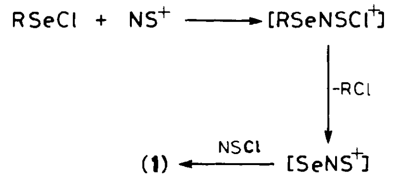
A Simple Synthesis of $[NS]^+[AlCl_4]^-$ and the Insertion Reaction with Alkylselenium Halides: *X*-Ray Structure of $[N_2S_2SeCl]^+[AlCl_4]^-$

Allen Apblett, Tristram Chivers,* and James F. Fait

Department of Chemistry, The University of Calgary, Calgary, Alberta, T2N 1N4, Canada

The reaction of $(NSCl)_3$ with aluminium trichloride at 50 °C without solvent, preferably with ultrasonic irradiation, produces $[NS]^+[AlCl_4]^-$ in good yields; the thiazyl salt reacts with alkylselenium halides to give $[N_2S_2SeCl]^+[AlCl_4]^-$, in which the cation is shown by *X*-ray crystallography to be a five-membered ring with chlorine attached to selenium.

As the simplest example of a triply bonded species the thiazyl cation, NS^+, is of central importance in sulphur–nitrogen chemistry. Although a salt of this cation was first reported almost 20 years ago,[1] the development of its chemistry has been sporadic due to the lack of an easy synthetic procedure. The methods available for the preparation of NS^+ salts include (i) the reaction of NSF[1—3] or $(NSF)_x$ (x = 3,4)[4,5] with BF_3, AsF_5, or SbF_5 and (ii) the treatment of $(NSCl)_3$ with silver(I) salts.[6,7] The latter method is suitable for the preparation of $[NS]^+[AsF_6]^-$,[7] but it requires the preparation (or purchase)



Scheme 1

of $AgAsF_6$ and the use of SO_2 as a solvent. The reaction of $(NSCl)_3$ with $AlCl_3$, $FeCl_3$, or $SbCl_5$ has been used frequently as a convenient *in situ* source of NS^+ salts of chloro-anions,[8—11] but definitive evidence for the formation of $[NS]^+[MCl_4]^-$ in these systems is lacking. We report here a simple procedure for the high yield synthesis of $[NS]^+[AlCl_4]^-$ and the unexpected formation of $[N_2S_2SeCl]^+[AlCl_4]^-$ from the reaction of NS^+ with alkylselenium chlorides.

A mixture of $(NSCl)_3$ (10 mmol) and freshly sublimed aluminium trichloride (30 mmol) was ground together under nitrogen and transferred to a Schlenk tube, which was immersed in an ultrasonic bath for 2 h at *ca.* 50 °C. Sublimation of the orange–yellow melt at 60 °C/0.1 Torr (1 Torr = 133.322 Pa) gave pale yellow crystals of $[NS]^+[AlCl_4]^-$ (21 mmol).† The S≡N stretching frequency (Nujol mull) is observed at 1405 cm^{-1} in the i.r. spectrum, *cf.* ν(NS) 1437 cm^{-1} for $[NS]^+[AsF_6]^-$.[1] The ^{14}N n.m.r. spectrum of $[NS]^+[AlCl_4]^-$ (in 1,2-$C_2H_4Cl_2$) shows a single resonance at 196 p.p.m. [ref. $MeNO_2$(l)] *cf.* $\delta(^{14}N)$ 202 p.p.m. for $[NS]^+[AsF_6]^-$ in SO_2.[12]

$$(NSCl)_3 + 3AlCl_3 \rightarrow 3[NS]^+[AlCl_4]^- \qquad (1)$$

If reaction (1) is carried out in 1,2-dichloroethane at 23 °C, the initial product is $[S_3N_3Cl_2]^+[AlCl_4]^-$ [$\delta(^{14}N)$ −118 and −291 p.p.m.] *cf.* formation of $S_3N_3Cl_2{}^+SbCl_6{}^-$ from $(NSCl)_3$ and $SbCl_5$.[4,5] When this solution is heated to 80 °C for 1 h the cations NS^+ and $N(SCl)_2{}^+$ {$\delta(^{14}N)$ 19 p.p.m., *cf.* 19 p.p.m. for $[N(SCl)_2]^+AsF_6{}^-$ in SO_2 [12]} are formed in a ratio of *ca.* 2 : 1. $[NS]^+[AlCl_4]^-$ can also obtained by heating the $(NSCl)_3$/$3AlCl_3$ mixture without solvent, but the yields are lower than when ultrasound is used due to an increase in the amount of $[N(SCl)_2]^+[AlCl_4]^-$ formed.

