Contribution from the Department of Chemistry,
University of Calgary, Calgary, Alberta, Canada T2N 1N4

Reaction of Dimethylcyanamide with Sulfur Dichloride: X-ray Crystal Structures of the *N*,*N*′-(Chlorosulfoniumylidene)bis(*N*^{1},*N*^{1}-dimethylchloroformamidine) Complexes $[(Me_2NC(Cl)N)_2SCl]^+X^-$ ($X^- = Cl^-, Cl_3^-$) and the Hydrolysis Product $[Me_2NC(Cl)NH_2]^+Cl^-{\cdot}H_2O$

T. CHIVERS,* J. F. RICHARDSON, and N. R. M. SMITH

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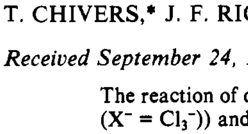
The reaction of dimethylcyanamide with SCl_2 in carbon tetrachloride containing NH_4Cl produces $[(Me_2NC(Cl)N)_2SCl]^+X^-$ (**4** ($X^- = Cl_3^-$)) and $[(Me_2NC(Cl)N)_3S]^+Cl_3^-$ (**8**). The former is hydrolyzed in wet acetone to $[Me_2NC(Cl)NH_2]^+Cl^-{\cdot}H_2O$ (**7**). In 1,2-dichloroethane, Me_2NCN and SCl_2 react to give **4** ($X^- = Cl^-$). The structures of **4** ($X^- = Cl^-, Cl_3^-$) and **7** have been determined by X-ray crystallography. Crystal data: $[(Me_2NC(Cl)N)_2SCl]^+Cl_3^-$, triclinic, space group $P\bar{1}$, $a = 10.275$ (4) Å, $b = 11.170$ (5) Å, $c = 6.767$ (2) Å, $\alpha = 104.98$ (3)°, $\beta = 95.41$ (3)°, $\gamma = 89.82$ (3)°, $V = 746.7$ (6) Å^3, $Z = 2$; $[(Me_2NC(Cl)N)_2SCl]^+Cl^-{\cdot}C_2H_4Cl_2$, triclinic, space group $P\bar{1}$, $a = 10.224$ (2) Å, $b = 12.158$ (3) Å, $c = 7.188$ (2) Å, $\alpha = 95.74$ (2)°, $\beta = 106.64$ (2)°, $\gamma = 93.97$ (2)°, $V = 847.3$ (4) Å^3, $Z = 2$; $[Me_2NC(Cl)NH_2]^+Cl^-{\cdot}H_2O$, monoclinic, space group $P2_1/c$, $a = 9.186$ (2) Å, $b = 5.5992$ (5) Å, $c = 14.745$ (3) Å, $\beta = 95.09$ (1)°, $V = 755.4$ (2) Å^3, $Z = 4$. The chlorosulfonium ion in **4** has pyramidal geometry at sulfur with bond angles in the range 97–104°, and d(S–Cl) = 2.128 (4) and 2.233 (1) Å for $X^- = Cl_3^-$ and Cl^-, respectively. The sum of the bond angles is ca. 360° for the carbon and terminal nitrogen atoms, and the C–N bond lengths are in the range 1.30–1.34 Å. The chemically equivalent halves of the chlorosulfonium ion are essentially planar, but twisted with respect to each other. The Cl_3^- ion in **4** ($X^- = Cl_3^-$) is almost linear (Cl–Cl–Cl = 177.5 (2)°) and unsymmetrical (d(Cl–Cl) = 2.249 (4) and 2.340 (4) Å). The cation in the hydrolysis product, **7**, is planar with trigonal geometry at the carbon and two nitrogen atoms and has C–N bond lengths of 1.282 (6) and 1.325 (5) Å. The reaction of **4** ($X^- = Cl^-$) with $SbCl_5$ produces the dicationic complex $[(Me_2NC(Cl)N)_2S]^{2+}[SbCl_6^-]_2$, **5** ($X^{2-} = 2SbCl_6^-$). The spectroscopic data (IR/Raman and ^{1}H and ^{13}C NMR) for **4**, **5**, **7**, and **8** are discussed in the light of the X-ray structural information for **4** and **7** and the vibrational spectra of $Ph_4As^+Cl_3^-$. The solid-state Raman spectra of salts containing the Cl_3^- ion show a strong band at ca. 270 cm^{-1} attributed to ν_1.

Introduction

Polymers containing the repeating unit –C(R)NSN–, **1**, are predicted to have useful conducting properties,[1] but attempts to prepare them from amidines and sulfur dichloride yielded eight-membered rings (**2**).[2] Sulfides of type **3** (see Figure 1) could be useful building blocks for such polymers, but the reaction of sulfur dichloride with organic nitriles (1:2 molar ratio) gives **3** only for R = R′SO_2 and with use of $Bu_4N^+Cl^-$ as a catalyst.[3,4] When R is an electron-releasing dialkylamino group, the products of this reaction are the sulfur(IV) derivatives $(RC(Cl)N)_2SCl_2$, the structures of which have been the subject of disagreement. Schindler has formulated them as chlorosulfonium salts (**4** (R = Et, $PhCH_2$, c-C_6H_{11}; $X^- = Cl^-$)) on the basis of analytical and spectroscopic (NMR, IR, and Raman) data.[5] By contrast, Russian workers have proposed that these compounds are sulfur diimides (R = Me, Et, *n*-Bu) that ionize in solution to the dicationic complexes **5** ($X^{2-} = 2Cl^-$).[6,7]



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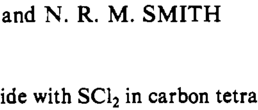

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We became interested in this problem in connection with attempts to prepare the five-membered ring **6** (R = NMe_2) as part of our investigations of the reactions of **2** (R = NMe_2) with halogens.[8] One route to **6** involves the reaction of RCN (R = Me, Ph, *p*-ClC_6H_4) with sulfur dichloride *at reflux in the presence of ammonium chloride*.[9] The monomer NSCl is thought to be generated as a reactive species in this system. For R = Me_2N, however, we obtained **4** and, surprisingly, the counteranion was Cl_3^-. We report here the X-ray structural determination of this salt, the corresponding chloride (**4** (R = Me_2N; $X^- = Cl^-$)), and the hydrolysis product (**7**). We have also isolated and characterized the trisubstituted sulfonium salt **8** (R = Me_2N) and the dicationic complex **5** (R = Me_2N; $X^{2-} = 2SbCl_6^-$).

Experimental Section

Reagents and General Procedures. $Ph_4As^+Cl_3^-$ was prepared by the slow addition of $Ph_4As^+Cl^-$ (ca. 1.0 g) to liquid chlorine (ca. 10 mL) at –78 °C. The reaction mixture was stirred at –78 °C for 1 h, and then excess chlorine was removed under vacuum to give $Ph_4As^+Cl_3^-$ as a pale cream-colored solid, which was stored at –20 °C. Dimethylcyanamide (Aldrich) and ammonium chloride (Fisher) were used as received. Sulfur dichloride (Fisher), antimony pentachloride (Baker), and tin tetrachloride (MCB) were distilled before use. All solvents were dried and distilled before use: CCl_4, CH_2Cl_2, CH_2ClCH_2Cl (P_2O_5); anhydrous diethyl ether (molecular sieves 4A). All reactions and the manipulation of moisture-sensitive products were carried out under an atmosphere of dry nitrogen (99.99% purity).

