrogen, fluorine, and sulfur[15]. For chlorine (ECP10MWB)[16] and selenium (ECP28MWB)[17] quasi-relativistic pseudopotentials and the following basis sets were used: Se, (5s5p)/[3s3p]-DZ+P (extended with a set of five d functions, d_{exp} = 0.338)[18]; Cl, (5s5p1d)/

[3s3p1d]-DZ+P[19]. The geometries for **1**–**4** were fully optimized at the HF level employing standard procedures. In addition, the geometries of cations **1** and **2** were fully optimized (no symmetry restrictions, start in C_1 symmetry) at the electron-correlated 2nd order Møller-Plesset level using the frozen core approximation [MP2(FC)].

$[(SeCl_2)_2N]^+[AsF_6]^-$ (**1**[AsF_6]) was prepared from $SeCl_3^+$-AsF_6^- (1.00 g, 2.67 mmol) and $N(SiMe_3)_3$ (0.52 g, 2.23 mmol) in $CFCl_3$ solution at 0°C (reaction time 3 h). Removal of all volatile material gave red-orange $[(SeCl_2)_2N]^+[AsF_6]^-$ in 83% yield (0.56 g) which was used for chemical and spectral analyses. Crystals suitable for single-crystal X-ray diffraction studies were obtained by recrystallization from CH_2Cl_2/MeCN (95:5) at −40°C. The crystal $[(SeCl_2)_2N]^+[AsF_6]^- \cdot CH_3CN$ was attached on the end of a glass fibre and immediately placed in a stream of cold dry nitrogen. – IR and Raman data see Table 3. – ^{77}Se NMR (CD_3CN, rel to Me_2Se, 76.31 MHz, 28°C): $\delta = 1800$.

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