A New Fluorinated Dithiaselenatelluratetrazocinium Cation: Synthesis, Properties and Structure

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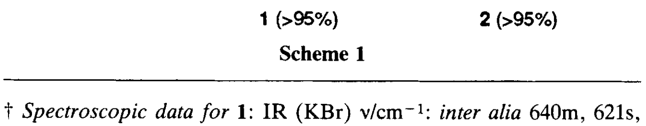
The first fluorinated cationic eight-membered chalcogen–nitrogen ring system, containing Te and Se, $[\mathrm{F\overline{TeNSNSeNSN}}]^+[\mathrm{TeF_5}]^-$ has been prepared by reacting $\mathrm{Se(NSO)_2}$ with $\mathrm{TeF_4}$; its molecular structure has been determined by X-ray crystallography (as a byproduct $\mathrm{[Se_2N_2S]_2[TeF_5]_2}$ was isolated).

Sulfur nitrogen heterocyclic chemistry has been enriched by substituting sulfur by selenium[1–6] and most recently also by tellurium[7–12] providing interesting structures with Se–N and Te–N moieties. Precursors in this type of chemistry are $\mathrm{Te(NSO)_2}$,[13] $\mathrm{Te[N(SiMe_3)_2]_2}$,[14] and $\mathrm{Se(NSO)_2}$.[1] Since the reaction between $\mathrm{Se(NSO)_2}$ and $\mathrm{TeCl_4}$ in $\mathrm{CH_2Cl_2}$ at 60 °C (28 d) yielded $\mathrm{Cl_2\overline{TeNSNSe}}$, $\mathrm{[\overline{SeNSNSe}]_2[TeCl_5]_2}$ and $\mathrm{Cl_6Te_2N_2S}$, it was interesting to consider the reaction between $\mathrm{Se(NSO)_2}$ and $\mathrm{TeF_4}$.

We report here the synthesis of 7-fluoro-$1\lambda^4\delta^2$,$5\lambda^4\delta^2$,3,$7\lambda^3$,2,4,6,8-dithiaselenatelluratetrazoicinium pentafluorotellurate **1**, the first fluorinated cationic eight-membered $\mathrm{\overline{TeNSNSeNSN}}$ species and bis(1,3,4,2,5-thiadiselenadiazolium) bis(pentafluorotellurate) **2**, a new derivative of the well known $\mathrm{[\overline{SeNSNSe}]_2}^{2+}$ cation.[1] Both compounds were obtained as crystalline products by the reaction of equimolar amounts of $\mathrm{Se(NSO)_2}$ and $\mathrm{TeF_4}$ (2.01 mmol) in $\mathrm{CH_2Cl_2}$ (10 cm^3) after a period of 7 d and heating up to 60 °C (Scheme 1). The crystals formed were washed several times with $\mathrm{CH_2Cl_2}$, dried *in vacuo* and separated mechanically with exclusion of moisture in a glove box fitted with a polarisation microscope yielding pure **1** (0.63 mmol) and **2** (0.31 mmol). Both substances are extremely air-sensitive and insoluble in $\mathrm{CH_2Cl_2}$ as well as in $\mathrm{SO_2}$. They do not explode on mechanical shock or heating and melt under decomposition at 145 °C **1**, 173–180 °C **2**, respectively. The results of a vibrational spectroscopic study of **1** are in good agreement with the proposed eight-membered ring structure, showing several bands which are tentatively assigned to N=S=N stretching vibrations (1138vs, 1090m, 1007w, 980m and 945s cm^{-1}).† Further frequencies belong to SeN (621 and 600 cm^{-1}), TeN (552 and 540 cm^{-1}) and TeF (640, 520, 455 and 430 cm^{-1}) vibrations.

Vibrational spectroscopical investigation of **2**‡ provides a spectrum which corresponds very well to the well-known $\mathrm{[\overline{SeNSNSe}]_2}^{2+}$ spectra.[1]

A crystal of **1** was examined by X-ray crystallography and its structure was elucidated to be an eight-membered ring with one fluorine atom attached to the tellurium atom which probably carries most of the positive charge and a $\mathrm{TeF_5}^-$ anion



1 (>95%) **2** (>95%)

Scheme 1

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† *Spectroscopic data for* **1**: IR (KBr) ν/cm^{-1}: *inter alia* 640m, 621s, 600vs, 552s, 540vs, 520vs, 455s, 430vs. MS (140 °C, main fragments): $\mathrm{TeSeS_2N_3}^+$, $\mathrm{FTeSeN_2S}^+$, $\mathrm{TeSeN_2S}^+$, $\mathrm{FTeS_2N_2}^+$, TeSeN^+, TeSe^+, FTeSN^+, $\mathrm{TeF_3}^+$, TeSN^+, $\mathrm{TeF_2}^+$, TeS^+, TeF^+, Te^+, SeSN^+, SeN^+, $\mathrm{S_2N_2}^+$, Se^+, $\mathrm{S_2}^+$, SN^+, S^+. Elemental analyses for N and S are in good agreement with calculated data.

