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The $\mathrm{ClSeNSeCl^+}$ Cation. An Unusual Structurally Very Flexible Ion Adopting Different Solid-State Structures As Deduced by X-ray and ab Initio Methods

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The new salt $[\mathrm{ClSeNSeCl}]^+[\mathrm{SbCl_6}]^-$ was prepared in 89% yield from the reaction of $[\mathrm{SeCl_3}]^+[\mathrm{SbCl_6}]^-$ and $\mathrm{N(SiMe_3)_3}$. This method provides the first synthesis that is suitable for the preparation of a $[\mathrm{ClSeNSeCl}]^+$ salt on a preparative scale. The new salt was characterized by elemental analysis and vibrational (IR, Raman), $^{77}\mathrm{Se}$ NMR, and mass spectroscopy. The low-temperature structure was determined by a single-crystal X-ray diffraction analysis. The compound crystallizes in the orthorhombic space group $P2_1nb$ with $Z = 8$ and unit cell dimensions $a = 7.0068(17)$, $b = 14.6678(23)$, and $c = 37.365(13)$ Å. The structure is made up of octahedral $\mathrm{SbCl_6^-}$ anions and s-shaped (s-isomer) $[\mathrm{ClSeNSeCl}]^+$ cations with some cation–anion interactions. In the $[\mathrm{ClSeNSeCl}]^+$ cation the two Se–N bond lengths (1.644(21), 1.753(22) Å) are just slightly different (double esd's) in agreement with quantum mechanical computations predicting that the asymmetrical geometry provides a better net positive overlap for the $\mathrm{LP(N)} \rightarrow \sigma^*(\mathrm{Se{-}Cl})$ negative hyperconjugation (LP, lone pair). The structures of the cationic species of the series $[\mathrm{ClXNXCl}]^+$ (X = S, Se) were determined ab initio using all-electron computations for first-row elements and sulfur and quasi relativistic pseudopotentials for Se and Cl. Split valence basis sets with polarization and diffuse functions (6-31+G* and dz+p, respectively) were employed. The MP2 results for the u-isomer (C_{2v}) of the cations $[\mathrm{ClXNXCl}]^+$ (X = S, Se) are in excellent agreement with the experimental (X-ray) XNX angles: $[\mathrm{ClSeNSeCl}]^+[\mathrm{GaCl_4}]^-$, 146.6(3)° (X-ray), 142.5° (MP2); $[\mathrm{ClSNSCl}]^+[\mathrm{AlCl_4}]^-$, 151.0(2)° (X-ray), 152.2° (MP2). The novel structural s-isomer (C_s) of the $[\mathrm{ClSeNSeCl}]^+$ cation in the new salt $[\mathrm{ClSeNSeCl}]^+[\mathrm{SbCl_6}]^-$ and the hitherto unknown w-isomer (C_{2v}) were fully optimized with the MP2/6-31+G* basis sets. It was shown that both experimentally observed isomers (u- and s-isomers) of $[\mathrm{ClSeNSeCl}]^+$ are essentially identical in their total energy ($\Delta E = 1$ kcal/mol in favor for the u-isomer) whereas the only other local minimum (w-isomer) was found to be 9.2 kcal/mol less stable than the u-isomer. Frequency calculations were performed at MP2/6-31+G* on the optimized structures for both the u- and the s-isomers of both salts $[\mathrm{ClXNXCl}]^+$ (X = S, Se). In general, agreement between the calculated and observed geometries and frequencies is very good at the correlated MP2 level.

Introduction

Numerous binary S–N–Cl cations have been prepared and structurally characterized.[1] In contrast, only two Se analogues have been reported: $[\mathrm{Cl_2SeNSeCl_2}]^+$ [2] and $[\mathrm{ClSeNSeCl}]^+$.[3] Whereas the first one can be obtained in a simple high-yield reaction (83%),[2] the five-atomic species $[\mathrm{ClSeNSeCl}]^+$ is only accessible from $\mathrm{Se_2NCl_3}$.[3,4] The main drawbacks of this reaction include the following: (i) $[\mathrm{ClSeNSeCl}]^+$ is only accessible from $\mathrm{Se_2NCl_3}$, which is not commercially available; (ii) the yields of the starting material $\mathrm{Se_2NCl_3}$ are far less than quantitative (about 57%); (iii) the chloride abstraction from $\mathrm{Se_2NCl_3}$ to yield $[\mathrm{ClSeNSeCl}]^+$ requires the expensive $\mathrm{Cl^-}$ ion acceptor $\mathrm{GaCl_3}$ (ca. \$70/5 g).

