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Preparation of $[NS][AlCl_4]$ and $[NS][CF_3SO_3]$ and Reactions of the Thiazyl Cation with Thiadiazoles and Organoselenium Halides: X-ray Crystal Structure of $[N_2S_2SeCl][AlCl_4]$

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The reaction of $(NSCl)_3$ with 3 mol of $AlCl_3$ at ca. 50 °C in the absence of a solvent provides a simple, high-yield synthesis of $[NS][AlCl_4]$. The treatment of $(NSCl)_3$ with 3 mol of $AgSO_3CF_3$ in 1,2-$C_2H_4Cl_2$ is a convenient in situ source of $[NS][SO_3CF_3]$. However, a solution of $[NS][AlCl_4]$ in boiling 1,2-$C_2H_4Cl_2$ produces $[(H_2N)HCCH(NH_2)][AlCl_4]_2$ after 24 h. The reactivity of thiazyl salts toward thiadiazoles, organoselenium halides, and chalcogens was monitored by ^{14}N NMR spectroscopy, and stable products were isolated and characterized. The reactions of 2,1,3- and 1,2,3-benzothiadiazole with NS^+X^- give either Lewis acid adducts ($X^- = AlCl_4^-, AsF_6^-$) and NSY (Y = Cl, F) or intensely colored charge-transfer complexes ($X^- = CF_3SO_3^-, AsF_6^-$) in which the NS^+ cation is attached to the heterocyclic ring on the basis of ^{13}C NMR data. By contrast, 3,5-dimethyl-1,2,4-thiadiazole reacts with $[NS][SO_3CF_3]$ to give a protonated adduct of the thiadiazole. The reaction of EtSeCl with $[NS][AlCl_4]$ yields $[N_2S_2SeCl][AlCl_4]$ via a thermally unstable intermediate. The same final product and a small amount of $[NS_2][AlCl_4]$ are formed in the reaction of $[NS][AlCl_4]$ with selenium. By contrast, the reaction of PhSeCl with $[NS][AlCl_4]$ produces a dark green charge-transfer complex. The structure of the $N_2S_2SeCl^+$ cation was shown by X-ray crystallography to be a five-membered ring with chlorine attached to selenium. The crystals of $[N_2S_2SeCl][AlCl_4]$ are monoclinic, space group $P2_1/n$, with $a = 9.237$ (1) Å, $b = 10.685$ (2) Å, $c = 11.332$ (2) Å, $\beta = 92.65$ (1)°, $V = 1117.2$ (2) Å^3, and $Z = 4$. The least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms converged at $R = 0.049$ and $R_w = 0.045$ for 2817 unique observed reflections. The Se atom is 0.187 (5) Å out of the plane formed by the S_2N_2 unit with d(Se–Cl) = 2.191 (1) Å and d(S–Se) = 2.293 (1) Å. The S–N bond lengths indicate a tendency toward localized π bonding in the NSN unit of the cation. Significant cation–anion interactions between one Cl atom of $AlCl_4^-$ and the Se and nearest S atom are observed.

Introduction

As the simplest example of a triply bonded species, the thiazyl cation, NS^+, is a fundamental species in sulfur–nitrogen (S–N) chemistry. The following approaches have been used for the synthesis of thiazyl salts: (a) the treatment of gaseous NSX monomer (X = F,[1,2] Cl[3]) with halide ion acceptors, (b) the reaction of $(NSF)_x$ (x = 3, 4) with BF_3, AsF_5, or Sb_5,[4] (c) the treatment of $(NSCl)_3$ with Lewis acids,[5-8] and (d) the reaction of $(NSCl)_3$ with silver(I) salts.[9,10] The last method is suitable for the high-yield synthesis of $[NS][AsF_6]$,[10] whereas method c has usually been used for the in situ generation of NS^+ salts of chloroanions.

The reactions of both isolated and in situ generated NS^+ have been investigated sporadically during the last 20 years. The most notable findings include insertion into the S–N bonds of S_4N_4 to give $S_5N_5^+$,[6,11,12] insertion into S–Cl[5,7,12] or Re–X (X = Cl, Br)[13] bonds, and the formation of charge-transfer complexes with arenes.[14] Recently, we described a simple synthesis of $[NS][AlCl_4]$ in the absence of solvent using method c.[15] This discovery and the realization that ^{14}N NMR spectroscopy is a powerful technique for monitoring reactions of NS^+[16] have facilitated a more extensive survey of the potential of NS^+ as a synthon in S–N chemistry. Here we describe the results of the reactions of thiazyl salts with thiadiazoles, organoselenium halides, and selenium. Our preliminary investigations indicated the need for a thiazyl salt with a noncoordinating anion for reactions with substrates containing Lewis base sites. Consequently, the silver(I) salt method was employed for the in situ generation of $[NS][SO_3CF_3]$.[17] The X-ray structure of $[N_2S_2SeCl][AlCl_4]$ was determined, and the structural details are compared with those of $[N_2S_2SeCl]Cl$.[18]

Experimental Section

Reagents and General Procedures. All experiments were performed under an atmosphere of dry nitrogen (99.99% purity). Solvents were dried by heating under reflux with the appropriate drying agent: methylene dichloride (P_4O_{10}), chloroform (P_4O_{10}), 1,2-dichloroethane (P_4O_{10}), $CFCl_3$ (P_4O_{10}), and SO_2 (molecular sieves). They were then distilled and stored in bottles fitted with a Teflon stopcock and septa-sealed T-joint. Solvents were transferred when required to the appropriate vessel either by syringe or under nitrogen by use of a stainless steel transfer needle. Reactions were performed in Schlenk tubes sealed with rubber septa, and all products were isolated and manipulated under an atmosphere of nitrogen in a Vacuum Atmospheres drybox.

The following reagents were prepared by published methods: $(NSCl)_3$,[19] 3,5-dimethyl-1,2,4-thiadiazole,[20] EtSeSeEt,[21] and $[NS][AsF_6]$.[10] The following commercial products were used without further purification: 2,1,3-benzothiadiazole (Aldrich), 1,2,3-benzothiadiazole (Fluka), $AgSO_3CF_3$ (Aldrich), $AgNO_3$ (Fisher), hexamethylbenzene (Fisher), *tert*-butyl chloride (Fisher), PhSeCl (Aldrich), selenium (Fisher), and AsF_5 (Ozark-Mahoning). $AlCl_3$ (Aldrich) was purified by sublimation at 80 °C/0.1 Torr.

Instrumentation. Infrared spectra were recorded as Nujol or Fluorolube mulls on KBr, CsI, or polyethylene plates by using a Nicolet DX-5 FTIR spectrometer (4000–400 cm^{-1}) or a Perkin-Elmer 457 grating infrared spectrometer. ^{14}N, ^{27}Al, and ^{77}Se NMR spectra were recorded on a Bruker AM-400 spectrometer, and chemical shifts are reported versus external nitromethane, $Al(NO)_3$(aq), and Me_2Se(ℓ), respectively. ^1H and ^{13}C NMR spectra were obtained on a Bruker ACE 200 spectrometer, and chemical shifts are reported relative to Me_4Si in $CDCl_3$. All NMR spectra were recorded at ca. 25 °C unless otherwise stated. Mass spectra were obtained by using a Kratos MS80 RFA instrument

