$[(SeCl)_2N][FeCl_4]$: Synthesis, Quantumchemical Calculations, Vibrational Data and Single-Crystal X-ray Structure

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The tetrachloroferrate salt of the $[(SeCl)_2N]^+$ cation, $[(SeCl)_2N][FeCl_4]$ (**1**), has been prepared and structurally characterized. The $[(SeCl)_2N]^+$ cation exists in a C_{2v} "u"-shaped geometry with the following structural parameters: d(Se–Cl) = 2.16 Å, *d*(SeN) = 1.70 Å, $\measuredangle$ (ClSeN) = 108° and $\measuredangle$ (SeNSe) = 147°. The harmonic vibrational frequencies for two isomers ("u" and "s" isomer) have been computed by ab initio methods and are compared with the experimental IR and Raman spectra.

Numerous ternary S–N–Cl cations have been prepared and structurally characterized[1]. In contrast, only two Se-containing analogous have been reported: $[(SeCl_2)_2N]^+$[2] and $[(SeCl)_2N]^+$[3,4]. Whereas the first one can be obtained in high yield (83%), the five-atom species $[(SeCl)_2N]^+$ was first prepared as its $[GaCl_4]^-$ salt by Dehnicke et al.[3] from neutral Se_2NCl_3 which is not commerically available, and yields of Se_2NCl_3 are far from being quantitative (about 57%). We recently described a convenient synthesis of $[(SeCl)_2N][SbCl_6]$ and established that the $[(SeCl)_2N]^+$ cation may exist either in an u-shaped form ($[GaCl_4]^-$ salt) or as an s-shaped isomer ($[SbCl_6]^-$ salt)[4].

The recent discoveries of such Se–N chlorides that are potential building blocks (as sources of the SeNSe unit) in selenium-nitrogen chemistry have facilitated the investigation of the reactivities of Se–N compounds in general[5]. Moreover, the construction of molecular conductors based on odd-electron Se–N species with strong intermolecular interactions in the solid state is a distinct possibility[6]. Since the synthesis of polymeric $(SeN)_x$ is still an interesting challenge, the preparation of new and easily accessible precursors (such as Se–N–Cl cations) is of great interest. In this paper we report on the preparation and characterization of $[(SeCl)_2N][FeCl_4]$ (**1**) which is readily available in one reaction step from $[SeCl_3][FeCl_4]$ and $N(SiMe_3)_3$ (80% yield).

Results and Discussion

The tetrachloroferrate salt **1** of the $[(SeCl)_2N]^+$ cation was prepared from $[SeCl_3][FeCl_4]$ and $N(SiMe_3)_3$ (Eq. 1, 2).

$$2\ SeCl_4 + 2\ FeCl_3 \xrightarrow{CCl_4,\ 2\ h,\ 25°C} \{2\ [SeCl_3][FeCl_4]\} \qquad (1)$$

$$2\ \{[SeCl_3][FeCl_4]\} + N(SiMe_3)_3 \xrightarrow{CCl_4,\ 2\ h,\ 25°C} \underset{\mathbf{1}}{[(SeCl)_2N][FeCl_4]}$$
$$+\ FeCl_3 + Cl_2 + 3\ Me_3SiCl \qquad (2)$$

The crude material of compound **1** was recrystallized from liquid sulfur dioxide yielding red needles (80%). Compound **1** was identified by elemental analyses and vibrational spectroscopy (IR, Raman) (see Experimental, also for MS data). The mass spectrum does not show any nitrogen-containing fragments. Moreover, from the fragmentation pattern there is no evidence for significant intermolecular interactions (no Se_n fragments with $n > 2$, no SeFe fragments).