We recently described a convenient synthesis of $[\mathrm{Cl_2SeNSeCl_2}]^+[\mathrm{AsF_6}]^-$ and established that $[\mathrm{SeCl_3}]^+[\mathrm{AsF_6}]^-$ is a potentially useful building block in Se–N–Cl chemistry.[2] In this paper we report the reaction of $[\mathrm{SeCl_3}]^+[\mathrm{SbCl_6}]^-$ with $\mathrm{N(SiMe_3)_3}$. Surprisingly, $[\mathrm{SeCl_3}]^+[\mathrm{SbCl_6}]^-$ does not react with $\mathrm{N(SiMe_3)_3}$ in the same way to form the hexafluoroarsenate salt (eq 1) but gives off chlorine to form the $[\mathrm{ClSeNSeCl}]^+$ cation in the new salt $[\mathrm{ClSeNSeCl}]^+[\mathrm{SbCl_6}]^-$ in high yield (89%) (eq 2). The results of this study are summarized in this paper.

$$6[\mathrm{SeCl_3}]^+[\mathrm{AsF_6}]^- + 5\mathrm{N(SiMe_3)_3} \rightarrow 9\mathrm{Me_3SiF} + 3\mathrm{AsF_3} + \mathrm{N_2} + 6\mathrm{Me_3SiCl} + 3[\mathrm{Cl_2SeNSeCl_2}]^+[\mathrm{AsF_6}]^- \quad (1)$$

$$2[\mathrm{SeCl_3}]^+[\mathrm{SbCl_6}]^- + \mathrm{N(SiMe_3)_3} \rightarrow [\mathrm{ClSeNSeCl}]^+[\mathrm{SbCl_6}]^- + \mathrm{SbCl_5} + \mathrm{Cl_2} + 3\mathrm{Me_3SiCl} \quad (2)$$

In the present work the X-ray structure determination revealed quite different geometries for $[\mathrm{ClSeNSeCl}]^+$ depending on the counteranions ($[\mathrm{GaCl_4}]^-$, u-isomer; $[\mathrm{SbCl_6}]^-$, s-isomer). Therefore, in order to understand the structures of these cationic, ternary chalcogen–halogen–nitrogen species more fully, the objective was to determine the ground-state structures of $[\mathrm{ClXNXCl}]^+$ (X = S, Se) cations. Ab initio computations including quasirelativistic pseudopotentials for Cl and Se were successfully applied to the structural elucidation of these electron-rich Se–N cations.

Experimental Section

The reactions were carried out in glass vessels in an inert-gas atmosphere ($\mathrm{N_2}$, drybox). Apparatus, techniques, and chemicals, unless specified, have been described.[2] $\mathrm{N(SiMe)_3}$ (Aldrich) was used as received; $\mathrm{SbCl_5}$

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(Aldrich) was purified by distillation. CCl_4 (Merck) was dried over P_4O_{10}, and SO_2 (Messer-Griesheim), over CaH_2.

^{77}Se NMR spectra were acquired at 76.26 MHz on a Bruker AM 250 spectrometer and referred externally to Me_2Se in CD_3CN with high-frequency direction positive. Infrared spectra were obtained as powders between KBr plates on a Perkin-Elmer 580 B instrument. The Raman data were obtained on a Jobin Yvon Ramanor U 1000 spectrometer using a Spectra Physics Kr ion laser (excitation line 647.09 nm) with samples contained in sealed, thin-walled 5-mm Raman tubes (either solid or SO_2 solution). Mass spectra were obtained at room temperature in the electron impact mode using 70-eV ionizing voltage on a Varian MAT 311A instrument. Elemental analyses were carried out either by the TU Berlin analytical service or by Analytische Laboratorien, Malissa, Engelskirchen, Germany.