Infrared spectra were recorded as Nujol mulls (CsI windows) on a Perkin-Elmer 467 grating spectrophotometer (4000–250 cm^{-1}) or a Nicolet 7000 FTIR spectrometer (300–80 cm^{-1}). UV–visible spectra were measured by use of a Cary 219 spectrophotometer. Raman spectra were obtained on solid samples in glass capillaries and on ca. 10^{-2} M solutions in 3-mL cells by using a Jarrell-Ash Model 25-100 double monochromator calibrated with carbon tetrachloride. A Coherent Radiation CR3 argon ion laser was used to produce an exciting line at 514 nm. ^{1}H and ^{13}C NMR spectra were recorded with use of a Varian XL-200 spectrometer. Chemical shifts are reported in ppm downfield from Me_4Si. Mass spectra were obtained with a Varian CH-5 instrument operating at 70 eV. Chemical analyses were performed by the Analytical Services of the Department of Chemistry, University of Calgary, and by MHW Laboratories, Phoenix, AZ.

Reaction between Me_2NCN and SCl_2 with Ammonium Chloride. (a) Preparation of $[(Me_2NC(Cl)N)_2SCl]^+Cl_3^-$ (4 (R = Me_2N; $X^- = Cl_3^-$)). Dimethylcyanamide (10 mL, 0.12 mol) was added dropwise, with vigorous stirring, to an ice-cooled solution of sulfur dichloride (23 mL, 0.37

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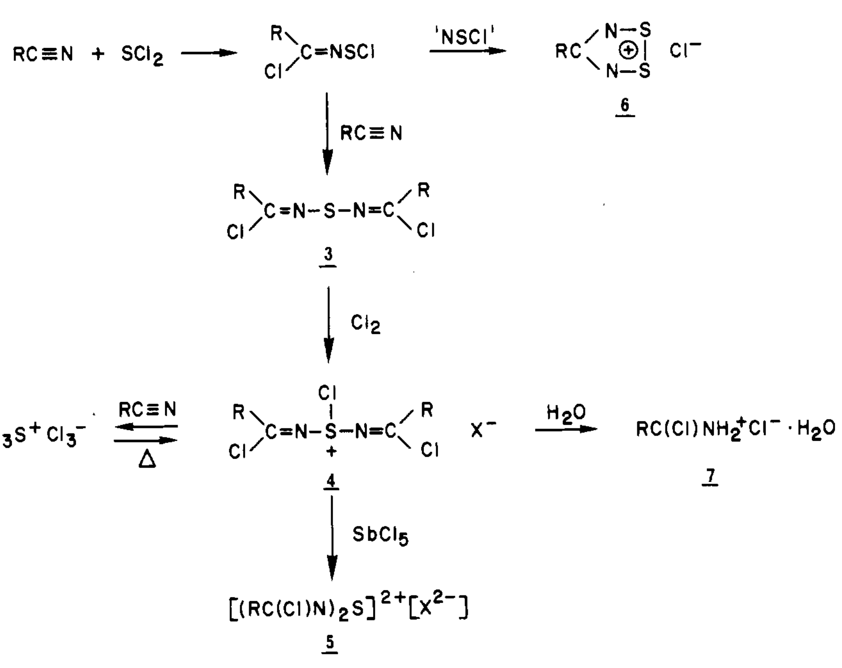

Figure 1. Scheme showing the products formed in the reaction of organic nitriles with sulfur dichloride.

mol) containing ammonium chloride (6.4 g, 0.12 mol) in carbon tetrachloride (50 mL). The mixture was stirred for 2 h at 23 °C, and additional solvent (25 mL) was added to break up the solid conglomerate. After filtration, the solid mixture was Soxhlet extracted with (a) carbon tetrachloride (5 h; 200 mL) and (b) methylene dichloride (2 h; 120 mL). The dark red-orange CH_2Cl_2 solution was reduced to half-volume and cooled (12 h; −20 °C). The yellow precipitate was filtered off, washed with CCl_4 (2 × 5 mL) and diethyl ether (2 × 5 mL) until free-flowing (1.5 g; 7% based on Me_2NCN), and recrystallized from 1,2-dichloroethane (ca. 15 mL g^{-1}) to give $[(Me_2NC(Cl)N)_2SCl]^+Cl_3^-$, mp 128–133 °C dec. Anal. Calcd for $C_6H_{12}N_4SCl_6$: C, 18.70; H, 3.12; N, 14.55; S, 8.33; Cl, 55.31. Found: C, 18.85; H, 4.05; N, 14.83; S, 8.01; Cl, 53.55. IR: 1590 s, br, 1420 s, 1402 vs, 1330 vs. br, 1235 s, 1150 m, br, 1050 m, 970 s, 948 vs, 870 vs, 856 vs, 640 m, 628 sh, 619 m, 510 m, 422 vs, 380 w, 332 w, 290 sh, 268 ms cm^{-1}. Raman (10^{-2} M in CH_3CN; 1650–100 cm^{-1}): 1613 s, 1441 m, 1416 m, 962 w, br, 860 w, br, 747 w, br, 696 w, 518 w, br, 423 m, 254 vs, br, 192 w cm^{-1}. UV (CH_3CN) λ_{max}, (ϵ): 202 (3.1×10^4), 256 (4.5×10^3). ^1H NMR ($CDCl_3$): 3.56 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 42.72 (s), 43.12 (s), 154.01 (s).

(b) Preparation of $[(Me_2NC(Cl)N)_3S]^+Cl_3^-$ (8 (R = Me_2N)). The CH_2Cl_2 solution remaining after the isolation of **4** (R = Me_2N, X^- = Cl_3^-) was reduced to one-third volume, and diethyl ether was added with cooling (−10 °C) to induce precipitation of a light-sensitive, bright yellow-orange, microcrystalline powder. This was filtered off, dried in vacuo, and identified as $[(Me_2NC(Cl)N)_3S]^+Cl_3^-$ (7.1 g; 39% based on Me_2NCN). Anal. Calcd for $C_9H_{18}N_6SCl_6$: C, 23.73; H, 3.95; N, 18.45; S, 7.04; Cl, 46.80. Found: C, 23.54; H, 4.21; N, 18.23; S, 6.88; Cl, 46.61. IR: 1600 s, br, 1420 s, 1315 s, 1238 s, 1170 m, 1152 m, 1070 w, 970 s, 962 s, 875 s, 859 s, 640 m, 520 w, 440 m, 396 s, 365 w, 310 s cm^{-1}. Raman (10^{-2} M in CH_3CN; 1650–100 cm^{-1}): 1613 s, 1445 m, 1415 m, 957 w, 864 w, 745 w, 701 w, 516 w, 424 m, 323 w, 292 w, 244 s, 200 m cm^{-1}. UV–visible (CH_3CN) λ_{max}, nm (ϵ): 200 (1.9×10^4), 257 (4.3×10^3), 307 (2.08×10^3), 360 sh (1.2×10^3), 400 sh (400), 463 (760). ^1H NMR ($CDCl_3$): 3.55 (s). $^{13}C\{^1H\}$ NMR: 42.68 (s), 43.04 (s), 154.06 (s). The light sensitivity has only been observed as a solid surface effect, resulting in a color change from yellow to green after several hours. An IR spectrum of a sample of the green solid (exposed to light for 72 h and shaken regularly) showed no significant changes except for a slight shoulder at 1660 cm^{-1} on the ν(C═N) absorption at 1590 cm^{-1}. Compound **8** dissolves readily in CH_2Cl_2 or $CHCl_3$ to give light-stable, intensely orange solutions.