Since two different structures of the $[(SeCl)_2N]^+$ cation have already been observed experimentally (u isomer, C_{2v}: $[GaCl_4]^-$ salt; s isomer, C_s: $[SbCl_6]^-$ salt)[4] we computed the harmonic vibrational frequencies for these two species ab initio {MP2/6-31+G*; effective core potentials for Se, (5s5p)/[3s3p]-DZ+P (extended by a set of 5d functions, d_{exp} = 0.338) and Cl, (5s5p)/[3s3p1d]-DZ+P}. We have checked the quality of such calculations for related molecules and ions and the used basis sets (with pseudopotentials) have proved to be very suitable[4,7]. Moreover, although harmonic ab-initio computed vibration frequencies are usually too large compared to experiment, it has been established that for these type molecules the applied pseudopotentials predict the experimental (anharmonic) frequencies remarkably well[4,7]. Table 1 summarizes the computed frequencies for the u and the s isomer of the $[(SeCl)_2N]^+$ cation and the observed (IR, Raman) data for the $[(SeCl)_2N]^+$ cation in **1**.

The most significant differences in the calculated vibrational frequencies of isolated u- and s-shaped

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Table 1. Computed (MP2) harmonic vibrational frequencies and observed IR and Raman frequencies (cm^{-1}) for the $[(SeCl)_2N]^+$ cation (experimental data for the $[FeCl_4]^-$ salt **1**); n.o. = not observed

IR[a]	Raman[b]	MP2[c], s isomer	MP2[c], u isomer	Assignment
933 s	n.o.	878 vs	944 vs	ν_{as}SeNSe
432 vs	434 (2)	565 m	446 vs	ν_sSeNSe
428 s (?)	397 (10)	442 m	424 m	ν_sSeCl
n.o.	381 (1)	416 m	409 m	ν_{as}SeCl
n.o.	272 (1)	273 vw	287 w	γSeNCl

[a] KBr, 25°C. – [b] 647.09 nm, 20 mW, −50°C. – [c] MP2/6-31+G*, effective core potentials for Se: (5s5p)/[3s3p]-DZ+P (extended by a set of 5 d functions, d_{exp} = 0.338) and for Cl: (5s5p)/[3s3p1d]-DZ+P).

$[(SeCl)_2N]^+$ cations are the symmetric and asymmetric SeNSe stretching modes of the cation: ν_{as}SeNSe, u 944, s 878 cm^{-1} and ν_sSeNSe, u 446, s 565 cm^{-1}. Since the $[(SeCl)_2N]^+$ cation in **1** shows these vibrations at 933 and 433 ± 1 cm^{-1}, respectively, the experimental spectra clearly show the u isomer to be present (scaling factor 0.979).

The single-crystal X-ray structure determination of **1** confirmed the above conclusions. The $[(SeCl)_2N^+$ cation in **1** has an u-shaped structure of C_{2v} symmetry (Figures 1 and 2) that closely resembles that of the same cation in the $[GaCl_4]^-$ salt[3]. As one can see from the torsion angles (Figure 1) the $[(SeCl)_2N]^+$ cation in **1** is virtually planar.

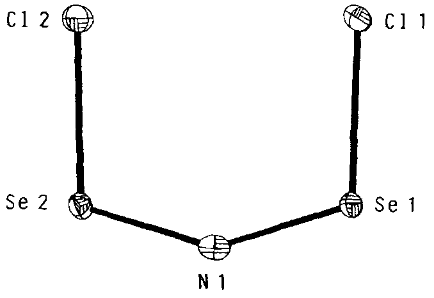

Figure 1. ORTEP presentation of the $[(SeCl)_2N]^+$ cation in $[(SeCl)_2N]$-$[FeCl_4]$ (**1**)[8]. Selected interatomic distances [Å] and bond angles [°]: Se(1)–Cl(1) 2.154(3), Se(1)–N(1) 1.695(9), Se(2)–Cl(2) 2.157(2), Se(2)–N(1) 1.699(9), Fe(1)–Cl(11) 2.216(3), Fe(1)–Cl(12) 2.185(3), Fe(1)–Cl(13) 2.196(3), Fe(1)–Cl(14) 2.192(3); Cl(1)–Se(1)–N(1) 108.2(3), Cl(2)–Se(2)–N(1) 108.0(3), Se(1)–N(1)–Se(2) 146.9(5), Cl(11)–Fe(1)–Cl(12) 111.1(1), Cl(11)–Fe(1)–Cl(13) 107.2(1), Cl(11)–Fe(1)–Cl(14) 107.2(1), Cl(13)–Fe(1)–Cl(14) 110.7(1); Cl(1)–Se(1)–N(1)–Se(2) −5.4(2), Cl(2)–Se(2)–N(1)–Se(1) 3.5(2)