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(1) Glemser, O.; Koch, W. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 127.
(2) Miller, K. V.; Emken, W. C.; Duncan, L. C. *J. Fluorine Chem.* **1984**, *26*, 125.
(3) Hey, R. G. Ph.D. Thesis, University of Durham, England, 1980.
(4) Mews, R.; Wagner, D. L.; Glemser, O. *Z. Anorg. Allg. Chem.* **1975**, *412*, 148.
(5) (a) Glemser, O.; Wegener, J. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 623. (b) Glemser, O.; Kindler, E.; Krebs, B.; Mews, R.; Schnepel, F. M.; Wegener, J. *Z. Naturforsch.* **1980**, *35B*, 657.
(6) Banister, A. J.; Clarke, H. G. *Inorg. Synth.* **1977**, *17*, 188.
(7) Alange, G. G.; Banister, A. J.; Dainty, P. J. *Inorg. Nucl. Chem. Lett.* **1979**, *15*, 175.
(8) Banister, A. J.; Kendrick, A. G. *J. Chem. Soc., Dalton Trans.* **1987**, 1565.
(9) Herberhold, M.; Haumaier, L. *Z. Naturforsch.* **1980**, *35B*, 1277.
(10) Apblett, A.; Banister, A. J.; Biron, D.; Kendrick, A. G.; Passmore, J.; Schriver, M.; Stojanac, M. *Inorg. Chem.* **1986**, *25*, 4451.
(11) Banister, A. J.; Clarke, H. G. *J. Chem. Soc., Dalton* Trans. **1972**, 2661.
(12) Mews, R. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 691.
(13) Hartmann, G.; Mews, R. *Z. Naturforsch.* **1985**, *40B*, 343.
(14) Brownstein, S.; Louie, B. *Can. J. Chem.* **1987**, *65*, 1361.
(15) For a preliminary communication, see: Apblett, A.; Chivers, T.; Fait, J. F. *J. Chem. Soc., Chem. Commun.* **1989**, 1596.
(16) The common practice of quoting $\nu_{1/2}$ values for ^{14}N NMR signals is followed; we note, however that line widths are highly dependent on factors such as temperature or solvent viscosity.
(17) Passmore, J.; Schriver, M. J. *Inorg. Chem.* **1988**, *27*, 2749.
(18) Gillespie, R. J.; Kent, J. P.; Sawyer, J. F. *Inorg. Chem., in press.*
(19) Jolly, W. L.; Maguire, K. D. *Inorg. Synth.* **1967**, *9*, 102.
(20) Kresze, G.; Maschke, A.; Albrecht, R.; Bederke, K.; Patzschke, H. P.; Smalla, H.; Trede, A. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 89.
(21) Shlyk, Y. N.; Bogolyubov, G. M.; Petrov, A. A. *Zh. Obshch. Khim.* **1968**, *38*, 1199.

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operating at 70 eV. Chemical analyses were performed by the Analytical Services Division of the Department of Chemistry, The University of Calgary, and by Canadian Microanalytical Service, New Westminster, BC, Canada. Melting points were obtained in sealed glass capillaries and are uncorrected.

Preparation of [NS][AlCl$_4$]. A mixture of (NSCl)$_3$ (2.44 g, 10 mmol) and freshly sublimed AlCl$_3$ (4.00 g, 30 mmol) was triturated and then transferred to a vacuum sublimation apparatus (4.5 × 15 cm). This vessel was immersed in an ultrasonic bath for 2 h at ca. 50 °C, and the reaction mixture became a molten orange-yellow semisolid. Sublimation of the melt so formed at 60 °C/0.1 Torr gave pale yellow crystals of [NS][AlCl$_4$] (4.58 g, 21 mmol). Anal. Calcd for AlCl$_4$NS: Cl, 66.00; N, 6.52; S, 14.92; Al, 12.56. Found: Cl, 66.26; N, 6.68; S, 14.65; Al, 12.41 (by difference). Sometimes a pale green or red color was observed in the sublimate. ^{14}N NMR spectrum in CH$_2$Cl$_2$ (δ, ppm; $\nu_{1/2}$, Hz): +196, 390[16] [lit. +202, 240 for [NS][AsF$_6$] in SO$_2$].[17] IR (Nujol, cm^{-1}): 1406 w [ν(NS)], 483 s [ν(AlCl$_4^-$)].

Preparation of [NS][CF$_3$SO$_3$]. A mixture of (NSCl)$_3$ (0.81 g, 3.3 mmol) and AgSO$_3$CF$_3$ (2.57 g, 10 mmol) was heated at reflux for 1 h in 1,2-dichloroethane (20 mL). The solution was then filtered to remove silver chloride (1.39 g, 9.7 mmol). The ^{14}N NMR spectrum of the filtrate indicated that NS$^+$, δ(^{14}N) +204 ppm, $\nu_{1/2}$ 250 Hz, was the only nitrogen-containing species in solution. Removal of the solvent under vacuum yielded a sticky red oil from which only a small amount of [NS][CF$_3$SO$_3$] (0.21 g, 1.1 mmol) could be obtained by sublimation.[12]

Reaction of [NS][AlCl$_4$] with 1,2-Dichloroethane. A mixture of (NSCl)$_3$ (1.62 g, 6.7 mmol) and AlCl$_3$ (2.66 g, 20 mmol) in 1,2-dichloroethane (5 mL) was heated at ca. 80 °C for 24 h. Pale yellow crystals of ethylenediiminium tetrachloroaluminate [(H$_2$N)HCCH(NH$_2$)][AlCl$_4$]$_2$ (2.41 g, 6.1 mmol) were obtained upon cooling the solution to −30 °C. Anal. Calcd for C$_2$H$_6$Al$_2$N$_2$Cl$_8$: C, 6.07; H, 1.53; N, 7.08. Found: C, 5.84; H, 1.76; N, 7.38. NMR spectra (δ, ppm): ^{1}H in 1:1 CH$_3$NO$_2$/CDCl$_3$ 10.95 (s, 4 H, NH$_2$), 5.34 (s, 2 H, CH); ^{13}C in 1:1 CH$_3$NO$_2$/CDCl$_3$ 168.9 (s); ^{14}N in 1:1 CH$_3$NO$_2$/CDCl$_3$ −190 (t), J_{NH} = 67 Hz. IR (Nujol, cm^{-1}): 3278 s, 3146 m, 1659 m, 1410 vs, 1018 m, 609 m, 481 vs.

Preparation of [Arene·NS][CF$_3$SO$_3$] Complexes. The arene·NS$^+$ complexes were prepared by the following general procedure. A mixture of (NSCl)$_3$ (0.42 g, 1.7 mmol) and AgSO$_3$CF$_3$ (1.30 g, 5.1 mmol) was triturated and placed in a 10 mm o.d. glass tube fitted with a Teflon-lined screw cap. Methylene dichloride (4 mL) was added to the mixture, and the tube was heated at 60 °C for 1.5 h. The solution of [NS][CF$_3$SO$_3$] so formed was cooled to 0 °C, and the arene (5.0 mmol) was added quickly by syringe. The resulting brightly colored solutions were shaken for 15 min, and then ^{14}N NMR spectra were obtained. ^{13}C NMR spectrum in CH$_2$Cl$_2$ for [hexamethylbenzene·NS][CF$_3$SO$_3$] (δ, ppm): 17.4, 147.4 [lit. δ(^{13}C) 17.1, 147.2 ppm for [hexamethylbenzene·NS][AsF$_6$] in CH$_2$Cl$_2$].[14]

Reaction of [NS][AlCl$_4$] with 2,1,3-Benzothiadiazole. 2,1,3-Benzothiadiazole (0.14 g, 1.0 mmol) was added to a solution of [NS][AlCl$_4$] (0.22 g, 1.0 mmol) in methylene dichloride (3 mL) in a 10 mm o.d. glass tube fitted with a Teflon-lined screw cap. An immediate reaction occurred to give an orange-brown solution. The ^{14}N NMR spectrum showed signals at +328 ppm attributed to NSCl [lit.[17] δ(^{14}N) +323 ppm in SO$_2$] and at −85 ppm due to 2,1,3-benzothiadiazole·AlCl$_3$. The latter assignment was confirmed by the observation of a resonance at −85 ppm for an authentic sample of the adduct prepared from 2,1,3-benzothiadiazole (0.14 g, 1.0 mmol) and AlCl$_3$ (0.13 g, 1.0 mmol) in methylene dichloride (3 mL).