Synthesis of $[ClSeNSeCl]^+[SbCl_6]^-$. A solution of $N(SiMe_3)_3$ (0.56 g, 2.40 mmol) in 100 mL of CCl_4 was added dropwise over 1 h to a stirred slurry of $[SeCl_3]^+[SbCl_6]^-$ (2.50 g, 4.80 mmol) in 100 mL of CCl_4 at 0 °C. The reaction mixture was stirred for 12 h at room temperature giving an orange powdery solid. After filtration the orange residue was washed three times with CCl_4 and dried in vacuum (yield 1.23 g, 89%).

Needle-shaped, orange crystals suitable for single-crystal X-ray diffraction studies were obtained by recrystallization from liquid SO_2 at room temperature.

Anal. Calcd for Cl_8NSbSe_2: N, 2.43; Cl, 49.13. Found: N, 2.19, Cl, 48.98. Mp: 120 °C dec. ^{77}Se NMR (CD_3CN, 31 °C): $\delta = 1702$ ppm, s. Infrared spectrum: see Table VI. Raman spectrum: see Table VI and Figure 6.

Crystal Structure Determination of $[ClSeNSeCl]^+[SbCl_6]^-$. Single crystals of $[ClSeNSeCl]^+[SbCl_6]^-$ were obtained by recrystallization from SO_2 solution. Suitable crystals were selected under fluorocarbon oil under a microscope. Data collection was carried out at −170 °C on a Rigaku AFC 6S diffractometer by the routine DIFRAC[5] with graphite-monochromated Mo Kα radiation ($\lambda = 0.709\ 30$ Å) using the $\theta/2\theta$ scan mode ($2\theta_{max}$ of 45°), and empirical correction was made for absorption using DIFABS;[5] the range of relative transmission factors was 0.87–1.12. The structure was refined by full-matrix least-squares analysis[6] to residuals of $R_F = 0.042$ and $R_w = 0.037$ for 1779 reflections [$I \geq 2.5\sigma(I)$] (2757 total) and 324 parameters. All atoms were assigned anisotropic thermal parameters. Scattering factors were taken from ref 7 and corrected for anomalous dispersion. Details of the data collection and structure refinement are summarized in Table I.

Computational Methods. The computations were carried out with the Gaussian 92 program using the 6-31+G* basis set for nitrogen and sulfur.[8] For chlorine (ECP10MWB)[9] and selenium (ECP28MWB)[10] quasi-relativistic pseudopotentials and the following basis sets were used: Se, (5s5p)/[3s3p]-dz+p (extended with a single d-function, $d_{exp} = 0.338$);[11] Cl, (5s5p1d)/[3s3p1d]-dz+p.[12] The pseudopotential for Se was used since all-electron computations are too expensive. In the case of chlorine we know from our own experience that the applied pseudopotential gives very good results in comparison with the experimental data.[13] For sulfur an all-electron computation was carried out as we do not have reliable data from pseudopotential calculations for comparison of computed and observed structures. In addition, the geometries of all three isomers (u-, s-, w-isomers) for both cations $[ClXNXCl]^+$ (X = S, Se) were fully optimized at the electron-correlated second-order Møller–Plesset level using the frozen core approximation (MP(FC)).

Table I. Details of the Data Collection and Structure Refinement for $[ClSeNSeCl]^+[SbCl_6]^-$ at −170 °C

formula	Cl_8NSbSe_2
fw	577.30
cryst system	orthorhombic
space group	$P2_1nb$
cryst dimens (mm)	0.20 × 0.20 × 0.40
cryst color	orange red
a (Å)	7.0068(17)
b (Å)	14.6678(23)
c (Å)	37.365(13)
Z	8
V (Å^3)	3840.2(2)
D_{calc} (g/cm^3)	2.996
radiation (λ, Å)	Mo Kα (0.709 30)
abs coeff, μ (mm^{-1})	6.58
abs corr type	empirical
abs factor range (intensity)	0.87–1.12
F(000) (e)	3144
temp (K)	100
diffractometer	Rigaku AFC6S
scan mode	$\theta/2\theta$
2θ range (deg)	1–45
tot. no. of reflns measd	2757
no. of unique reflns	2757
no. of reflns used for refinement	1779 [$I > 2.5\sigma(I)$]
no. of params refined	324
max final shift/error	0.017
max resid density (e/Å^3)	1.150
$R_F = \sum(F_o - F_c)/\sum(F_o)$	0.042
$R_w = [\sum(w(F_o - F_c)^2)/\sum(w(F_o)^2]^{1/2}$	0.037
GOF = $[\sum(w(F_o - F_c)^2/$(no. of reflns − no. of params)$]^{1/2}$	1.17