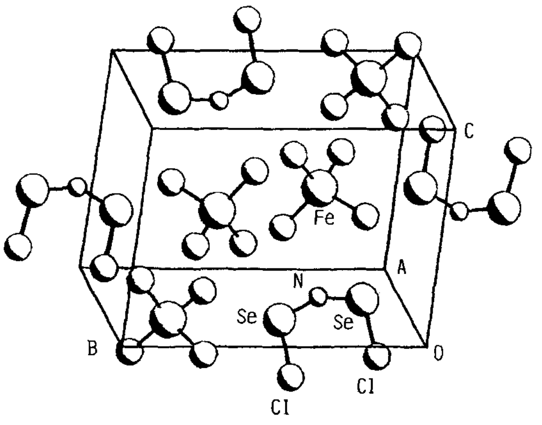

Figure 2. Packing diagram of **1** (PLUTO plot)[8]

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Experimental

Synthesis of **1**: $SeCl_4$ (1.00 g, 4.53 mmol) was allowed to react with $FeCl_3$ (0.74 g, 4.53 mmol) in 150 ml of CCl_4 for 2 h yielding white, unsoluble $[SeCl_3][FeCl_4]$. This suspension in CCl_4 was then treated with a solution of $N(SiMe_3)_3$ (0.53 g, 2.27 mmol) in 50 ml of CCl_4 and stirred for 2 h at room temp. The precipitated orange solid was isolated by filtration and recrystallized from liquid SO_2 affording $[(SeCl)_2N][FeCl_4]$ (**1**) as red needles. Yield: 0.80 g (80%). – Cl_6FeNSe_2 (440.5): calcd. N 3.17, Se 35.85; found N 3.00, Se 34.90. – MS (EI, 70 eV, 120°C), *m/z* (%): 254 (15) $[Fe_2Cl_4]^+$, 230 (12) $[Se_2Cl_2]^+$, 193 (13) $[Se_2Cl]^+$, 161 (14) $[FeCl_3]^+$, 150 (84) $[SeCl_2]^+$, 126 (15) $[FeCl_2]^+$, 115 (100) $[SeCl]^+$, 91 (11) $[FeCl]^+$. – IR (KBr): $\tilde{\nu}$ = 933 cm^{-1} s, 800 s, 481 s, 432 vs, 428 s, 418 w. – Raman (647.09 nm, 20 mW, −50°C): $\Delta\tilde{\nu}$ (Int.) = 434 cm^{-1} (2), 397 (10), 381 (1), 373 (1), 332 (4) 314 (1), 272 (1), 128 (5), 113 (4).

X-Ray Structure Determination of **1**: Empirical formula Cl_6FeNSe_2; mol. mass 440.49; crystal size 0.45 × 0.40 × 0.30 mm; space group: monoclinic, $P2_1/c$; $Z = 4$; Rigaku AFC 6S; routine DIFRAC program, NRCVAX interactive program system for structure analysis[9]; temperature −150°C; $a = 9.4396(5)$, $b = 11.5294(2)$, $c = 10.3378(6)$ Å; $\beta = 112.108(5)°$; $V = 1042.38(8)$ Å^3; $\varrho_{calcd.} = 2.807$ g cm^{-3}; $\mu = 9.85$ mm^{-1}; $F(000) = 815.62$; radiation Mo-K_α, $\lambda = 0.71073$ Å; $2\Theta_{max.} = 50°$; total no. of unique reflections 1831; no. of reflections with $I_{net.} \geqslant 2.5\sigma(I)$ 1292; the structure was refined by full-matrix least-squares analysis[9,10]; residuals: $R_F = 0.043$, $R_w = 0.051$, GoF = 1.49 (for significant reflections): $R_F = 0.079$, $R_w = 0.055$ (for all reflections); residual electron density: −1.080 (min.), +1.380 (max.) e Å^{-1}; empirical correction for absorption was made by using DIFABS[11]; min. and max. transmission factors are 0.0258 resp. 0.1052. – Further details of the crystal structure determination are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-58267, the names of the authors, and the journal citation.