Reaction of [NS][CF$_3$SO$_3$] with 2,1,3-Benzothiadiazole. 2,1,3-Benzothiadiazole (0.68 g, 5.0 mmol) was added to a solution of [NS][CF$_3$SO$_3$] (0.98 g, 5.0 mmol) in 1,2-dichloroethane (25 mL). A slow reaction occurred to give a bright green solution. After 24 h the solution was filtered to remove silver chloride (0.69 g, 4.8 mmol). The successive addition of 5-mL aliquots of chloroform, followed by cooling the solution to −30 °C, produced several crops of [2,1,3-benzothiadiazole·NS][CF$_3$SO$_3$] (1.26 g, 3.8 mmol) as a green-black solid. Anal. Calcd for C$_7$H$_4$F$_3$N$_3$O$_3$S$_3$: C, 25.38; H, 1.22; N, 12.68, S, 29.03. Found: C, 25.46; H, 1.27; N, 12.78; S, 28.78. IR (Nujol, cm^{-1}): 1607 m, 1553 s, 1502 m, 1409 m [ν(NS$^+$)], 1295 vs, 1286 vs, 1231 vs, 1215 s, 1169 s, 1160 s, 1027 vs, 930 m, 871 m, 811 m, 761 s, 636 vs, 581 s, 525 s, 514 s, 495 m, 411 m, 395 m. MS [m/e (%) ion]: 136 (60) C$_6$H$_4$N$_2$S$^+$, 108 (20) C$_6$H$_4$S$^+$, 90 (20) C$_6$H$_4$N$^+$, 76 (20) C$_6$H$_4^+$, 69 (55) ?, 64 (50) S$_2^+$, 46 (100) NS$^+$. ^{13}C and ^{14}N NMR data are given in Table I.

Reaction of [NS][AsF$_6$] with 2,1,3-Benzothiadiazole. A solution of [NS][AsF$_6$] (1.18 g, 5.0 mmol) in SO$_2$ (5 mL) was added to a solution of 2,1,3-benzothiadiazole (0.68 g, 5.0 mmol) in SO$_2$ (5 mL) in a two-bulb vessel. An immediate reaction occurred to give a bright green solution. The SO$_2$ was removed and a CFCl$_3$/SO$_2$ mixture (10:1, 10 mL) was added to the vessel by vacuum transfer. Several washings with this solvent mixture extracted a yellow solid identified as 2,1,3-benzothiadiazole·AsF$_5$ (0.79 g, 2.6 mmol) by comparison of the IR spectrum with that of an authentic sample prepared from 2,1,3-benzothiadiazole and AsF$_5$.[22] The green solid residue was tentatively identified as [2,1,3-benzothiadiazole·NS][AsF$_6$] (0.88 g, 2.4 mmol) by comparison of the IR and ^{13}C NMR data with those of [2,1,3-benzothiadiazole·NS][CF$_3$SO$_3$]. IR (Nujol, cm^{-1}): 1609 m, 1551 s, 1502 m, 1412 s [ν(NS$^+$)], 1294 vs, 1170 s, 930 m, 868 m, 811 m, 759 s, 700 vs (AsF$_6^-$), 580 s, 525 s, 514 s, 495 m, 411 m, 395 vs (AsF$_6^-$). ^{13}C NMR spectrum in CD$_3$NO$_2$ (δ, ppm): 150.6, 133.9, 119.8.

Table I. ^{13}C and ^{14}N NMR Chemical Shifts for Benzothiadiazole·NS$^+$ Charge-Transfer Complexes

	δ(^{13}C)[a]		δ(^{14}N)[b]	
heterocycle, L	L	L·NS$^+$	L	L·NS$^+$
hexamethylbenzene[c]	132.1	147.4[d]		−200[c]
2,1,3-benzothiadiazole[c]	154.4	150.9	−49	−57
	128.8	133.6		−68[e]
	121.1	120.3		
1,2,3-benzothiadiazole[f]	156.2	147.6	−45	−51
	138.8	146.9	−59	−113
	127.2	134.9		−135[e]
	124.9	134.0		
	121.7	123.0		
	117.3	119.0		

[a] Relative to Me$_4$Si. [b] Relative to MeNO$_2$(l). [c] Counterion is CF$_3$SO$_3^-$. [d] Literature[14] δ(^{13}C) 147.0, 147.2, and 147.3 ppm for [NS]$^+$[BF$_4$]$^-$, [NS]$^+$[AsF$_6$]$^-$, and [NS]$^+$[SbF$_6$]$^-$, respectively. [e] Assigned to NS$^+$. [f] Counterion is AsF$_6^-$.

Reaction of 1,2,3-Benzothiadiazole with [NS][AsF$_6$]. The reaction of 1,2,3-benzothiadiazole (0.68 g, 5 mmol) and [NS][AsF$_6$] was carried out by using the procedure described above for 2,1,3-benzothiadiazole. The products were colorless crystals of 1,2,3-benzothiadiazole·AsF$_5$ (0.49 g, 1.6 mmol), which were characterized by comparison of the IR spectrum with that of an authentic sample prepared from 1,2,3-benzothiadiazole and AsF$_5$,[22] and a dark purple solid tentatively identified as [1,2,3-benzothiadiazole·NS][AsF$_6$] (1.18 g, 3.2 mmol). Satisfactory elemental analysis could not be obtained for this product due to ready hydrolysis. IR (Nujol, cm^{-1}): 1592 m, 1550 s, 1455 vs, 1424 vs [ν(NS$^+$)], 1345 s, 1294 vs, 1222 s, 1166 s, 1141 m, 1121 m, 1077 m, 1012 s, 898 vs, 775 vs, 761 s, 730 vs, 699 vs (AsF$_6^-$), 598 s, 591 s, 510 m, 497 s, 427 s, 397 vs (AsF$_6^-$). ^{13}C and ^{14}N NMR data are given in Table I.

Reaction of 3,5-Dimethyl-1,2,4-thiadiazole with [NS][AlCl$_4$]. A solution of 3,5-dimethyl-1,2,4-thiadiazole (0.29 g, 2.5 mmol) in CH$_2$Cl$_2$ (1 mL) was added by syringe to a solution of [NS][AlCl$_4$] (0.54 g, 2.5 mmol) in methylene chloride (2 mL). An immediate reaction occurred to give a pale brown solution. The ^{14}N NMR spectrum of this solution showed signals at +328 ppm, $\nu_{1/2}$ 190 Hz,[16] assigned to NSCl [lit.[17] δ(^{14}N) +323 ppm, $\nu_{1/2}$ 60 Hz, for NSCl in SO$_2$] and at −89 ($\nu_{1/2}$ 1060) and −164 ppm ($\nu_{1/2}$ 725 Hz) attributed to 3,5-dimethyl-1,2,4-thiadiazole·AlCl$_3$ plus a minor unidentified product at −123 ppm. The identity of the AlCl$_3$ adduct was confirmed by the preparation of an authentic sample [δ(^{14}N) −89, −165 ppm] from 3,5-dimethyl-1,2,4-thiadiazole (0.29 g, 2.5 mmol) and AlCl$_3$ (0.33 g, 2.4 mmol) in methylene dichloride (3 mL).

Reaction of 3,5-Dimethyl-1,2,4-thiadiazole with [NS][CF$_3$SO$_3$]. 3,5-Dimethyl-1,2,4-thiadiazole (0.57 g, 5.0 mmol) was added to a stirred solution of [NS][CF$_3$SO$_3$] (0.98 g, 5.0 mmol) in methylene dichloride (10 mL). After 3 h a reddish black color had developed. After 24 h the ^{14}N NMR spectrum of the solution showed the complete absence of the signals for the reactants and the appearance of two new signals at −107 (very broad) and −170 ppm ($\nu_{1/2}$ 220 Hz). The solvent was removed under vacuum, and the black solid residue was extracted with chloroform to give a pale red solution from which colorless crystals of [3,5-dimethyl-1,2,4-thiadiazole·H][CF$_3$SO$_3$] (0.49 g, 1.9 mmol) were obtained. Anal. Calcd for C$_5$H$_7$F$_3$N$_2$O$_3$S$_2$: C, 22.73; H, 2.67; N, 10.60. Found: C, 22.79; H, 2.42; N, 10.91. IR (Nujol, cm^{-1}): 1625 s, 1597 vs, 1293 vs, 1238 vs, 1221 m, 1158 vs, 1029 s, 967 s, 813 s, 759 m, 732 s, 638 vs, 574 m, 533 m, 516 m. An authentic sample of [3,5-dimethyl-1,2,4-thiadiazole·H][CF$_3$SO$_3$] [δ(^{14}N) −106, −168 ppm] was prepared from the thiadiazole and HSO$_3$CF$_3$ in CH$_2$Cl$_2$ for comparison of spectroscopic data.