‡ *Spectroscopic data of* **2**: IR (KBr) ν/cm^{-1}: 1001m, 949s, 656m, 633s, 617vs, 538s, 492s. MS (120 °C, main fragments): $\mathrm{Se_2N_2S}^+$, $\mathrm{TeF_4}^+$, $\mathrm{TeF_3}^+$, $\mathrm{Se_2N}^+$, $\mathrm{TeF_2}^+$, $\mathrm{Se_2}^+$, TeF^+, Te^+, SeSN^+, SeN^+, Se^+, SNF^+, SN^+, S^+. Satisfactory elemental analysis for N and S were obtained.

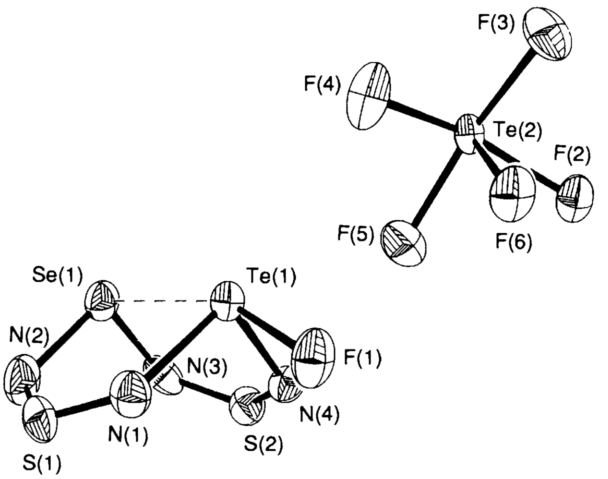

Fig. 1 Structure of $[\mathrm{F}\overline{\mathrm{TeNSNSeNSN}}]^+[\mathrm{TeF_5}]^-$. Bond distances (Å) and angles (°): Te(1)–Se(1) 2.902(2), Te(1)–F(1) 1.926(8), Te(1)–N(1) 2.041(13), Te(1)–N(4) 2.032(12), Te(2)–F(2) 2.008(8), Te(2)–F(3) 1.995(9), Te(2)–F(4) 1.960(9), Te(2)–F(5) 1.953(9), Te(2)–F(6) 1.897(8), Se(1)–N(2) 1.866(14), Se(1)–N(3) 1.891(14), S(1)–N(1) 1.527(13), S(1)–N(2) 1.561(15), S(2)–N(3) 1.560(14), S(2)–N(4) 1.545(13); Se(1)–Te(1)–F(1) 155.9(3), Se(1)–Te(1)–N(1) 80.1(4), F(1)–Te(1)–N(1) 82.8(5), Se(1)–Te(1)–N(4) 81.2(3), F(1)–Te(1)–N(4) 84.1(4), N(1)–Te(1)–N(4) 97.0(5), F(2)–Te(2)–F(3) 91.9(4), F(2)–Te(2)–F(4) 157.1(4), F(3)–Te(2)–F(4) 87.2(4), F(2)–Te(2)–F(5) 87.5(4), F(3)–Te(2)–F(5) 159.3(4), F(4)–Te(2)–F(5) 85.4(4), F(2)–Te(2)–F(6) 77.0(4), F(3)–Te(2)–F(6) 78.9(4), F(4)–Te(2)–F(6) 80.4(4), F(5)–Te(2)–F(6) 80.9(4), Te(1)–Se(1)–N(2) 94.8(4), Te(1)–Se(1)–N(3) 94.3(4), N(2)–Se(1)–N(3) 96.8(6), N(1)–S(1)–N(2) 122.9(8), N(3)–S(2)–N(4) 123.5(7), Te(1)–N(1)–S(1) 125.5(8), Se(1)–N(2)–S(1) 116.6(8), Se(1)–N(3)–S(2) 116.4(8), Te(1)–N(4)–S(2) 124.6(7).