Several examples of the insertion of NS^+ into the polar S–Cl bond of SCl_2 [8—10] or sulphenyl chlorides[2] have been reported and the products obtained are thermally stable. We have found that the corresponding reaction with RSeCl (R = Et, Bu^n) gives products that decompose readily at 20 °C. For example, a solution of ethylselenium chloride (2.5 mmol) in CH_2Cl_2 (10 ml) was transferred dropwise *via* a stainless steel cannula into a solution of $[NS]^+[AlCl_4]^-$ (1.08 g, 5.0 mmol) in CH_2Cl_2 (10 ml) at −78 °C. An immediate reaction occurred to give a red solution and a yellow precipitate. The solution was allowed to warm slowly to 23 °C and the yellow precipitate was isolated by filtration and identified as (**1**), $[N_2S_2SeCl]^+[AlCl_4]^-$ (0.74 g, 2.0 mmol) by *X*-ray crystallography. The same product was also obtained from the reaction of Bu^{n}SeCl with $[NS]^+[AlCl_4]^-$. The related compound $N_2S_2SeCl_2$ has been prepared in 85% yield by the reaction of $(NSCl)_3$ with Se_2Cl_2 in SO_2.[13] The i.r. spectrum of (**1**) (Nujol mull) shows major bands at 917s, 722s, 635s, 508s, 488vs, 471vs, and 354vs cm^{-1}. The ^{14}N n.m.r. spectrum of (**1**) (in CH_2Cl_2) exhibits signals at −49 and −137 p.p.m.

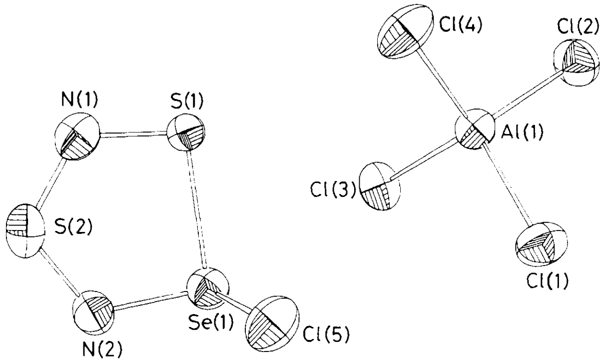


Figure 1. ORTEP plot (50% probability ellipsoids) for $[N_2S_2SeCl]^+[AlCl_4]^-$, (**1**). Selected bond lengths (Å) and angles (°): Se(1)–S(1) 2.293(1), S(1)–N(1) 1.630(4), N(1)–S(2) 1.545(4), S(2)–N(2) 1.578(4), N(2)–Se(1) 1.741(4), Se(1)–Cl(5) 2.191(1), Al(1)–Cl(1) 2.128(2), Al(1)–Cl(2) 2.131(2), Al(1)–Cl(3) 2.148(2), Al(1)–Cl(4) 2.108(2); S(1)–Se(1)–Cl(5) 101.46(5), S(1)–Se(1)–N(2) 92.7(1), Cl(5)–Se(1)–N(2) 103.7(1), Se(1)–S(1)–N(1) 96.1(1), N(1)–S(2)–N(2) 110.2(2), S(1)–N(1)–S(2) 121.6(2), Se(1)–N(2)–S(2) 118.6(2).

The structure of (**1**) was determined by *X*-ray crystallography.‡ The molecular geometry and atomic numbering scheme are shown in Figure 1. The SeS_2N_2 ring is nearly planar with the selenium atom 0.187(5) Å out of the plane formed by the S_2N_2 moiety. A comparison of the structure of (**1**) with that of $[N_2S_2SeCl]Cl$[13] will be given in the full account of this work.