Reaction of PhSeCl with [NS][AlCl$_4$]. A solution of benzeneselenyl chloride (1.92 g, 10 mmol) in methylene dichloride (20 mL) was added dropwise to a stirred solution of [NS][AlCl$_4$] (2.15 g, 10 mmol) in

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[22] Apblett, A.; Chivers, T.; Richardson, J. F. *Can. J. Chem.* **1986**, *64*, 849.

Table II. Crystallographic Data for $[N_2S_2SeCl][AlCl_4]$

chem formula $AlCl_5N_2S_2Se$
$a = 9.237\ (1)$ Å
$b = 10.685\ (2)$ Å
$c = 11.332\ (2)$ Å
$\beta = 92.65\ (1)°$
$V = 1117.2\ (2)$ Å^3
$Z = 4$
fw 375.34
space group $P2_1/n$
$T = 23\ (2)$ °C
$\lambda = 0.71069$ Å
$\rho_{calcd} = 2.23$ g cm^{-3}
$\mu = 48.14$ cm^{-1}
$R = 0.049$
$R_w = 0.045$

methylene dichloride (20 mL). An immediate reaction occurred to give a dark green solution. Removal of the solvent under vacuum and recrystallization of the residue (3.68 g, 9.1 mmol) from $CHCl_3/CH_2Cl_2$ (1:1) gave $[PhSeCl{\cdot}NS][AlCl_4]$ as a dark green solid. Anal. Calcd for $C_6H_5AlCl_5NSSe$: C, 17.23; H, 1.24; N, 3.45. Found: C, 16.94; H, 1.33; N, 3.72. IR (Nujol, cm^{-1}): 1652 m, 1412 s [$\nu(NS^+)$], 1090 s, 971 m, 805 s, 571 m, 491 vs, br. NMR spectra in CH_2Cl_2 (δ, ppm): ^{14}N −137; ^{13}C 143.7, 140.8, 134.1, 132.6; ^{77}Se 1052.

Reaction of Ethylselenium Chloride with $[NS][AlCl_4]$. A solution of ethylselenium chloride [prepared from diethyl diselenide (0.54 g, 2.5 mmol) and SO_2Cl_2 (0.34 g, 2.5 mmol)] in methylene dichloride (10 mL) was transferred dropwise via a stainless steel cannula into a solution of $[NS][AlCl_4]$ (1.08 g, 5.0 mmol) in methylene dichloride (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 room temperature, and the precipitate was isolated by filtration and identified as $[N_2S_2SeCl][AlCl_4]$ (0.74 g, 2.0 mmol) by X-ray crystallography. IR (Nujol, cm^{-1}): 917 s, 722 s, 635 s, 508 s, 488 vs, 471 vs, 354 vs. NMR (δ, ppm): ^{14}N (in CH_2Cl_2) −49 ($\nu_{1/2}$ 500 Hz), −137 ($\nu_{1/2}$ 550 Hz); [lit.[18] ^{15}N NMR (δ, ppm) −51.7 (d, $^2J_{NN} = 5.6$ Hz), −137.8 (d, $^2J_{NN} = 5.6$ Hz)]; ^{77}Se (in CH_2Cl_2) 328. In a separate experiment this reaction was monitored by ^{14}N NMR spectroscopy and shown to proceed via a thermally unstable intermediate [$\delta(^{14}N)$ −124 ppm ($\nu_{1/2}$ 725 Hz)].

Reaction of $[NS][AlCl_4]$ with Selenium. Selenium (0.16 g, 2.0 g atom) was added to a solution of $[NS][AlCl_4]$ (0.43 g, 2.0 mmol) in methylene dichloride (10 mL) in a 10 mm o.d. glass tube, which was placed in an ultrasonic bath for 4 h. Some unreacted selenium was still evident, but the ^{14}N NMR spectrum of the reaction mixture showed that NS^+ had been completely consumed. The yellow precipitate was isolated by filtration and identified as $[N_2S_2SeCl][AlCl_4]$ (0.26 g, 0.70 mmol) by comparison of the IR spectrum with that of an authentic sample.

X-ray Structural Analysis. A suitable pale orange transparent block-shaped crystal (0.54 × 0.53 × 0.68 mm) was wedged in a Lindemann glass capillary, which was mounted on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters and their standard deviations were derived from the setting angles of 25 reflections in the range $10.23° < \theta < 16.63°$. Reduced cell calculations did not indicate any higher metric symmetry. Data were collected by using $\theta/2\theta$ scans with variable scan speeds from 0.7 to 6.7°/min. Crystal and instrumental instability were monitored through the measurement of 3 standard reflections every 1 h of X-ray exposure time; there was a small amount of crystal decomposition. The net intensities of the data were corrected for reflection width, scale variation, Lorentz, and polarization effects. Variance $\sigma^2(I)$ was calculated on the basis of counting statistics. Crystal data and experimental details of the structure determination are compiled in Table II.

The selenium was located in an E map with phases derived from symbolic addition.[23] The remaining atoms were located in difference maps after refining the scale and thermal parameters. All atoms were refined with anisotropic temperature factors. Convergence was reached at $R = 0.049$. The final values of the refined positional parameters are presented in Table III. Tables of thermal parameters, comprehensive lists of bond distances and angles, and tables of F_o, F_c, and $\sigma(F)$ are available as supplementary material for this paper. Neutral-atom scattering factors were used with anomalous dispersion corrections applied.[24] No corrections for absorption or extinction were made. All calculations were carried out on a Zenith 386 computer at the University of Calgary with the program package XTAL.[25]

Results and Discussion

Table III. Atom Coordinates for $[S_2N_2SeCl][AlCl_4]$

atom	x	y	z	10^3U_{eq}, Å^2
Se(1)	0.93750 (4)	0.78177 (4)	0.11075 (4)	39.8
S(1)	0.95898 (1)	0.75108 (10)	0.31104 (9)	35.5
Cl(5)	1.14805 (13)	0.86514 (13)	0.07608 (11)	56.4
S(2)	1.00820 (13)	0.53335 (11)	0.18613 (11)	47.4
N(1)	1.0045 (4)	0.6039 (4)	0.3050 (3)	46.2
N(2)	0.9618 (4)	0.6235 (4)	0.0808 (3)	44.2
Al(1)	1.02598 (12)	1.14157 (12)	0.31196 (10)	33.7
Cl(1)	1.14426 (12)	1.21343 (12)	0.17008 (9)	46.9
Cl(2)	0.92918 (13)	1.29382 (11)	0.40072 (10)	50.1
Cl(3)	0.85201 (11)	1.02633 (10)	0.24163 (10)	43.6
Cl(4)	1.16552 (12)	1.03578 (12)	0.42564 (11)	52.1