displaying a distorted square pyramidal environment as illustrated in Fig. 1.§ The structure shows a short Te–Se distance (2.902 Å) but no significant secondary S–S bonding (3.793 Å) and so represents a partially opened three-dimensional cage, as it is found in $S_4N_4Cl_2$.[15] The Te–N (2.041 Å and 2.032 Å) as well as the Se–N bond distances (1.866 Å and 1.891 Å) correspond to single bond distances as is expected for a non-delocalized, cationic ring-system. In the lattice the molecule is stabilized by strong Te···F (2.687 Å) and Se···F (2.729 Å) and weak S···F (2.952 Å) and Te(1)···Te(2) (4.185 Å) cation–anion interactions, which are smaller than the corresponding van der Waal's radii.[16,17]

For the first time it can be demonstrated that $\mathrm{Se(NSO)_2}$ formed with TeF_4 a stable eight-membered cage like ring. Such a species was postulated as an intermediate[1] before decomposing to the isolated stable five-ring moieties.

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References

1 A. Haas, J. Kasprowski, K. Angermund, P. Betz, C. Krüger, Y.-H. Tsay and S. Werner, *Chem. Ber.*, 1991, **124**, 1895.
2 E. G. Awere, J. Passmore, P. S. White and T. Klapötke, *J. Chem. Soc., Chem. Commun.*, 1989, 1415.
3 E. G. Awere, J. Passmore and P. S. White, *J. Chem. Soc., Dalton Trans.*, 1992, 1267.
4 R. Wollert, B. Neumüller and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1992, **616**, 191.
5 M. Broschag, T. M. Klapötke, I. C. Tornieporth-Oetting and P. S. White, *J. Chem. Soc., Chem. Commun.*, 1992, 1390.
6 J. Siivari, T. Chivers and R. Laitinen, *Angew. Chem.*, 1992, **104**, 1539; *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1518.
7 A. Haas and R. Pohl, *Eur. J. Solid State Inorg. Chem.*, 1992, **29**, 791.
8 H. W. Roesky, J. Münzenberg and M. Noltemeyer, *Angew. Chem.*, 1990, **102**, 73; *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 61.
9 J. Münzenberg, H. W. Roesky, S. Besser, R. Herbst-Irmer and G. M. Sheldrick, *Inorg. Chem.*, 1992, **31**, 2986.
10 A. Haas, J. Kasprowski and M. Pryka, *Chem. Ber.*, 1992, **125**, 789.
11 A. Haas, J. Kasprowski and M. Pryka, *Chem., Ber.*, 1992, **125**, 1537.
12 A. Haas, J. Kasprowski and M. Pryka, *J. Chem. Soc., Chem. Commun.*, 1992, 1144.
13 A. Haas and R. Pohl, *Chimia*, 1989, **43**, 261.
14 M. Björgvinsson, H. W. Roesky, F. Pauer, D. Stalke and G. M. Sheldrick, *Inorg. Chem.*, 1990, **29**, 5140.
15 Z. Zák, *Acta Crystallogr. Sect. B*, 1981, **37**, 23.
16 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, NY, 3rd edn., 1960, ch. 7.
17 S. C. Nyburg and C. H. Faerman, *Acta Crystallogr. Sect. B*, 1985, **41**, 274.

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§ *Crystal data for*: $F_6N_4S_2SeTe_2$. Yellow prism, 0.4 × 0.4 × 0.3 mm, orthorhombic, space group *Pbca*, $a = 7.3780(10)$, $b = 12.697(3)$, $c = 22.596(5)$ Å, $U = 2116.8(7)$ Å^3, $Z = 8$, $M = 568.3$, $D_c = 3.567$ Mg m^{-3}, absorption coefficient = 9.062 mm^{-1}, $F(000) = 2016$. Solution and refinement: Siemens SHELXTL PLUS (VMS), direct methods solution, full-matrix least-squares refinement, $\Sigma w(F_o - F_c)^2$, hydrogen atoms riding model, fixed isotropic U, $w^{-1} = \sigma^2(F) + 0.0001F^2$, 136 parameters refined, final R indices (obs. data) $R = 4.68\%$, $wR = 4.41\%$, R indices (all data) $R = 7.52\%$, $wR = 4.64\%$, goodness-of-fit = 1.84. Data collection: Siemens P4 diffractometer, Mo-Kα ($\lambda = 0.71073$ Å), 293 K, highly oriented graphite crystal monochromator, $2\theta = 3.0$ to 50.0°, ω scan type, scan range (ω) = 1.60°, $-8 \leqslant h \leqslant 0$, $-14 \leqslant k \leqslant 0$, $-25 \leqslant l \leqslant 0$, 2129 reflections collected, 1821 ($R_{int} = 1.94\%$) independent reflections, 1264 [$F > 4.0\sigma(F)$] observed reflections, semi-empirical absorption correction. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.