Preparation of $[Me_2NC(Cl)NH_2]^+Cl^-$ (7) by Hydrolysis of $[(Me_2NC(Cl)N)_2SCl]^+Cl_3^-$. A small amount (ca. 0.5 g) of $[(Me_2NC(Cl)N)_2SCl]^+Cl_3^-$ was hydrolyzed by addition to wet acetone (10 mL). Chloroform was then added to dissolve the precipitated white solid. Slow evaporation of this solution yielded colorless crystals of $[Me_2NC(Cl)NH_2]^+Cl^-\cdot H_2O$ suitable for X-ray crystallography (vide infra). Anal. Calcd for $C_3H_{10}Cl_2N_2O$: C, 22.4; H, 6.2; N, 17.4. Found: C, 21.9; H, 5.9; N, 16.9. IR: 3510 w, 3480 w, 3150 br, 1670 vs, 1625 s, 1085 w, 1060 m, 875 m, 770–730 w, br, 685 m, 628 w, 468 w cm^{-1}. ^1H NMR (CD_3NO_2): 3.43 (s), 3.47 (s), 10.25 (s), 10.60 (s). $^{13}C\{^1H\}$ NMR (CD_3NO_2): 42.76 (s), 43.51 (s), 155.57 (s).

Reaction between Me_2NCN and SCl_2 in 1,2-Dichloroethane. Preparation of $[(Me_2NC(Cl)N)_2SCl]^+Cl^-$ (4 (R = NMe_2; X^- = Cl^-)). Dimethylcyanamide (3.0 mL, 0.037 mol) in 1,2-dichloroethane (10 mL) was added dropwise, with vigorous stirring, to an ice-cooled solution of SCl_2 (3.5 mL, 0.055 mol) in 1,2-dichloroethane (40 mL). After being stirred for 1 h at 23 °C, the solution was filtered to give a pale yellow crystalline solid, which was washed with diethyl ether (2 × 10 mL), dried in vacuo, and recrystallized from 1,2-dichloroethane (ca. 15 mL g^{-1}) to give $[(Me_2NC(Cl)N)_2SCl]^+Cl^-\cdot C_2H_4Cl_2$ (1.6 g; 28% based on Me_2NCN), mp 134 °C dec. Anal. Calcd for $C_8H_{16}Cl_6N_4S$: C, 23.24; H, 3.87; N, 13.56. Found: C, 22.35; H, 4.10; N, 14.28. IR: 1580 s, br, 1428 s, 1415 s, 1400 s, 1335 vs, br, 1270 m, 1235 s, 1140 s, br, 1060 w, br, 1030 w, 945 s, sh, 862 vs, 855 vs, 670 m, 650 m, 640 w, 630 sh, 620 m, 518 m, 450 w, 432 m, 410 w, 385 vs, 325 w, 270 w cm^{-1}. Raman (10^{-2} M in CH_3CN, 500–100 cm^{-1}): 424 s, 326 w, 295 w, 253 s, 198 m cm^{-1}. UV (CH_3CN) λ_{max} nm (ϵ): 225 (2.5×10^3), 258 (1.3×10^3), 290 sh (590), 360 (185). ^1H NMR ($CDCl_3$): 3.53 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 42.59 (s), 43.03 (s), 153.89 (s).

Thermal Decomposition of $[(Me_2NC(Cl)N)_3S]^+Cl_3^-$ to $[(Me_2NC(Cl)N)_2SCl]^+Cl^-$. In an attempted recrystallization, $[(Me_2NC(Cl)N)_3S]^+Cl_3^-$ (1.5 g) was heated to reflux in 1,2-dichloroethane (10 mL). After the mixture was filtered and the filtrate cooled to −10 °C for 12 h, there was precipitation of a bright yellow crystalline solid (0.58 g). This material was no longer photosensitive and was characterized as $[(Me_2NC(Cl)N)_2SCl]^+Cl^-$ (IR spectrum).

Preparation of $[(Me_2NC(Cl)N)_2S]^{2+}[SbCl_6^-]_2$ (5 (X^{2-} = $2SbCl_6^-$)). Antimony pentachloride (0.25 mL, 2.0 mmol) was added dropwise, by syringe, to a solution of $[(Me_2NC(Cl)N)_2SCl]^+Cl^-$ (0.25 g, 0.79 mmol) in methylene dichloride (10 mL) at 23 °C with stirring. There was immediate precipitation of a bright yellow solid (0.52 g; 72% based on $[(Me_2NC(Cl)N)_2SCl]^+Cl^-$), which was filtered off after 3 h, washed with diethyl ether (2 × 10 mL), and recrystallized from liquid sulfur dioxide (ca. 60 mL g^{-1}) to give $[(Me_2NC(Cl)N_2S]^{2+}[SbCl_6^-]_2$. Anal. Calcd for $C_6H_{12}Cl_{14}N_4SSb_2$: C, 7.89; H, 1.32; N, 6.14. Found: C, 8.02; H, 1.48; N, 6.35. IR: 1668 m, 1599 s, 1408 m, 1335 m, 1285 vs, 1255 m, 1230 m, 1165 m, 1055 m, 985 m, 980 m, 889 m, 640 m, 520 w, 450 w, and 342 vs cm^{-1}. ^1H NMR (CD_3NO_2): 3.92 (s), 4.01 (s). $^{13}C\{^1H\}$ NMR (CD_3NO_2): 47.48 (s), 47.93 (s), 160.25 (s).

X-ray Analysis. Crystals suitable for an X-ray structural determination were obtained by the following procedures: $[(Me_2NC(Cl)N)_2SCl]^+Cl_3^-$, by recrystallization from CCl_4/CH_2Cl_2 (1:1); $[(Me_2NC(Cl)N)_2SCl]^+Cl^-\cdot C_2H_4Cl_2$ by recrystallization from 1,2-dichloroethane solution (3 weeks at −20 °C) and cutting to a suitable size; $[Me_2NC(Cl)NH_2]^+Cl^-\cdot H_2O$, by slow evaporation of an acetone/$CHCl_3$ solution at 23 °C.