Computational Methods: The computations were carried out applying the Gaussian 92 program package using the 6–31+G* basis set for nitrogen[12]. For chlorine (ECP10MWB)[13] and selenium (ECP28MWB)[14] quasi-relativistic pseudopotentials and the following basis sets were used: Se, (5s5p)/[3s3p]-DZ+P (extended by a set of 5 d functions, $d_{exp.}$ = 0.338)[15]; Cl, (5s5p)/[3s3p1d]-DZ+P[16,17].

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[1] J. D. Woollins, *Non-Metal Rings, Cages and Clusters*, Wiley, New York, **1988**, and references therein.

[2] M. Broschag, T. M. Klapötke, I. C. Tornieporth-Oetting, P. S. White, *J. Chem. Soc., Chem. Commun.* **1992**, 1390.

[3] R. Wollert, A. Höllwarth, G. Frenking, D. Fenske, H. Goesmann, K. Dehnicke, *Angew. Chem.* **1992**, *104*, 1216; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1251.

[4] M. Broschag, T. M. Klapötke, A. Schulz, P. S. White, *Inorg. Chem.* **1993**, *32*, 5734.

[5] K. B. Borisenko, M. Broschag, I. Hargittai, T. M. Klapötke, D. Schröder, A. Schulz, H. Schwarz, I. C. Tornieporth-Oetting, P. S. White, *J. Chem. Soc., Dalton Trans.*, in press.

[6] T. Chivers, *Main Group Chem. News* **1993**, *1*, 6, and references therein.

[7] A. Schulz, P. Buzek, P. v. R. Schleyer, M. Broschag, I. C. Tornieporth-Oetting, T. M. Klapötke, P. S. White, submitted for publication in *Chem. Ber.*

[8] [8a] C. K. Johnson, *ORTEP – A Fortran Thermal Ellipsoid Plot Program*, Technical Report ORNL-5138, Oak Ridge, **1976**. – [8b] S. Motherwell, *PLUTO Plotting*, Univ. Chemical Lab, Cambridge, England, **1978**.

[9] E. J. Gabe, Y. Le Page, J.-P. Charland, F. L. Lee, P. S. White, *J. Appl. Crystallogr.* **1989**, *22*, 384.

[10] Scattering factors: *International Tables for X-ray Crystallography*, vol. IV, Kynoch, Birmingham, England, **1974**.

[11] E. J. Gabe, P. S. White, to be published.

[12] M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, K. Andres, K. Raghavachari, J. S. Binkley, C. Gonzales, R. L. Martin, D. J. Fox, D. J. De Frees, J. Baker, J. J. P. Stewart, J. A. Pople, *Gaussian 92; Revision B*, Gaussian Inc., Pittsburgh, PA, **1992**.

[13] M. Kaupp, P. v. R. Schleyer, H. Stoff, H. Preuss, *J. Am. Chem. Soc.* **1991**, *113*, 6012.

[14] A. Bergner, M. Dolg, W. Kuechle, H. Stoll, H. Preuß, *Molec. Phys.* **1993**, *80*, 1431.

[15] J. Andzelm, L. Klobukowski, L. Radzip-Andzelm, Y. Sakai, H. Tatewaki in *Gaussian Basis Sets for Molecular Calculations* (Ed.: S. Huzinaga), Elsevier, New York, **1984**.

[16] M. Dolg, PhD Thesis, Universität Stuttgart, **1989**.

[17] W J. Hehre, L. Radom, P. v. R. Schleyer, J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, **1986**.

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