Preparation of $[NS][AlCl_4]$ and $[NS][CF_3SO_3]$. Previous detailed studies of the reaction of $(NSCl)_3$ with Lewis acids, e.g. $SbCl_5$, have shown that a variety of products are formed depending on the solvent.[4,26] The initial product is $[S_3N_3Cl_2][SbCl_6]$, which, in CH_2Cl_2 or SO_2, subsequently decomposes to $[S_5N_5][SbCl_6]$, $[S_4N_4][SbCl_6]_2$, $S_4N_4{\cdot}SbCl_5$, and other unidentified compounds.[26] In this work we found that the ^{14}N NMR spectrum of a solution of $(NSCl)_3$ plus 3 molar equiv of $AlCl_3$ in 1,2-dichloroethane at 25 °C shows a small resonance attributed to $[NS]^+[AlCl_4]^-$ [δ(^{14}N) 185 ppm; cf. 202 ppm for $[NS]^+[AsF_6]^-$][17] in addition to much stronger signals for $[S_3N_3Cl_2]^+[AlCl_4]^-$ at −118 ($\nu_{1/2}$ 675 Hz) and −291 ppm ($\nu_{1/2}$ 1300 Hz). When this solution was heated at 80 °C for 1 h, the latter cation was converted to NS^+ and $N(SCl)_2^+$ [$\delta(^{14}N)$ 19 ppm; cf. 19 ppm for $[N(SCl)_2][AsF_6]$ in SO_2[16]] in a ratio of ca. 2:1. It was difficult to completely remove the solvent from $[NS][AlCl_4]$, so the reaction was performed without solvent. A mixture of $(NSCl)_3$ and 3 molar equiv of $AlCl_3$ was subjected to ultrasound for 2 h to give a yellow-orange semisolid. The temperature of the mixture reached ca. 50 °C during this process, and $[NS][AlCl_4]$ was obtained as moisture-sensitive, yellow crystals in 71% yield by sublimation of the melt. The thiazyl salt can also be obtained by simply heating the $(NSCl)_3/AlCl_3$ mixture to ca. 60 °C, but the yields are lower than when ultrasound is used due to an increase in the amount of $N(SCl)_2^+$ that is formed.

$$(NSCl)_3 + 3AlCl_3 \xrightarrow[50\ °C]{)))} 3[NS][AlCl_4] \qquad (1)$$

Spectroscopic evidence indicates significant anion–cation contacts in $[NS][AlCl_4]$ both in the solid state and in solution. The $S{\equiv}N$ stretching frequency is observed at 1405 cm^{-1} in the IR spectrum of solid samples compared to a value of 1437 cm^{-1} for $[NS][AsF_6]$.[1] The ^{14}N chemical shift of $[NS][AlCl_4]$ in 1,2-$C_2H_4Cl_2$ occurs at 196 ppm compared to 202 ppm for $[NS]^+[AsF_6]^-$ in SO_2.[17] The shielding of the signal observed for $[NS][AlCl_4]$ *generated in solution* [$\delta(^{14}N)$ 185 ppm] may result from the presence of excess $AlCl_3$. The ^{27}Al NMR signal for $[NS][AlCl_4]$ in 1,2-$C_2H_4Cl_2$ is considerably broadened [$\delta(^{27}Al)$ 98 ppm, $\nu_{1/2}$ 435 Hz] compared to that observed for $Na[AlCl_4]$ in 1:1 CH_2Cl_2/CH_3NO_2 [$\delta(^{27}Al)$ 101 ppm, $\nu_{1/2}$ 25 Hz].

For reactions with substrates containing Lewis base sites it was desirable to have a thiazyl salt with a noncoordinating anion. For this reason we prepared $[NS][CF_3SO_3]$ by the silver(I) salt method. When $(NSCl)_3$ was heated with 3 molar equiv of $AgSO_3CF_3$ in 1,2-$C_2H_4Cl_2$ at 80 °C, $[NS][CF_3SO_3]$ was produced almost quantitatively, as indicated by the ^{14}N NMR spectrum of the solution [$\delta(^{14}N)$ 204 ppm]. This method provides a convenient in situ preparation of $[NS][CF_3SO_3]$. However, attempts to isolate pure $[NS][CF_3SO_3]$ by sublimation failed due to difficulties in removing the last traces of solvent. Furthermore, we found that NS^+ reacts with 1,2-$C_2H_4Cl_2$ on heating at 80 °C for 24 h to give ethylenediiminium tetrachloroaluminate, $[(NH_2)HCCH(NH)_2][AlCl_4]_2$, which was identified on the basis of elemental analyses and the following spectroscopic data. The ^1H-coupled ^{14}N NMR spectrum of this product showed a triplet at −190 ppm ($J_{NH} = 67$ Hz), indicating the presence of an NH_2 group. This assignment was confirmed by the observation of bands

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(23) Schenk, H.; Hall, S. R. SIMPEL, XTAL 2.4 User's Manual. Hall, S. R., Stewart, J. M., Eds; Universities of Western Australia and Maryland, 1988.

(24) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(25) Hall, R.; Stewart, J. M., Eds. XTAL 2.4 User's Manual. Universities of Western Australia and Maryland, 1988.

(26) Gillespie, R. J.; Sawyer, J. F.; Slim, D. R.; Tyrer, J. D. *Inorg. Chem.* **1982**, *21*, 1296.

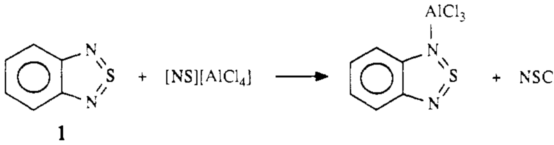
in the IR spectrum at 3278 and 3146 cm^{-1} attributed to $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$, respectively. The IR spectrum also exhibited bands at 1659 [ν(C=N)] and 481 cm^{-1} [$\nu_3(AlCl_4^-)$]. Finally, the ^{1}H and ^{13}C NMR spectra showed singlets at 5.34 and 168.9 ppm, respectively, for the CH groups, consistent with a symmetrical structure.

^{14}N NMR Spectra of Arene·NS$^+$ Charge-Transfer (CT) Complexes. Brownstein et al. have prepared CT complexes of various NS$^+$ salts with arenes.[14] These complexes were characterized by IR, ^{1}H and ^{13}C NMR, and UV–visible spectroscopy. A shift to lower frequency of ca. 40 cm^{-1} was noted for ν(N≡S), and the ^{1}H and ^{13}C NMR signals were dishielded relative to the uncomplexed arene. A weak, broad CT band was observed at 310–400 nm.

Several reactions of NS$^+$ that we have studied involve substrates with aromatic rings. These reactions were monitored by ^{14}N NMR spectroscopy, so the ^{14}N NMR spectra of some typical arene·NS$^+$ complexes were obtained for comparison. The salt [NS][CF$_3$SO$_3$] was chosen in order to obtain solutions that are reasonably stable at room temperature.[27] There is a dramatic upfield shift (300–400 ppm) of the ^{14}N NMR resonance of NS$^+$ upon complexation to an arene. The values for Ar·NS$^+$ are −103 ppm, $\nu_{1/2}$ = 935 Hz (Ar = benzene), −145 ppm, $\nu_{1/2}$ = 990 Hz (Ar = toluene), and −200 ppm, $\nu_{1/2}$ = 250 Hz (Ar = hexamethylbenzene, HMB) {cf. δ(^{14}N) +204 ppm, $\nu_{1/2}$ 250 Hz, for [NS][CF$_3$SO$_3$]}. No structural data are available for arene·NS$^+$ complexes,[14] but this large shift indicates that the nitrogen atom is held within the shielding region of the aromatic ring. The smaller differences in chemical shift among the arene·NS$^+$ complexes can be attributed to the increasing donor ability of the arenes along the series benzene < toluene < HMB.

The [arene·NS][CF$_3$SO$_3$] complexes, once formed, were found by ^{14}N NMR spectroscopy to be stable for several days at room temperature in CH$_2$Cl$_2$. However, the ^{14}N NMR spectra indicated that the CT complexes are not formed cleanly. Several minor products are also produced as a result of the reaction of NS$^+$ with alkyl groups[28] and/or electrophilic aromatic substitution.

Reactions of Thiazyl Salts with Thiadiazoles. The insertion reaction of NS$^+$ with S$_4$N$_4$ to give S$_5$N$_5^+$[6,11,12] is potentially capable of extension to other S–N heterocycles. In connection with our interest in eight-π-electron ring systems[29,30] we have attempted to prepare the unknown dithiatriazepinium cation, C$_2$N$_3$S$_2^+$,[31] by the reaction of NS$^+$ with thiadiazoles. 2,1,3-Benzothiadiazole (**1**) behaved as a Lewis base toward [NS][AlCl$_4$] to produce NSCl and the AlCl$_3$ adduct of **1**.