The crystal data and experimental conditions are given in Table I. Cell constants and orientation matrices were determined by least-squares refinement of the diffraction geometry for 25 accurately centered, high-angle reflections (minimum θ = 14°). The space groups were determined by using the indexing routines of the diffractometer and by

Table I. Crystal Data

	$[(Me_2NC(Cl)N)_2SCl]^+Cl_3^-$	$[(Me_2NC(Cl)N)_2SCl]^+Cl^-\cdot C_2H_4Cl_2$	$[Me_2NC(Cl)NH_2]^+Cl^-\cdot H_2O$
formula	$C_6H_{12}Cl_6N_4S$	$C_8H_{16}Cl_6N_4S$	$C_3H_{10}Cl_2N_2O$
fw	384.97	413.03	161.03
cryst description	pale yellow blocks	yellow plates	colorless plates
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a, Å	10.275 (4)	10.224 (2)	9.186 (2)
b, Å	11.170 (5)	12.158 (3)	5.5992 (5)
c, Å	6.767 (2)	7.188 (2)	14.745 (3)
α, deg	104.98 (3)	95.74 (2)	90
β, deg	95.41 (3)	106.64 (2)	95.09 (1)
γ, deg	89.82 (3)	93.97 (2)	90
V, Å	746.7 (6)	847.3 (4)	755.4 (2)
Z	2	2	4
D_c, g cm^{-3}	1.712	1.619	1.416
radiation[a]	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
temp, °C	−160 (2)	−160 (2)	21 (1)
max θ, deg	25	30	25
scan range $\Delta\omega$, deg	$1.5(0.66 + 0.347 \tan\theta)$	$1.5(0.70 + 0.347 \tan\theta)$	$1.5(0.60 + 0.347 \tan\theta)$
scan speed, deg min^{-1}	0.7–6.7	0.7–5.0	0.7–4.0
octants collcd	$\pm h,\pm k,+l$	$\pm h,\pm k,+l$	$\pm h,+k,-l$
cryst dimens, mm	0.1 × 0.2 × 0.25	0.25 × 0.3 × 0.4	0.1 × 0.3 × 0.4
μ (Mo Kα), cm^{-1}	12.60	11.17	7.75
no. of unique data	2613	4900	1327
no. of obsd data ($I > 3\sigma(I)$)	898	3439	665
no. data used in final cycle	1716[b]	3439	1017[b]
no. variables in final cycle	155	172	73
GOF	1.10	1.59	0.89
residual electron density, e Å^{-3}	0.8	0.9	0.4
R, R_w[c]	0.043, 0.050	0.038, 0.047	0.038, 0.042

[a] Graphite monochromator. [b] Observed data plus those for which $I_c > 3\sigma(I_o)$. [c] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. GOF and R_w for $[(Me_2NC(Cl)N)_2SCl]^+Cl_3^-$ were based on a value of $w = 0.2$.

examination of the intensities measured during data collection. In two cases the final choice of space group $P\bar{1}$ was based on the centric distribution of *E* values (K-curve)[11] and the successful solution of the structure. The data were collected on an Enraf-Nonius CAD 4F automated diffractometer fitted with a low-temperature device using the ω–2θ scan technique. A scan of 96 steps was recorded, of which the central 64 steps were taken as the peak (*P*) and the 16 steps on either side were taken as backgrounds (B_1 and B_2). The intensity was calculated as $I = [P - 2(B_1 + B_2)]Q$, where *Q* is the scan rate, and the standard deviation of the intensity as $\sigma(I) = [P + 4(B_1 + B_2)]^{1/2}Q$. The data were corrected for Lorentz and polarization effects, but an absorption correction was not applied.

Atomic scattering factors for non-hydrogen atoms were those of Cromer and Mann,[12] the H scattering factors were taken from ref 13, and real and anomalous dispersion corrections were applied to all non-hydrogen atoms.[14] The initial model for each structure was determined by using MULTAN 78.[15] Structure factor and difference Fourier calculations revealed the positions of all non-hydrogen atoms not included in the initial model. Refinement was carried out by full-matrix least-squares techniques based on *F*, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where *w* was defined as 0.2, $[\sigma^2(F_o) + 0.0003(F_o^2)]^{-1}$, and $[\sigma^2(F_o) + 0.0001(F_o^2)]^{-1}$ for **4** ($X = Cl_3^-$), **4** ($X^- = Cl^-$), and **7**, respectively. With the exception of the H atoms on C(6) of structure **4** ($X^- = Cl_3^-$), all H atoms were located on difference Fourier maps. C–H atoms were included in idealized positions (sp^3 hybridization, *d*(C–H) = 1.00 Å), and the N–H and O–H atoms of **7** were included in the positions determined from the map. For the final cycles, positional and anisotropic thermal parameters for non-hydrogen atoms were refined and C–H positions were recalculated. With **4** ($X^- = Cl_3^-$) it was possible to refine an isotropic extinction coefficient, the final value being 3.85×10^{-4}. An extinction coefficient could not be refined for **4** ($X^- = Cl^-$) or **7**. All models converged with a maximum shift/error of 0.1 or less, and final difference Fourier syntheses showed only minor peaks of electron density that were of no chemical significance.

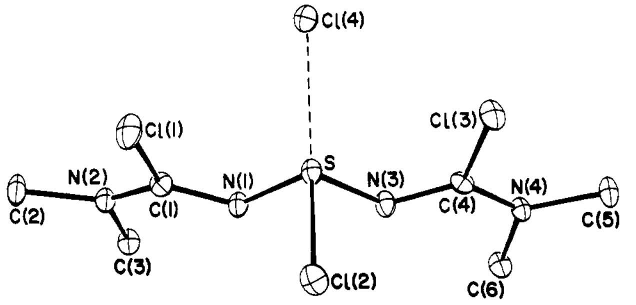

Figure 2. ORTEP drawing of $[(Me_2NC(Cl)N)_2SCl]^+Cl^-$ showing the atomic numbering scheme.

Results and Discussion

Reaction of Me_2NCN with SCl_2. Formation of $[(Me_2NC(Cl)N)_2SCl]^+X^-$ ($X^- = Cl^-$ or Cl_3^-) and $[(Me_2NC(Cl)N)_3S]^+Cl_3^-$. The reaction of Me_2NCN with SCl_2 in carbon tetrachloride *containing NH_4Cl* produces **4** ($X^- = Cl_3^-$) and **8** as the major products. Since the reaction occurs at 0 °C, the formation of NSCl (from NH_4Cl and SCl_2) is unlikely. Consequently the absence of **6** among the products is not surprising. The formation of **4** can be viewed as occurring via a double insertion of the nitrile (RCN) into the two X–Cl bonds of SCl_2 to give **3**, followed by oxidative addition of Cl_2. A third insertion reaction then produces the trisubstituted sulfonium complex, **8**.[16] The reaction appears to be subject to chloride ion catalysis since in CCl_4, a low-polarity solvent, no reaction occurs in the absence of NH_4Cl. In 1,2-dichloroethane (ϵ = 10.4), however, the reaction proceeds without addition of NH_4Cl, presumably because the ionization $SCl_2 \rightarrow SCl^+ + Cl^-$ is favored in this solvent.