Results

Preparative Aspects. The successful preparation of $[Cl_2SeNSeCl_2]^+[AsF_6]^-$ (eq 1) led naturally to the attempted synthesis of the analogous $SbCl_6^-$ salt since $[SeCl_3]^+[SbCl_6]^-$ is much less expensive than $[SeCl_3]^+[AsF_6]^-$. However, we were surprised to find that $[ClSeNSeCl]^+[SbCl_6]^-$ (**1**) had been formed in reaction 2. In fact, **1** was prepared in high yield according to eq 2 when a 1:2 stoichiometry ($N(SiMe_3)_3$:$SeCl_3^+$) was used. Therefore eq 2 provides the first convenient and high-yield synthesis for a salt containing the $[ClSeNSeCl]^+$ cation on a preparative scale.

Structural Aspects (X-ray). The $[ClSeNSeCl]^+$ cation in **1** has an s-shaped C_s structure (Figure 1) that does not resemble that of the same cation in the $[GaCl_4]^-$ salt which represents the u-isomer (C_{2v}).[3] This structural diversity can be qualitatively rationalized assuming the existence of several (at least two) minima (that are close in energy) on the (potential energy) hypersurface of $[ClSeNSeCl]^+$. Quite recently we reported on the structural diversity of $[Cl_2SeNSeCl_2]^+$ cations and showed that cation···anion interactions can account for the realization of solid-state cation structures that are up to 8 kcal/mol higher in energy than the minimum energy structures of the gaseous (isolated) cations.[13] Nicely in agreement with this, there are significant cation···anion interactions with bond distances substantially shorter than the sum of the van der Waals radii also in **1** (e.g. the Se···Cl distance, solid black atoms in Figure 1 marked by →: 3.274(7) Å. Cf. van der Waals radii: Cl, 1.80 Å; Se, 2.10 ± 10 Å).[14] The internal structural parameters of the $[ClSeNSeCl]^+$ cation in **1** are summarized in Table II. It is worthwhile mentioning that the two Se–N and Se–Cl bond distances are just slightly different (double esd's). An explanation for this is given in the theoretical part (see below). The $SbCl_6^-$ anions are nearly octahedral with some distortion due to cation···anion interactions: d(Sb–Cl) = 2.349(7)–2.380(6) Å and ∠(ClSbCl) = 86.1(3)–92.1(3)°.

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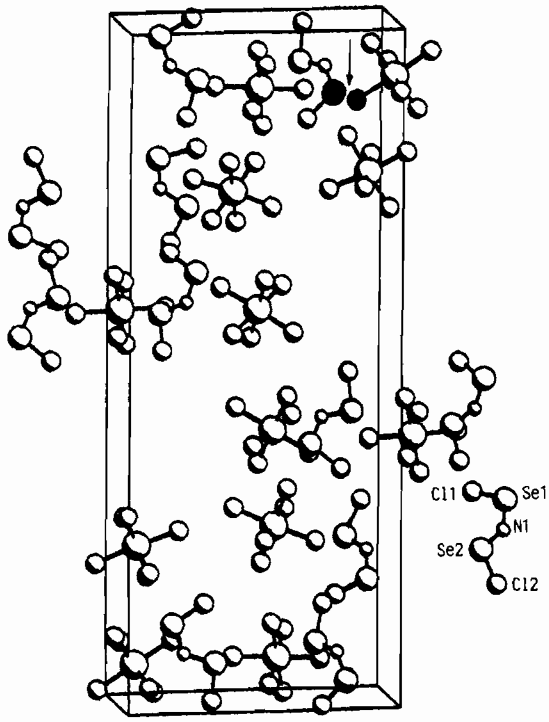