1

(2)

By contrast, the reaction of **1** with [NS][AsF$_6$] in SO$_2$ produced a bright green complex in addition to **1**·AsF$_5$. The ^{13}C NMR spectrum of this green complex showed only three signals indicative of C_2 symmetry, and the mass spectrum exhibited a fragmentation pattern similar to that of **1** with an additional strong peak at *m/e* 46 (NS$^+$). On the basis of ^{13}C and ^{14}N NMR spectra (Table I), the same green species is obtained from **1** and [NS][CF$_3$SO$_3$], and elemental analysis of this adduct is consistent with a stoichiometry of 1 mol of [NS][CF$_3$SO$_3$]/thiadiazole. The intense color of these adducts is indicative of a CT complex rather than an insertion product. There are two possible sites for complex formation between **1** and NS$^+$: the C$_6$ ring or the C$_2$N$_2$S ring. The small changes in the ^{13}C NMR chemical shifts of **1** upon complexation compared to that observed for HMB (Table I) and the fact that there is not a uniform deshielding of the ^{13}C resonances of **1** indicate that NS$^+$ is bound to the heterocyclic ring.[32]

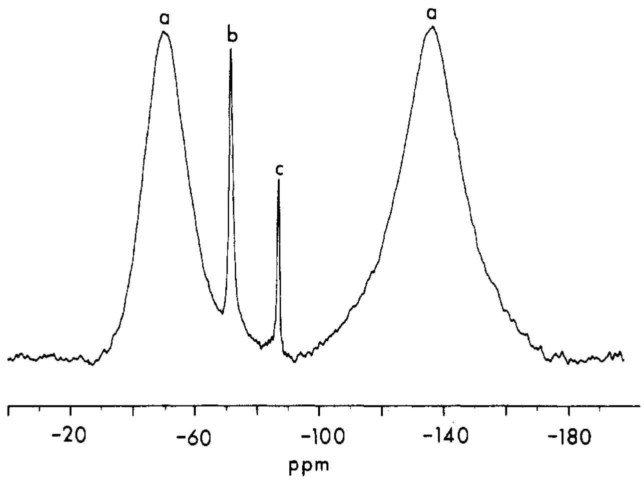
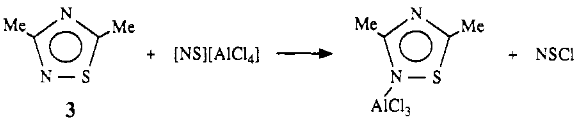


Figure 1. ^{14}N NMR spectrum of the reaction of [NS][AlCl$_4$] with selenium in CH$_2$Cl$_2$: (a) [N$_2$S$_2$SeCl][AlCl$_4$]; (b) dissolved N$_2$; (c) S$_2$N$^+$.

The reaction of 1,2,3-benzothiadiazole (**2**) with [NS][AsF$_6$] produced a mixture of the AsF$_5$ adduct of **2**[22] and a bright purple complex. A CT interaction with the heterocyclic ring is also likely for this complex, since the ^{13}C NMR chemical shifts (Table I) are not uniformly deshielded compared to those of **2**.

In order to avoid an arene·NS$^+$ interaction, we also investigated the reaction of thiazyl salts with 2,5-dimethyl-1,2,4-thiadiazole (**3**). Treatment of **3** with [NS][AlCl$_4$] resulted in the adduct formation shown in eq 3.



3

(3)

The addition of **3** to a solution of [NS][CF$_3$SO$_3$] in methylene dichloride produced a dark red solution from which an amorphous black product, presumably polymeric, and colorless crystals were isolated. The latter were identified as the protonated triflate salt of **3**. Thus, the insertion of NS$^+$ into the S–N bond of **3** does not occur. Instead the reaction appears to involve a methyl group, leading to the production of HSO$_3$CF$_3$ and subsequent protonation of **3**.[28]

Reactions of [NS][AlCl$_4$] with Organoselenium Chlorides. Previous reports of the insertion of NS$^+$ into the S–Cl bonds of SCl$_2$[5,7,12] or RSCl (R = CF$_3$, (CF$_3$)$_2$C=N)[12] prompted us to investigate the reactions of [NS][AlCl$_4$] with compounds containing Se–Cl bonds.

The reaction of ethylselenium chloride with [NS][AlCl$_4$] in methylene chloride produced a thermally unstable intermediate, possibly EtSeNSCl$^+$, which decomposed to give [N$_2$S$_2$SeCl][AlCl$_4$] (**4**) identified by X-ray crystallography (vide infra), in 79% yield.[33] The chloride salt of **4** has been prepared (in 85% yield) by the reaction of (NSCl)$_3$ with Se$_2$Cl$_2$ in SO$_2$,[18] and this

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(27) Brownstein and Louie report in ref 14 that solutions of [arene·NS][MF$_n$] (M = B, n = 4; M = As, Sb, n = 6) at ambient temperatures decompose via fluorination of the aromatic ring.

(28) We have also observed that thiazyl salts react vigorously with alkanes. [NS][AlCl$_4$] undergoes a rapid exothermic reaction with pentane at 0 °C to give a red solution and a white precipitate. The major product is an alkylammonium salt, [RNH$_3$][AlCl$_4$], δ(^{14}N) −355 ppm (q, J_{NH} = 55 Hz).

(29) Burford, N.; Chivers, T.; Cordes, A. W.; Laidlaw, W. G.; Noble, M.; Oakley, R. T.; Swepston, P. N. *J. Am. Chem. Soc.* **1982**, *104*, 1282.

(30) Chivers, T.; Edelmann, F.; Richardson, J. F.; Smith, N. R. M.; Treu, O., Jr.; Trsic, M. *Inorg. Chem.* **1986**, *25*, 2119.

(31) The corresponding anion C$_2$N$_3$S$_2^-$, a 10-π-electron system, has been proposed as a component of a CNS heterocycle base on the phenazulene system: Codding, P. W.; Koenig, H.; Oakley, R. T. *Can. J. Chem.* **1983**, *61*, 1562.

(32) The observation of only three ^{13}C NMR resonances for [2,1,3-benzothiadiazole·NS]$^+$ implies that these CT complexes are fluxional. A propeller-like rotation of NS$^+$ could account for this observation.

(33) On the basis of ^{14}N NMR spectroscopy, the same product is formed in the reactions of [NS][AlCl$_4$] with ^{n}BuSeCl or CF$_3$SeBr.

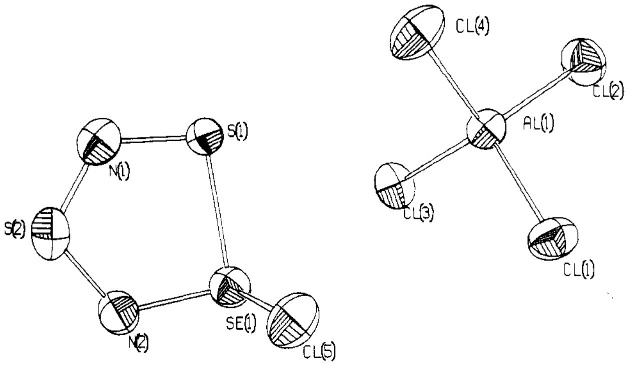

Figure 2. ORTEP plot (50% probability ellipsoids) for [N$_2$S$_2$SeCl][AlCl$_4$] (**4**).