The isolation of **4** as the Cl_3^- salt is probably a consequence of the formation of Cl_2 from the disproportionation of excess SCl_2

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(11) All computations were performed by using the XRAY 76 system of programs implemented on a Honeywell Computer with a MULTICS operating system: Stewart, J. M., Ed. "XRAY 76" Technical Report TR-446; Computer Science Center, University of Maryland: College Park, MD, 1976.

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Table II. Positional Parameters (×10^4) and B_{eq} (×10) for the Non-Hydrogen Atoms

atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq}, Å^2
		$[(Me_2NC(Cl)N)_2SCl]^+Cl_3^-$		
Cl(1)	1814 (2)	6289 (2)	9520 (4)	17
Cl(2)	1425 (2)	5051 (2)	3580 (4)	18
Cl(3)	20 (2)	2010 (2)	3820 (4)	15
Cl(4)	1412 (3)	2419 (3)	9137 (4)	28
Cl(5)	2306 (3)	567 (3)	7919 (4)	25
Cl(6)	3177 (3)	−1396 (3)	6732 (5)	31
S	1910 (2)	4083 (2)	5869 (4)	12
N(1)	3274 (7)	4766 (7)	6924 (12)	14
N(2)	4344 (8)	6378 (8)	9284 (14)	18
N(3)	2514 (7)	2827 (7)	4655 (12)	11
N(4)	2144 (7)	783 (7)	3035 (12)	11
C(1)	3244 (9)	5767 (9)	8482 (15)	13
C(2)	4479 (10)	7406 (9)	11108 (17)	17
C(3)	5503 (10)	6045 (11)	8203 (18)	23
C(4)	1678 (8)	1850 (9)	3846 (15)	13
C(5)	3575 (9)	605 (9)	3073 (16)	15
C(6)	1351 (9)	−372 (9)	2189 (17)	18
		$[(Me_2NC(Cl)N)_2SCl]^+Cl^-{\cdot}C_2H_4Cl_2$		
Cl(1)	3609.3 (7)	1156.5 (6)	1073.0 (12)	16
Cl(2)	3701.1 (7)	4109.8 (6)	735.4 (11)	15
Cl(3)	3371.3 (7)	5018.2 (6)	5674.8 (11)	13
Cl(4)	1783.1 (7)	1963.6 (6)	5084.6 (11)	14
Cl(5)	3690.0 (8)	8931.9 (7)	4758.1 (13)	20
Cl(6)	2607.4 (9)	6995.9 (7)	907.0 (13)	21
S	2463.1 (7)	3201.5 (6)	2313.4 (11)	11
N(1)	1460 (2)	2360 (2)	529 (4)	11
N(2)	1114 (2)	639 (2)	−1236 (4)	11
N(3)	1394 (2)	4094 (2)	2436 (4)	11
N(4)	998 (2)	5704 (2)	4034 (4)	10
C(1)	1921 (3)	1417 (2)	49 (4)	12
C(2)	1597 (3)	−357 (2)	−2042 (5)	16
C(3)	−304 (3)	855 (2)	−2214 (4)	13
C(4)	1798 (3)	4916 (2)	3894 (4)	10
C(5)	1378 (3)	6668 (2)	5552 (5)	14
C(6)	−281 (3)	5722 (2)	2449 (4)	13
C(7)	4726 (3)	8427 (3)	3278 (6)	26
C(8)	4341 (4)	7251 (3)	2484 (6)	26
		$[Me_2NC(Cl)NH_2]^+Cl^-{\cdot}H_2O$		
Cl(1)	4308.3 (11)	7193.4 (23)	743.0 (8)	44
Cl(2)	1953.1 (11)	1993.3 (22)	9261.1 (8)	41
O	2601 (3)	6942 (6)	8146 (2)	59
N(1)	1530 (3)	7779 (7)	638 (2)	38
N(2)	2431 (3)	4540 (6)	1484 (2)	31
C(1)	2600 (4)	6382 (8)	987 (3)	32
C(2)	963 (5)	3834 (8)	1687 (3)	40
C(3)	3643 (5)	3116 (9)	1887 (3)	49

Table III. Selected Bond Distances (Å) and Bond Angles (deg)

	dist			
bond	4 ($X^- = Cl_3^-$)	$4{\cdot}C_2H_4Cl_2$ ($X^- = Cl^-$)	bond	dist 7
S–Cl(2)	2.128 (4)	2.233 (1)		
S–N(1)	1.610 (8)	1.607 (2)		
S–N(3)	1.590 (8)	1.607 (3)		
N(1)–C(1)	1.327 (11)	1.321 (4)	N(1)–C(1)	1.325 (5)
N(3)–C(4)	1.356 (11)	1.324 (4)		
C(1)–N(2)	1.319 (12)	1.308 (3)	C(1)–N(2)	1.282 (6)
C(4)–N(4)	1.289 (12)	1.317 (4)		
C(1)–Cl(1)	1.723 (10)	1.737 (3)	C(1)–Cl(1)	1.703 (4)
C(4)–Cl(3)	1.711 (9)	1.733 (3)		
N(2)–C(2)	1.449 (12)	1.468 (4)	N(2)–C(2)	1.462 (5)
N(2)–C(3)	1.453 (14)	1.474 (4)	N(2)–C(3)	1.453 (6)
N(4)–C(5)	1.481 (12)	1.467 (4)		
N(4)–C(6)	1.483 (12)	1.472 (3)	O–H(1)	1.06
			H(1)–Cl(2)	2.30
Cl(4)–Cl(5)	2.249 (4)		O–H(1)···Cl(2)	3.303 (4)
Cl(5)–Cl(6)	2.340 (4)		O–H(2)	1.10
			H(2)–Cl(2)	2.27
C(7)–Cl(5)		1.799 (4)	O–H(2)···Cl(2)	3.352 (4)
C(7)–C(8)		1.467 (5)	N(1)–H(11)	0.94
C(8)–Cl(6)		1.796 (3)	H(11)–Cl(2)	2.30
S–Cl(4)		2.822 (1)	N(1)–H(11)···Cl(2)	3.219 (3)
			N(1)–H(12)	1.08
			H(12)–Cl(2)	2.13
			N(1)–H(12)···Cl(2)	3.159 (4)