In a separate experiment it was shown by ^{14}N n.m.r. spectroscopy that NS^+ is quickly consumed in the reaction with EtSeCl to give a thermally unstable intermediate [$\delta(^{14}N)$ −124 p.p.m.], which decomposes to (**1**) at 23 °C. This observation may be explained by the initial insertion of NS^+ into an Se–Cl bond to give $RSeNSCl^+$ followed by elimination of RCl to produce $SeNS^+$, which undergoes a [2 + 4]cycloaddition with NSCl followed by Cl^- migration to Se to yield (**1**) (Scheme 1), *cf.* the formation of $S_3N_2X^+AsF_6{}^-$ from $NS_2{}^+AsF_6{}^-$ and NSX (X = F[14], Cl[12]).

In support of the proposed *in situ* generation of the novel cation $SeNS^+$, we have shown by ^{14}N n.m.r. spectroscopy that the reaction of $[NS]^+[AlCl_4]^-$ with elemental selenium produces (**1**) as the major product with a small amount of $[NS_2]^+[AlCl_4]^-$ [$\delta(^{14}N)$ −87 p.p.m., $\Delta\nu_{1/2}$ 40 Hz, *cf.* −91 p.p.m. for $[NS_2]^+[AsF_6]^-$ in SO_2 [12]]. By contrast, the reaction of the thiazyl cation with elemental sulphur produces the corresponding $NS_2{}^+$ salts.[11,12]

The simple synthesis of $[NS]^+[AlCl_4]^-$ described here should facilitate investigations of the chemistry of the thiazyl cation.

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† Satisfactory analytical data for N, S, and Cl were obtained.

‡ *Crystal data*: $AlCl_5N_2S_2Se$ (**1**), M = 375.3, monoclinic, space group $P2_1/n$ (No. 14); at 298 K, a = 9.237(1), b = 10.685(2), c = 11.332(2) Å, β = 92.65(1)°, U = 1117 Å^3, Z = 4, μ(Mo-K_α) = 48.14 cm^{-1}, F(000) = 712, D_c = 2.23 g cm^{-3}. Intensity data were collected at 298 K on an Enraf–Nonius CAD-4F diffractometer operating in the ω-2θ mode and using Mo-K_α radiation (λ = 0.71069 Å, graphite monochromator). Total number of unique reflections 3229, of which 2817 had $I > 2.0\,\sigma(I)$. Crystal dimensions 0.54 × 0.53 × 0.68 mm. The structure was solved by symbolic addition and was refined by full-matrix least-squares techniques with anisotropic thermal parameters to R = 0.049 and R_w = 0.045.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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References

1 O. Glemser and W. Koch, *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 127.
2 R. Mews, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 691.
3 K. V. Miller, W. C. Emken, and L. C. Duncan, *J. Fluorine Chem.*, 1984, **26**, 125.
4 R. Mews, D. L. Wagner, and O. Glemser, *Z. Anorg. Allg. Chem.*, 1975, **412**, 148.
5 R. J. Gillespie, J. F. Sawyer, D. R. Slim, and J. D. Tyrer, *Inorg. Chem.*, 1982, **21**, 1296.
6 M. Herberhold and L. Haumaier, *Z. Naturforsch., B.*, 1980, **35**, 1277.
7 A. Apblett, A. J. Banister, D. Biron, A. G. Kendrick, J. Passmore, M. Schriver, and M. Stojanac, *Inorg. Chem.*, 1986, **25**, 4451.
8 O. Glemser and J. Wegener, *Inorg; Nucl. Chem. Lett.*, 1971, **7**, 622; O. Glemser, E. Kindler, B. Krebs, R. Mews, F.-M. Schnepel, and J. Wegener, *Z. Naturforsch., B.*, 1980, **35**, 657.
9 A. J. Banister and H. G. Clarke, *J. Chem. Soc. A*, 1972, 2661; *Inorg. Synth.*, 1977, **17**, 188.
10 G. G. Alange, A. J. Banister, and P. J. Dainty, *Inorg. Nucl. Chem. Lett.*, 1979, **15**, 175.
11 A. J. Banister and A. G. Kendrick, *J. Chem. Soc., Dalton Trans.*, 1987, 1565.
12 J. Passmore and M. Schriver, *Inorg. Chem.*, 1988, **27**, 2749.
13 R. J. Gillespie, J. P. Kent, and J. F. Sawyer, *Inorg. Chem.*, in press.
14 P. K. Padma and R. Mews, *Z. Naturforsch., B.*, 1987, **42**, 699.