Figure 1. Packing diagram of 1 with Se···Cl contacts.[15]

Table II. Structural Parameters of the $[ClSeNSeCl]^+$ Cation in 1

Distances (Å)			
N(1)–Se(1)	1.644(21)	Se(1)–Cl(1)	2.156(7)
N(1)–Se(2)	1.753(22)	Se(2)–Cl(2)	2.136(7)
Angles (deg)			
Se(1)–N(1)–Se(2)	127.0(13)	N(1)–Se(2)–Cl(2)	99.5(7)
N(1)–Se(1)–Cl(1)	102.2(8)		

Structural Aspects (Computations). Two different structures for the $[ClSeNSeCl]^+$ cation were observed experimentally (X-ray). These are (i) the u-isomer (C_{2v}) with two identical Se–N and Se–Cl bond distances and (ii) the s-isomer (C_s) with two different Se–N and two different Se–Cl bond lengths. In order to understand this structural diversity more fully three structures of $[ClSeNSeCl]^+$ were computed ab initio: our notation employs "u" for the u-isomer (C_{2v}), "s" for the s-isomer (C_s), and "w" for the w-isomer (C_{2v}). The optimized geometries are shown in Figure 2; the computed structural parameters are summarized in Table III.

The energies of the various structures with the different theoretical approximations are summarized in Table IV. In nice agreement with the experimental results at the HF/6-31+G* and correlated MP2 level, the total energies for both observed isomers (the s- and the u-shaped cations) are very similar. Therefore, only marginal differences in the cation···anion interactions can favor either of these species. Only one other local minimum was found, the experimentally unknown w-isomer, but this was 9.2 kcal/mol less stable than the u- and 8.2 kcal/mol less stable than the s-isomers (MP2/6-31+G*). Since the two isomers (u and s) which are very close in energy can interconvert by a 180° rotation along one of the Se–N axes (i.e. by variation of the dihedral Cl2Se2N1Se1 angle from 0 to 180°), we computed the energy required for this isomerization (Figure 3). It was shown that both isomers are separated by a barrier of 19 kcal/mol, which should allow interconversion in solution when there are no cation···anion interactions.

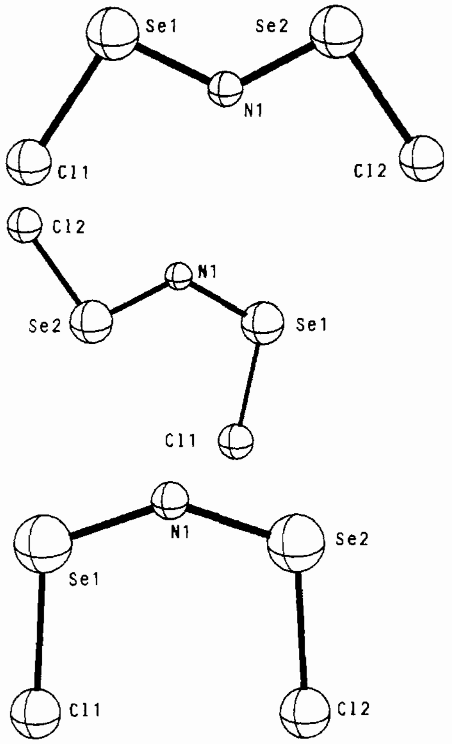

Figure 2. MP2-optimized geometries for the u-, w-, and s-isomers of $[ClSeNSeCl]^+$.