	angle			
atoms	4 ($X^- = Cl_3^-$)	$4{\cdot}C_2H_4Cl_2$ ($X^- = Cl^-$)	atoms	angle 7
N(1)–S–N(3)	96.9 (4)	97.3 (1)		
N(1)–S–Cl(2)	100.6 (4)	100.4 (1)		
N(3)–S–Cl(2)	104.2 (4)	99.1 (1)		
S–N(1)–C(1)	118.4 (7)	117.3 (2)		
S–N(3)–C(4)	117.2 (6)	117.0 (2)		
N(1)–C(1)–N(2)	119.2 (9)	120.8 (2)	N(1)–C(1)–N(2)	125.0 (4)
N(3)–C(4)–N(4)	119.1 (8)	120.2 (2)		
N(1)–C(1)–Cl(1)	122.2 (7)	122.0 (2)	N(1)–C(1)–Cl(2)	115.2 (3)
N(3)–C(4)–Cl(3)	121.6 (7)	122.7 (2)		
N(2)–C(1)–Cl(1)	118.6 (7)	117.2 (2)	N(1)–C(2)–Cl(1)	119.7 (3)
N(4)–C(4)–Cl(3)	119.3 (7)	117.0 (2)		
C(1)–N(2)–C(2)	125.1 (8)	123.7 (2)	C(1)–N(2)–C(2)	119.7 (3)
C(1)–N(2)–C(3)	117.8 (8)	118.7 (2)	C(1)–N(2)–C(3)	123.2 (4)
C(4)–N(4)–C(5)	120.7 (7)	124.1 (2)		
C(4)–N(4)–C(6)	124.8 (8)	119.2 (2)		
C(2)–N(2)–C(3)	117.0 (8)	116.6 (2)	C(2)–N(2)–C(3)	117.1 (3)
C(5)–N(4)–C(6)	114.2 (7)	116.2 (2)		
Cl(4)–Cl(5)–Cl(6)	177.5 (2)		O–H(1)···Cl(2)	158
			O–H(2)···Cl(2)	169
Cl(5)–C(7)–C(8)		112.8 (3)	N(1)–H(11)···Cl(2)	165
C(7)–C(8)–Cl(6)		112.4 (3)	N(1)–H(12)···Cl(2)	159

in the reaction mixture.[17] This could also account for the oxidative-addition step **3** → **4**. When SCl_2 is not in excess, **4** is obtained as the Cl^- salt.

The characterization of **8** as a trisubstituted sulfonium salt is based on complete elemental analyses, spectroscopic data (vide infra), and thermal decomposition to give **4** ($X^- = Cl^-$) (see Figure 1). The X-ray structures of **4** ($X = Cl^-$, Cl_3^-) are described in the following section.

Crystal and Molecular Structures of $[(Me_2NC(Cl)N)_2SCl]^+X^-$ ($X^- = Cl^-$, Cl_3^-). X-ray structural determinations have confirmed that the chlorosulfonium formulation **4** is the correct description for the solid-state structure of the product of the reaction between dimethylcyanamide and sulfur dichloride in 1,2-dichloroethane or in carbon tetrachloride in the presence of ammonium chloride. In the latter case, the counterion is the trichloride ion. The final atomic coordinates for non-hydrogen atoms are given in Table II. Figure 2 shows an ORTEP drawing with the atomic numbering scheme for the $[(Me_2NC(Cl)N)_2SCl]^+$ cation for $X^- = Cl^-$, and selected bond lengths and bond angles are presented in Table III.

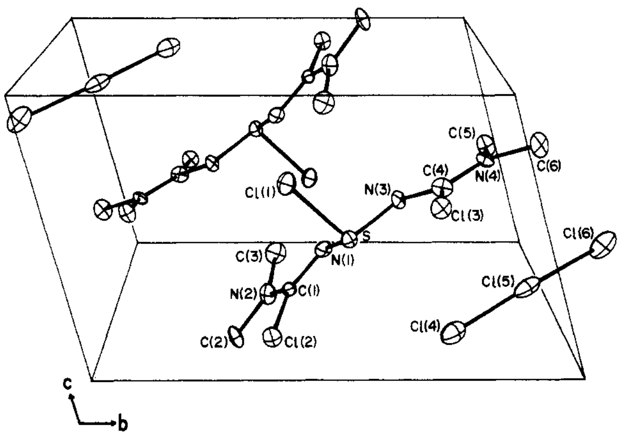

Figure 3. Unit cell of $[(Me_2NC(Cl)N)_2SCl]^+Cl_3^-$.

A unit cell illustrating the orientation of anions relative to the cation for $X^- = Cl_3^-$ is displayed in Figure 3.

Although the structures of the cation in **4** ($X^- = Cl^-$, Cl_3^-) are essentially similar, there are small differences that can be at-

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[17] Although the Cl_3^- ion is the least stable of the trihalide ions, R_4N^+ salts have been known for many years: Chattaway, F. D.; Hoyle, G. *J. Chem. Soc.* **1923**, *123*, 654.

tributed to counterion effects. The asymmetric disposition of the Cl_3^- ion (Figure 3) gives rise to inequalities in the lengths of bonds that are equal in the Cl^- salt (Table III). It should be noted, however, that these inequalities (S–N(1) vs. S–N(3), N(1)–C(1) vs. N(3)–C(4), and C(1)–N(2) vs. C(4)–N(4)) are slightly less than 3σ for the Cl_3^- salt.

The S–Cl(2) bond length is 2.128 (4) Å for $X^- = Cl_3^-$. We have been unable to find structural data for other chlorosulfonium salts, but this value is comparable to those found for *d*(S–Cl) in $(NSCl)_3$ (2.084 (4) and 2.150 (4) Å)[18] or $[S_3N_2Cl]^+$ (2.168 Å)[19] and is indicative of a two-electron covalent bond. For $X = Cl^-$, the S–Cl(2) distance is slightly longer (2.233 (1) Å), and there is a significant long-range interaction of 2.822 (1) Å between sulfur and Cl(4); cf. 2.811 (2) Å for *d*(S–Cl) in S_4N_5Cl,[20] which has a polymeric (predominantly ionic) structure in which $[S_4N_5]^+$ cations are bridged by Cl^- ions. The geometry at sulfur is pyramidal with bond angles in the range 97–104° ($X^- = Cl_3^-$; $\sum S = 301.7°$) and 97–100° ($X^- = Cl^-$; $\sum S = 296.8°$). The S–N bond lengths (1.60–1.61 Å) are similar to those found in $(NSCl)_3$ (*d*(S–N) = 1.61 Å).[18]

The bond lengths and bond angles involving the carbon and nitrogen atoms of the NCNSNCN chain are indicative of C=N multiple bonding. The average internal C–N distances, C(1)–N(1) and C(4)–N(3), are 1.323 (4) and 1.341 (11) Å for $X^- = Cl^-$ and Cl_3^-, respectively, while the terminal C–N bond lengths, C(1)–N(2) and C(4)–N(4), are 1.312 (4) and 1.304 (12) Å (cf. *d*(C=N) in oximes, ~1.29 Å).[21] The bond angles at the internal (two-coordinate) nitrogen atoms, N(1) and N(3), are 117–118°, suggesting sp^2 hybridization, while the terminal three-coordinate nitrogen atoms, N(2) and N(4), adopt a planar geometry. The sum of the angles at these two nitrogen atoms and at C(1) and C(4) are all close to 360° for both salts. The C–Cl bond lengths of 1.735 (3) ($X^- = Cl^-$) and 1.717 (10) Å ($X^- = Cl_3^-$) are typical for $C(sp^2)$–Cl single bonds. The chemically equivalent halves of the chlorosulfonium cation, which are bisected by S–Cl(2), are essentially planar but are twisted with respect to each other. The angles between the normals to the planes for each half of the cation are 12.2° ($X^- = Cl^-$) and 26.5° ($X^- = Cl_3^-$).