Table IV. Dihedral Angles (deg) for [N$_2$S$_2$SeCl][AlCl$_4$]

Cl(5)-Se(1)-S(1)-N(1)	-97.7 (1)
N(2)-Se(1)-S(1)-N(1)	6.8 (2)
S(1)-Se(1)-N(2)-S(2)	-8.6 (2)
Cl(5)-Se(1)-N(2)-S(2)	93.9 (2)
Se(1)-S(1)-N(1)-S(2)	-4.3 (3)
N(2)-S(2)-N(1)-S(1)	-0.5 (3)
N(1)-S(2)-N(2)-Se(1)	7.5 (3)

method is certainly preferable for the synthesis of the N$_2$S$_2$SeCl$^+$ cation. However, the possible in situ generation of the hitherto unknown selenathianitronium ion, SeNS$^+$, (eqs 4 and 5) is an

$$\mathrm{RSeCl} + [\mathrm{NS}][\mathrm{AlCl_4}] \rightarrow [\mathrm{RSeNSCl}][\mathrm{AlCl_4}] \qquad (4)$$

$$[\mathrm{RSeNSCl}][\mathrm{AlCl_4}] \xrightarrow{-\mathrm{RCl}} \text{“}[\mathrm{SeNS}][\mathrm{AlCl_4}]\text{”} \xrightarrow{\mathrm{NSCl}} \mathbf{4} \qquad (5)$$

$$\mathrm{R} = \text{alkyl}$$

interesting feature of the route to **4** reported here. The subsequent reaction of this cation with NSCl, followed by chloride migration to Se, could account for the formation of **4**; cf. the formation of S$_3$N$_2$X$^+$AsF$_6^-$ from NS$_2^+$AsF$_6^-$ and NSX (X = F,[34] Cl[16]).

In an attempt to provide evidence for the proposed formation of SeNS$^+$, the reaction of [NS][AlCl$_4$] with selenium (1:1 molar ratio) in CH$_2$Cl$_2$ was monitored by ^{14}N NMR spectroscopy. The selenium was not completely consumed, and the major product was **4**, which was isolated in 35% yield based on selenium. The formation of a small amount of [NS$_2$][AlCl$_4$] [δ(^{14}N) 87 ppm, $\nu_{1/2}$ 30 Hz] was readily detected by ^{14}N NMR spectroscopy (Figure 1).[17] By contrast, the reaction of the thiazyl cation with elemental sulfur is known to produce the corresponding NS$_2^+$ salts in good yields.[8,17] In the present work it was shown by ^{14}N NMR spectroscopy that a solution of [NS][AlCl$_4$] in methylene dichloride is converted quantitatively to [NS$_2$][AlCl$_4$] upon addition of sulfur.[35]

In contrast to the reactions with alkylselenium chlorides, the treatment of [NS][AlCl$_4$] with benzeneselenenyl chloride in methylene dichloride produced a thermally stable dark green solid with the composition [PhSeCl·NS][AlCl$_4$]. The intense color of this material is indicative of a CT complex, and the δ(^{14}N) value of −123 ppm, $\nu_{1/2}$ = 2310 Hz, is in the observed range for an arene·NS$^+$ complex.

Crystal and Molecular Structures of [N$_2$S$_2$SeCl][AlCl$_4$] (4). An ORTEP drawing of **4** with the atomic numbering scheme is displayed in Figure 2. The cation is an almost planar five-membered ring with chlorine attached to selenium. The dihedral angles are given in Table IV; the selenium atom is 0.187 (5) Å out of the plane formed by the S$_2$N$_2$ moiety. The other structural parameters for the cation in **4** are compared in Table V with those for the same cation in [N$_2$S$_2$SeCl]Cl.[18] The structure of the cation in the latter salt has been discussed thoroughly, and in view of the similarity of the structural trends with those of the cation in **4**, further consideration is not warranted. As with [S$_3$N$_2$Cl]X salts (X = Cl,[36] FeCl$_4$,[37] SbCl$_6$[38]), several anion–cation contacts in **4** are significantly less than van der Waals distances. The primary interaction is between the Cl(3) atom of the anion and the S–Se bond of the cation {d[Se(1)–Cl(3)] = 3.124 (1), d[S(1)–Cl(3)] = 3.190 (2) Å; cf. 2.917 (2) and 3.056 (2) Å for the corresponding interactions in [N$_2$S$_2$SeCl]Cl}.[18] This contact results in an Al–Cl(3) bond length of 2.148 (2) Å compared to an average value of 2.129 (2) Å for d(Al–Cl) in the anion.

Table V. Bond Lengths (Å) and Bond Angles (deg) for [N$_2$S$_2$SeCl]X

Distances	X = AlCl$_4^-$	X = Cl^{-a}
Se(1)-S(1)	2.293 (1)	2.277 (2)
S(1)-N(1)	1.630 (4)	1.653 (7)
N(1)-S(2)	1.545 (4)	1.569 (8)
S(2)-N(2)	1.578 (4)	1.561 (6)
N(2)-Se(1)	1.741 (4)	1.788 (7)
Se(1)-Cl(5)	2.191 (1)	2.249 (3)
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)	

Angles	X = AlCl$_4^-$	X = Cl^{-a}
S(1)-Se(1)-Cl(5)	101.46 (5)	98.29 (9)
N(2)-Se(1)-Cl(5)	103.7 (1)	100.4 (2)
N(2)-Se(1)-S(1)	92.7 (1)	92.9 (2)
Se(1)-S(1)-N(1)	96.1 (1)	97.2 (2)
S(1)-N(1)-S(2)	121.6 (2)	120.4 (4)
N(1)-S(2)-N(2)	110.2 (2)	110.0 (4)
S(2)-N(2)-Se(1)	118.6 (2)	118.3 (4)
Cl(1)-Al(1)-Cl(2)	108.81 (7)	
Cl(1)-Al(1)-Cl(3)	109.13 (7)	
Cl(1)-Al(1)-Cl(4)	109.53 (7)	
Cl(2)-Al(1)-Cl(3)	106.84 (7)	
Cl(2)-Al(1)-Cl(4)	112.26 (7)	
Cl(3)-Al(1)-Cl(4)	110.19 (7)	

[a] Data taken from ref 18.

Conclusions

[NS][AlCl$_4$] is readily obtained from the reaction of (NSCl)$_3$ with AlCl$_3$ in the absence of a solvent, and spectroscopic investigations indicate significant anion–cation interactions in this compound. This reagent forms AlCl$_3$ adducts with substrates containing Lewis base sites, and the use of a thiazyl salt with a noncoordinating anion, e.g. in situ generated [NS][CF$_3$SO$_3$], is necessary to avoid this reaction pathway. The formation of CT complexes between NS$^+$ and arenes is accompanied by very strong shielding of the thiazyl moiety, as indicated by ^{14}N NMR chemical shifts, and NMR data indicate preferential attachment to the C$_6$ ring in the reactions of NS$^+$ with benzothiadiazoles. An X-ray structural determination of an [arene·NS]$^+$ CT complex would be of considerable interest, but the formation of such complexes is often accompanied by side reactions, e.g. with alkyl substituents. The reactivity of NS$^+$ toward alkanes or chlorohydrocarbons imposes limitations on studies of the interaction of NS$^+$ with organic or organometallic substrates.[39] In contrast to the simple

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(34) Padma, P. K.; Mews, R. *Z. Naturforsch.* **1987**, *42B*, 699.

(35) [NS$_2$][AlCl$_4$] has been prepared previously in unspecified yield by the reaction of S$_4$N$_4$ with AlCl$_3$ in CH$_2$Cl$_2$, and the X-ray structure was determined: Thewalt, U.; Berhalter, K.; Müller, P. *Acta Crystallogr., Sect. B* **1982**, *B38*, 1280.

(36) Zalkin, A.; Hopkins, T. E.; Templeton, D. H. *Inorg. Chem.* **1966**, *5*, 1767.

(37) Shearer, H. M. M.; Banister, A. J.; Halfpenny, J.; Whitehead, G. *Polyhedron* **1983**, *2*, 149.

(38) Isenberg, W.; Homsy, N. K.; Anhaus, J.; Roesky, H. W.; Sheldrick, G. M. *Z. Naturforsch.* **1983**, *38B*, 808.