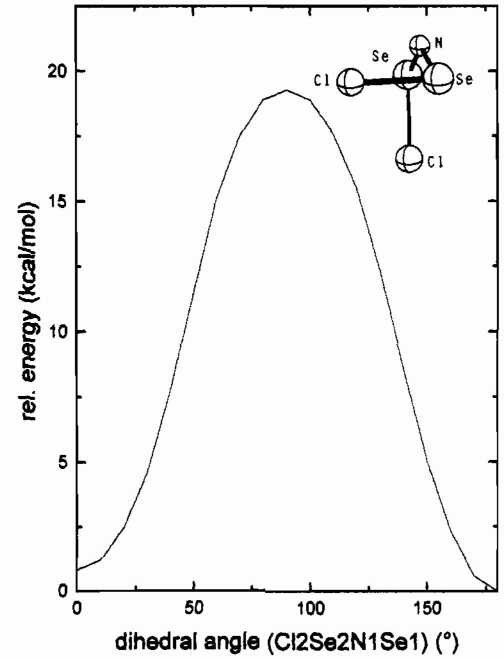

Figure 3. Energy profile for the interconversion of the u- (0°) to the s-isomer (180°) of $[ClSeNSeCl]^+$ by variation of the Cl2Se2N1Se1 dihedral angle (HF/6-31+G*).

Finally, it might be interesting to discuss whether the relatively small SeNSe angle of 127° found by X-ray analysis in agreement with the computational results (MP2 124°) for the s-isomer of $[ClSeNSeCl]^+$ could also be realized in the u-form for which the observed SeNSe angle is 147° (MP2 142.5°). The computed relationship (Figure 4) between the total energy for the u-isomer as a function of the SeNSe angle clearly shows a relatively steep potential (especially for smaller angles). Therefore, the hypothetical small-angle (127°) u-isomer is not likely to be found as this species does not represent a local minimum and is 12 kcal/mol (HF) less stable than the observed u-isomer with an SeNSe angle close to 150° at the HF level (142.5° at MP2).

As indicated by NBO (natural bond orbital) analysis,[16] the Se–N–Se unit in all three isomers of the $[ClSeNSeCl]^+$ cation has strongly polarized Se–N bonds. In all cases the NBO charges

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Table III. Experimental (X-ray) and Computed Structural Parameters for the Different Isomers of $[ClSeNSeCl]^+$ (Distances in Å, Angles in deg)

	s isomer			u isomer			w isomer	
	X-ray[a]	HF	MP2	X-ray[b]	HF	MP2	HF	MP2
d(Se1–N)	1.644(21)	1.717	1.759	1.695(4)	1.708	1.747	1.731	1.774
d(Se2–N)	1.753(22)	1.736	1.787	1.694(4)	1.708	1.747	1.731	1.774
d(Cl1–Se1)	2.156(7)	2.162	2.190	2.151(2)	2.156	2.184	2.146	2.164
d(Cl2–Se2)	2.136(7)	2.144	2.159	2.143(2)	2.156	2.184	2.146	2.164
∠(Se1NSe2)	127.0(13)	132.4	124.0	146.6(3)	151.0	142.5	133.5	126.8
∠(Cl1Se1N)	102.2(8)	103.8	105.7	108.3(1)	107.9	111.4	99.1	97.3
∠(Cl2Se2N)	99.5(7)	98.7	97.5	108.3(1)	107.9	111.4	99.1	97.3
dihedral ∠(ClSeNSe)	180	180	180	0	0	0	0	0

[a] This work. [b] Reference 3.

Table IV. Absolute (–au) and Relative (kcal/mol) Energies for Different Isomers of $[ClSeNSeCl]^+$

	w (C_{2v})	s (C_s)	u (C_{2v})
HF; –au (rel., kcal/mol)	101.864 03 (5.6)	101.873 00 (0.0)	101.871 79 (0.8)
MP2; –au (rel., kcal/mol)	102.527 54 (9.2)	102.540 59 (1.0)	102.542 26 (0.0)

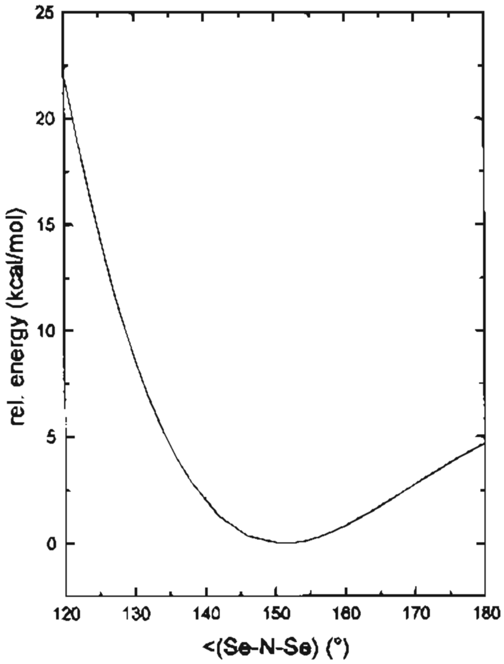

Figure 4. Energy profile for the variation of the SeNSe angle in the u-isomer. Energies are given relative to the local minimum at 151° (HF/6-31+G*).