The Cl_3^- ion in **4** ($R = NMe_2$) is almost linear (Cl–Cl–Cl = 177.5 (2)°) and unsymmetrical (*d*(Cl–Cl) = 2.249 (4) and 2.340 (4) Å). These data are remarkably similar to those found in the only other structural determination of the trichloride anion, viz. $Ph_4As^+Cl_3^-$, for which Cl–Cl–Cl = 177.45 (15)° and *d*(Cl–Cl) = 2.227 (4) and 2.305 (3) Å.[22] Thus the Cl_3^- ion follows the trend exhibited by other trihalide ions in that the overall length of the ion is 0.5–0.6 Å greater than the sum of two single-bond lengths (*d*(Cl–Cl) in Cl_2 is 1.99 Å).[23] This is consistent with the three-center, four-electron view of bonding in the Cl_3^- ion,[24] but it should be noted that ab initio MO calculations predict a symmetrical configuration ($D_{\infty h}$) for this anion.[25] In the present case, the inequality in Cl–Cl bond lengths is probably due, at least in part, to the asymmetric orientation of the Cl_3^- ion relative to that of the cation in the unit cell (Figure 3).

Crystal and Molecular Structures of the Hydrolysis Product $[Me_2NC(Cl)NH_2]^+Cl^-\cdot H_2O$. The hydrolysis of $[(Me_2NC(Cl)N)_2SCl]^+Cl_3^-$ in wet acetone produces N^1,N^1-dimethylchloroformamidinium chloride, the structure of which has been determined by X-ray crystallography. Figure 4 shows an ORTEP drawing of the cation of the hydrolysis product with the atomic numbering scheme. The final atomic coordinates for the non-hydrogen atoms are given in Table II, and selected bond lengths and bond angles can be found in Table III.

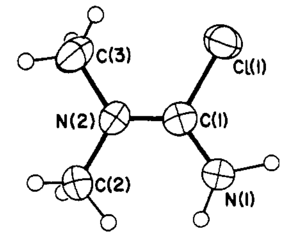

Figure 4. ORTEP drawing of the cation in $[Me_2NC(Cl)NH_2]^+Cl^-\cdot H_2O$ showing the atomic numbering scheme.

The $[Me_2NC(Cl)NH_2]^+$ cation is planar with trigonal geometry at C(1) and N(2). The C(1)–N(1) and C(1)–N(2) distances of 1.325 (5) and 1.282 (6) Å, respectively, are indicative of C=N double bonds (vide supra), whereas C(2)–N(2) and C(3)–N(2) have typical single-bond values (1.45–1.46 Å).[21]

A number of weak hydrogen bonds involving the Cl^- ion and hydrogen atoms of the NH_2 group and the water molecule are found in the structure of **7** ($R = Me_2N$) (Table III). The bond lengths are typical (cf. *d*(N–H···Cl) = 3.12 Å).[26]

Spectroscopic Data for $[(Me_2NC(Cl)N)_2SCl]^+X^-$ ($X^- = Cl^-$, Cl_3^-), $[(Me_2NC(Cl)N)_3S]^+Cl_3^-$, and $[Me_2NC(Cl)NH_2]^+Cl^-\cdot H_2O$. NMR Spectra. The NMR spectra of **4** ($X^- = Cl^-$, Cl_3^-) and **8** exhibit similar features characteristic of the $Me_2NC(Cl)N$ group. The ^{13}C spectra show two singlets at 42–43 ppm with small separations of 18–22 Hz, due to inequivalent methyl groups, and a singlet at 150–154 ppm attributed to the carbon atom bonded to chlorine. The inequivalence of the methyl groups, a result of restricted rotation about the C=N bond, is not resolved in the ^1H NMR spectra of **4** and **8**, which exhibit a single line at ca. 3.5 ppm. In the hydrolysis product (**7**) the two methyl signals appear at 3.43 and 3.47 ppm in the ^1H NMR spectrum and at 42.76 and 43.51 ppm in the ^{13}C NMR spectrum [cf. Me_2NCHO (^1H NMR 2.79 and 2.94 ppm; ^{13}C NMR 29.85 and 34.95 ppm)[27]]. The inequivalent protons of the NH_2 group in **7** give rise to singlets at 10.25 and 10.60 ppm.

In addition to the signals discussed above, the NMR spectra of analytically pure samples of **4** and **8** invariably contained *weak* signals at higher fields (ca. 3.3 ppm for ^1H NMR and 41 ppm for ^{13}C NMR). Although we have been unable to make definite assignments, we believe these signals are due either to products formed as a result of loss of Cl_2 when **4** or **8** are dissolved in a solvent (vide infra) or to $Me_2NC(Cl)NS(O)Cl$ formed at the same time as **7** in the hydrolysis of **4** and **8**.[28]

IR and Raman Spectra. The solid-state IR spectra of **4** ($X^- = Cl^-$, Cl_3^-) and **8** show several similar features, but as might be expected, there are distinctive differences. All three compounds show strong bands at 1580–1600, 850–970, and 620–640 cm^{-1} tentatively assigned to C=N, S—N (or C—S—N), and C—Cl stretching vibrations, respectively. Additional bands are observed at 1270, 1030, 670, and 650 cm^{-1} for **4** ($X^- = Cl^-$) due to 1,2-$C_2H_4Cl_2$ solvent of crystallization. The S–Cl stretching frequency in **4** is expected to occur at ca. 400 cm^{-1} [cf. $(NSCl)_3$ (ν(S–Cl) = 385 cm^{-1},[29] *d*(S–Cl) = 2.15 Å[18]) and $S_3N_2Cl^+$ (ν(S–Cl) = 400 cm^{-1},[30] *d*(S–Cl) = 2.17 Å[19])]. The strong bands at 423 cm^{-1} for **4** ($X^- = Cl_3^-$) and at 385 cm^{-1} for **4** ($X = Cl^-$) are therefore tentatively attributed to ν(S–Cl). The lower frequency for the

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Table IV. Vibrational Frequencies (cm^{-1}) of the Cl_3^- Ion

compd	state	ν_1	ν_2	ν_3
n-$Pr_4N^+Cl_3^-$[a]	solid	268 (R)		242 (IR)
	CH_3CN soln	275 (R)	165 (R)[a,b]	
	benzene soln	281 (IR)[a,c]		232 (IR)
$Ph_4As^+Cl_3^-$[d]	solid	271 (R)	148 (IR)	253 (IR)
4 ($X^- = Cl_3^-$)[d]	solid	269 (R)		268 (IR)
	CH_3CN soln	253 (R)		

[a] Reference 31. [b] Estimated frequency based on the observation of a weak band at 330 cm^{-1}, assigned to $2\nu_2$, in the Raman spectrum of acetonitrile solutions. [c] The observation of a band of medium intensity assigned to ν_1 in the IR spectrum of benzene solutions was attributed to loss of anion symmetry in solution. [d] This work (±3 cm^{-1}).

latter is consistent with the longer S–Cl bond length (2.23 vs. 2.13 Å). The photosensitive compound, **8**, shows a strong band at 396 cm^{-1}, but its shape is distinctly different from those assigned to ν(S–Cl) for **4**.