(39) The reaction of CpCr(NO)$_2$Me with in situ generated [NS][PF$_6$] has recently been claimed to give [CpCr(NO)$_2${(NSH)CH$_2$}][PF$_6$] on the basis of spectroscopic evidence; Legzdins, P.; Richter-Addo, G. B.; Wassink, B.; Einstein, F. W. B.; Jones, R. H.; Willis, A. C. *J. Am. Chem. Soc.* **1989**, *111*, 2097.

synthesis of NS_2^+ from thiazyl salts and sulfur, the corresponding reaction with selenium produces the five-membered ring $N_2S_2SeCl^+$. This cation is also formed from NS^+ and alkylselenium chlorides. The instability of the Se=N double bond in selenodiimides, RN=Se=NR,[40] is well documented, and the current work indicates that this functionality is not stabilized in the $[Se{=}N{=}S]^+$ cation (as the $AlCl_4^-$ salt).

Acknowledgment. We are grateful to Professor R. J. Gillespie for a preprint of ref 18. The financial support of the NSERC (Canada) in the form of operating and infrastructure grants and of the Alberta Heritage Scholarship Fund, and Killam Foundation (The University of Calgary), and the NSERC for postgraduate awards to A.A. is also acknowledged. We also acknowledge helpful discussions with Professor R. Mews.

Supplementary Material Available: Listings of thermal parameters, contact distances (<3.6 Å), and crystallographic parameters and a figure showing a stereoscopic view of the packing in $[N_2S_2SeCl][AlCl_4]$ (4 pages); a table of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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[40] See, for example: (a) Sharpless, K. B.; Hori, T.; Truesdale, L. K.; Dietrich, C. O. *J. Am. Chem. Soc.* **1975**, *98*, 269. (b) Roesky, H. W.; Weber, K.-L.; Seseke, U.; Pinkert, W.; Noltemeyer, M.; Clegg, W.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1985**, *565*. (c) Thrasher, J. S.; Bauknight, C. W., Jr.; DesMarteau, D. D. *Inorg. Chem.* **1985**, *24*, 1598. (d) Fockenberg, F.; Haas, A. *Z. Naturforsch.* **1986**, *41B*, 413. (e) Herberhold, M.; Jellen, W. *Z. Naturforsch.* **1986**, *41B*, 144.

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Synthesis, X-ray Structures, and Spectroscopic and Magnetic Properties of a Series of Isomeric Binuclear Molybdenum(III) Complexes of General Formula $Mo_2Cl_6L_3$ (L = Thioether): Large Structural Influence of Bridging Ligands in Confacial Bioctahedral Complexes

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The syntheses, spectroscopic characterization, and X-ray crystal structures of two isomeric forms of $Mo_2Cl_6(THT)_3$ (THT = C_4H_8S, tetrahydrothiophene) are reported and compared with those of $(Me_2S)Cl_2Mo(\mu\text{-}Me_2S)(\mu\text{-}Cl)_2MoCl_2(Me_2S)$ and the anion $[(Me_2S)Cl_2Mo(\mu\text{-}Cl)_3MoCl_2(Me_2S)]^-$. The most notable feature of these structures, which have a confacial bioctahedral framework, is that those which have the core structure $Mo(\mu\text{-}Cl)_3Mo$ have relatively long Mo–Mo bond lengths and display antiferromagnetic behavior, while those with one μ-Cl replaced by a μ-thioether have much shorter Mo–Mo bonds, in the range expected for Mo≡Mo bonding, and are diamagnetic. By following the interconversion of two isomers of $Mo_2Cl_6(Me_2S)_3$ in $C_2D_2Cl_4$ solution at 70 °C by ^1H NMR spectroscopy, it was inferred that the process is intramolecular, likely involving ligand exchange between terminal and bridging sites. The complex $(THT)Cl_2Mo(\mu\text{-}THT)(\mu\text{-}Cl)_2MoCl_2(THT)$ (**4**) crystallizes with 1 mol of CH_2Cl_2 in the triclinic space group $P\bar{1}$ with $Z = 2$ in a cell of dimensions $a = 8.595$ (1) Å, $b = 11.165$ (4) Å, $c = 15.143$ (3) Å, $\alpha = 70.60$ (2)°, $\beta = 73.94$ (1)°, and $\gamma = 77.33$ (2)°. The least-squares refinement, with anisotropic thermal parameters for all non-hydrogen atoms, converged at $R = 0.071$ and $R_w = 0.050$ for 5583 unique observed reflections. The complex *meso*-$(THT)Cl_2Mo(\mu\text{-}Cl)_3MoCl(THT)_2$ (**5a**) crystallized in the monoclinic space group $P2_1/n$ with $Z = 4$ in a cell of dimensions $a = 10.522$ (2) Å, $b = 12.124$ (2) Å, $c = 18.262$ (3) Å, and $\beta = 98.91$ (1)°. The least-squares refinement, with anisotropic thermal parameters for all non-hydrogen atoms, converged at $R = 0.083$ and $R_w = 0.043$ for 7938 unique observed reflections.

Introduction

There is currently renewed interest in confacial bioctahedral molybdenum(III) and tungsten(III) chemistry, both from the point of view of structural variations[2-4] and potential catalytic properties.[5] Earlier, we reported[6] on the syntheses and structures of two such complexes, $(Me_2S)Cl_2Mo(\mu\text{-}Me_2S)(\mu\text{-}Cl)_2MoCl_2(Me_2S)$ (**1**) (C_{2v}) and $[PPh_4][(Me_2S)Cl_2Mo(\mu\text{-}Cl)_3MoCl_2(Me_2S)]$ (**2**) the latter complex being derived from the structural isomer of **1**, $[(Me_2S)Cl_2Mo(\mu\text{-}Cl)_3MoCl(Me_2S)_2]$ (**3**). This complex (**3**) was shown, on the basis of spectroscopic data, to exist as two stereoisomers, namely a C_s isomer, which we termed the meso isomer, **3a**, and an enantiomeric pair ((+)/(−)) of C_1 isomers, **3b** (Figure 1; L = Me_2S). The surprising feature of the structural analysis of these complexes was that by replacing the μ-Me_2S ligand in **1** by a μ-Cl to give the anion of **2**, the Mo–Mo bond length increased from 2.462 (2) to 2.746 (9) Å. An accompanying change in the magnetic properties, as detected from ^1H NMR measurements at different temperatures, suggested that whereas **1** was diamagnetic, the anion of **2** and its precursor **3** were antiferromagnetic.

We now report on the synthesis of the tetrahydrothiophene (THT) analogues of **1** (**4**) and **3a** (meso isomer, **5a**), their crystal structures, and solution behavior and provide a more detailed analysis of the magnetic properties of **2** and **3** and the interconversion of the various isomers in solution. Complete experimental details of the synthetic procedures for making **1**, **2**, and **3** and their spectroscopic characterization are provided, to supplement the preliminary report of their syntheses and structures.[6]

The facile synthesis of the C_{2v} isomer of $[(C_4H_8S)Cl_2Mo(\mu\text{-}C_4H_8S)(\mu\text{-}Cl)_2MoCl_2(C_4H_8S)]$ (**4**) will enable its chemistry to be compared with that of the analogous complexes of niobium and tantalum, which have been shown to be highly reactive toward alkynes.[7,8] Preliminary results suggest that this comparison will prove to be of considerable interest and potential catalytic significance.

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[2] Chisholm, M. H.; Eichorn, B. W.; Folting, K.; Huffman, J. C.; Ontiveros, C. D.; Streib, W. E.; Van Der Sluys, W. G. *Inorg. Chem.* **1987**, *26*, 3182.

[3] Chacon, S. T.; Chisholm, M. H.; Streib, W. E.; Van Der Sluys, W. G. *Inorg. Chem.* **1989**, *28*, 5.

[4] Cotton, F. A.; Luck, R. L. *Inorg. Chem.* **1989**, *28*, 182.

[5] Bott, S. G.; Clark, D. L.; Green, M. L. H.; Mountford, P. *J. Chem. Soc., Chem. Commun.* **1989**, 418.

[6] Boorman, P. M.; Moynihan, K. J.; Oakley, R. T. *J. Chem. Soc., Chem. Commun.* **1982**, 899.

[7] Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1980**, *19*, 2352.

[8] Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1980**, *19*, 2354.

0020-1669/90/1329-1648$02.50/0