Table V. Calculated NBO Charges for $[ClSeNSeCl]^+$ (u-, s-, and w-Isomers)

isomer	Cl1	Se1	N1	Se2	Cl2
u	–0.17	+1.12	–0.90	+1.12	–0.17
s	–0.19	+1.10	–0.81	+1.03	–0.13
w	–0.14	+1.08	–0.89	+1.08	–0.14

on nitrogen are close to –1 whereas for each selenium they are nearly +1 (Table V). In agreement with NBO analysis the best Lewis representation for these cations would clearly be a species containing four σ-bonds and one π-bond that is delocalized within the Se–N–Se unit. Although this model agrees well with the planar structure of the observed isomers, how can one explain the two sets of different Se–N and Se–Cl bond distances in the s-isomer? The quantum mechanical computation indicates a fairly strong interaction of the p lone pair (p-LP) on nitrogen with one of the unoccupied, antibonding σ* orbitals of the Se–Cl bond (in our notation Se1–Cl1): p-LP(N) → σ*(Se1–Cl1), 10 kcal/mol. Obviously, the interaction with the other Se–Cl bond (Se2–Cl2) is rather weak for geometrical reasons: p-LP(N) → σ*(Se2–Cl2), 3 kcal/mol. This p-LP(N) → σ*(Se–Cl) (negative) hyperconjugation is illustrated in Figure 5. This not only explains

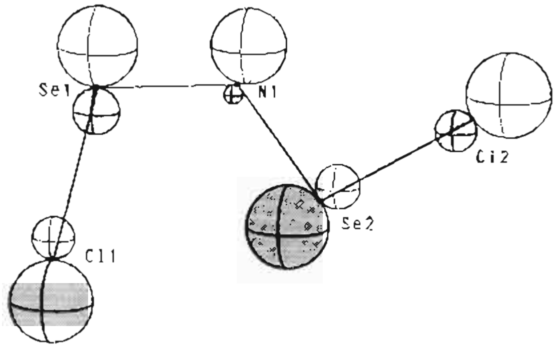

Figure 5. Negative p-LP(N) → σ*(Se–Cl) hyperconjugation in the s-isomer of $[ClSeNSeCl]^+$.

the two different N–Se distances but also accounts for the differences in the Se–Cl bond lengths.[13,17,18]

Comparison with the S analogue $[ClSNSCl]^+$. It is interesting to mention that a large number of sulfur analogues of **1** have been prepared. These compounds contain the $[ClSNSCl]^+$ cation in combination with the following anions: AsF_6^-, SbF_6^-;[19] $SbCl_6^-$,[20] $[MoCl_5(NSCl)]^-$,[21] BCl_4^-,[22] $AlCl_4$,[23] $Re_2Cl_9^-$.[24] For the $[ClSNSCl]^+$ cation we also computed the two most likely isomers (u, s) ab initio and found that at our highest level (MP2/6-31+G*) the u-isomer is more favorable. Again, the s-isomer is just slightly higher in energy (MP2: ΔE(u–s) = 2.8 kcal/mol). All of the experimentally observed $[ClSNSCl]^+$ structures ($SbCl_6^-$,[20] $[MoCl_5(NSCl)]^-$,[21] BCl_4^-,[22] $AlCl_4^-$ [23]) are all made up of u-shaped cations with SNS bond angles of 150 ± 1° (cf. MP2, 152.2°). The only exception is the $Re_2Cl_9^-$ salt which contains the $[ClSNSCl]^+$ cation as the u-isomer with an SNS angle of 134°.[24] However, no unusual cation⋯anion interactions have been observed in the latter case. On the basis of a MP2 computation with a fixed SNS angle of 134°, we found this geometry 5.5 kcal/mol less stable than the minimum structure (u-isomer, SNS = 152.2°). The optimized parameters are in

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Table VI. Computed (MP2) IR and Experimentally Observed IR and Raman Frequencies (cm^{-1}) for $[ClSeNSeCl]^+$ in **1**

IR[a]	Raman, solid[b]	Raman, SO_2 soln[c]	MP2/6-31+G* s-isomer[d]	MP2/6-31+G* u-isomer[d]	assgnt
875 (vs)	880 (1)	935 (2)	878 (vs)	944 (vs)	ν_{as}(SeNSe)
800 (s)		808 (2)			$2\nu_{as}$(SeCl)
		624 (2)			?
		533, 484 (≤1)			?
560, 530 (w)	566 (10)	437 (1)	565 (m)	446 (vs)	ν_s(SeNSe)
445 (w)					?
422 (m)	416 (1)	411 (2)	442 (m)	424 (m)	ν_s(SeCl)
400 (m)	395 (1)	402 (3)	416 (m)	409 (m)	ν_{as}(SeCl)
340 (s)					$\nu_3(SbCl_6^-)$
	334 (7)	333 (10)			$\nu_1(SbCl_6^-)$
	286 (1)				$\nu_2(SbCl_6^-)$
271 (m)	265 (3)	278(2), 271(2)	273 (vw), 270 (w)	287 (w)	γ-SeNCl

[a] Powder between KBr plates, 25 °C. [b] 647.09 nm, 25 °C, 50 mW. [c] 647.09 nm, 25 °C, 100 mW. [d] Computed intensities correspond to IR frequencies.

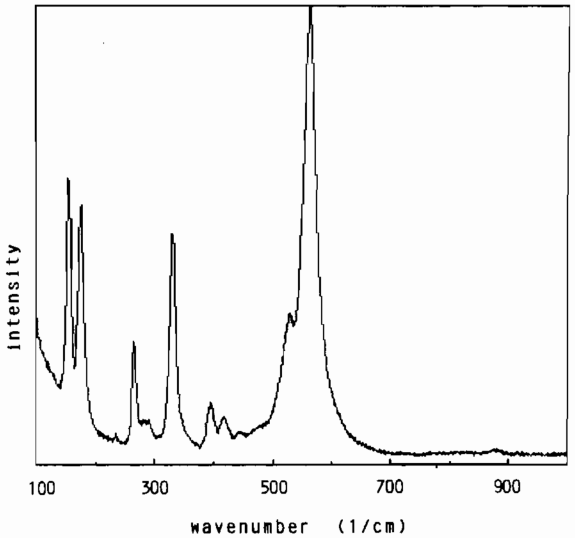

Figure 6. Raman spectrum of **1** (solid, 647.09 nm, 50 mW, 25 °C).

very good agreement with the X-ray data (e.g. ∠ClSN: X-ray, 117.6°; MP2, 116.8°). The energy difference for the minimum structure (5.5 kcal/mol) is much lower than the corresponding one for the hypothetical, distorted small-angle selenium u-isomer (12 kcal/mol; see above) and may explain why this sulfur cation was observed in the solid state. So far no s-shaped $[ClSNSCl]^+$ cation has been reported, which, in accord with our computations, is also likely to exist.

Vibrational Frequencies. The experimental IR spectrum of **1** was obtained on a solid sample (powder between KBr plates) containing the s-shaped $[ClSeNSeCl]^+$ cation. The observed frequencies are in excellent agreement with the calculated data ($\Delta\nu_{max(exp-calc)} \approx 10$ cm^{-1}) on correlated MP2 level (6-31+G*) (Table VI). The experimental Raman spectra of **1** changed dramatically after dissolving of the sample in liquid sulfur dioxide. Whereas the Raman spectrum of the crystalline solid (Figure 6) compares nicely with the computed frequencies of the s-isomer, as expected (see above), the solution spectrum clearly shows the u-isomer to be present.

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Supplementary Material Available: For **1**, tables of crystallographic details, anisotropic thermal parameters, atomic parameters (x, y, z and B_{iso}), and nonessential bond lengths and angles (6 pages). Ordering information is given on any current masthead page.