The Raman spectra of CH_3CN solutions of **4** ($X^- = Cl^-, Cl_3^-$) and of solid **4** ($X^- = Cl_3^-$) all show bands at ca. 425 cm^{-1}, which could be due to ν(S–Cl). A similar band was also observed for **8**, suggesting decomposition to **4** in the laser beam, but we found no evidence from the Raman spectrum for the loss of Me_2NCN from **8**.

Vibrational Spectra of the Cl_3^- Ion. In principle, vibrational spectroscopy can distinguish between symmetric ($D_{\infty h}$) and antisymmetric ($C_{\infty v}$) arrangements of a linear trihalide ion, X_3^-. In the former case the mutual exclusion rule applies; ν_1 is Raman active, while ν_2 and ν_3 are IR active. In the absence of a center of symmetry, however, all three vibrations become both IR and Raman active. The vibrational spectra of n-$Pr_4N^+Cl_3^-$ have been interpreted in terms of a symmetrical structure in the solid state and loss of anion symmetry in solution.[31] Unlike Br_3^- or I_3^-, ν_3 occurs at a lower frequency than ν_1 for the Cl_3^- ion.[32,33] In light of the known structure of Cl_3^- (vide infra and ref 22) and in order to investigate counterion effects on the vibrational spectra of this anion, we have measured the far-IR and Raman spectra of $Ph_4As^+Cl_3^-$ and **4** ($X^- = Cl_3^-$). The data are summarized in Table IV.

The IR spectrum of $Ph_4As^+Cl_3^-$ (solid) exhibits bands at 148 and 253 cm^{-1}, assigned to ν_2 and ν_3 (Cl_3^-), respectively, which are not apparent in the spectrum of $Ph_4As^+Cl^-$. The Raman spectrum showed a band at 271 cm^{-1}, assigned to ν_1. These data are consistent with the earlier results for n-$Pr_4N^+Cl_3^-$.[31] A medium-strong band is observed at 269 cm^{-1} in the solid-state IR spectrum of **4** ($X^- = Cl_3^-$), whereas there is only a weak, broad band at this frequency for **4** ($X^- = Cl^-$). The Raman spectrum of solid **4** ($X^- = Cl_3^-$) shows a strong band at 269 cm^{-1}, which, in acetonitrile solution, appears as a strongly polarized absorption at 253 cm^{-1} attributed to ν_1 (Cl_3^-).

The observation of a strongly polarized band at 244 cm^{-1} in the Raman spectrum of **8** (in CH_3CN) provides evidence for the presence of Cl_3^- in this salt. However, a similar, but less intense, Raman band at 254 cm^{-1} was also found for **4** ($X^- = Cl^-$). A possible explanation for this observation involves partial loss of Cl_2 from **4** ($X^- = Cl^-$) in solution and subsequent formation of Cl_3^- (from Cl^- and Cl_2).[28]

Preparation of $[(Me_2NC(Cl)N)_2S]^{2+}[SbCl_6^-]_2$. The instantaneous reaction of **4** ($X^- = Cl^-$) with $SbCl_5$ produced a bright yellow solid identified as **5** ($X^{2-} = 2SbCl_6^-$) on the basis of analytical and spectroscopic data. In the IR spectrum of **5**, the band attributed to ν(S—Cl) in **4** has disappeared and the ν(C=N) bands occur at higher frequencies (ca. 1670 and 1600 cm^{-1}) compared to the corresponding bands in **4**. Raman bands for **5** (in CH_3NO_2) at 327 and 282 cm^{-1} and a very strong IR band at 342 cm^{-1} are assigned to ν_1, ν_2, and ν_3, respectively, of the $SbCl_6^-$ ion.[34] The inequivalent methyl groups of the Me_2N substituents can be distinguished in both the ^1H (3.92 and 4.01 ppm) and ^{13}C (47.48 and 47.93 ppm) NMR spectra, but the chemical shifts are at lower fields than the corresponding signals for the chlorosulfonium monocation in **4**. The ^{13}C NMR signal for the tertiary carbons in **5** also appears at lower field (160.25 ppm).

Thus it seems reasonable to conclude that **5** contains a rare example of a two-coordinate sulfur dication.[35] The structural data for **4** suggest, however, that the positive charge will be highly delocalized in **5**, and consequently, the S–N bond orders are likely to be substantially greater than 1. Attempts to determine the structure of **5** by X-ray crystallography are in progress.

Conclusions

The products of the reaction of SCl_2 with Me_2NCN are correctly formulated as the chlorosulfonium salts $[(Me_2NC(Cl)N)_2SCl]^+X^-$ (**4**) in the solid state, and in the presence of Cl_2, a rare example of a stable compound containing the Cl_3^- ion is isolated. The chlorosulfonium cation reacts reversibly with excess Me_2NCN to give the trisubstituted sulfonium ion $[(Me_2NC(Cl)N)_3S]^+$ and with $SbCl_5$ to form $[(Me_2NC(Cl)_2S]^{2+}[SbCl_6^-]_2$ (**5**), which probably contains a 2-coordinate sulfur dication. The reactions of **4** with various reducing agents are under investigation with a view to producing **3**, a possible precursor of polymers of type **1**.[36]

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Registry No. **4** ($R = NMe_2$, $X = Cl_3^-$), 96445-65-7; **4** ($R = NMe_2$, $X = Cl^-$)·$Cl(CH_2)_2Cl$, 96445-69-1; **4** ($R = NMe_2$, $X = Cl^-$, nonsolvated), 96445-68-0; **5** ($R = NMe_2$, $X^{2-} = 2SbCl_6^-$), 96445-67-9; **7** ($R = NMe_2$)·H_2O, 96445-70-4; **7** ($R = NMe_2$, nonsolvated), 88949-04-6; **8** ($R = NMe_2$), 96445-72-6; $CNNMe_2$, 1467-79-4; SCl_2, 10545-99-0; $SbCl_5$, 7647-18-9.

Supplementary Material Available: Tables containing anisotropic thermal parameters for non-hydrogen atoms, positional and isotropic thermal parameters for hydrogen atoms, and structure factors for **4** ($X^- = Cl^-$), **4** ($X^- = Cl_3^-$), and **7** and a table of best planes for **4** (41 pages). Ordering information is given on any current masthead page.

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(31) Evans, J. C.; Lo, G. Y.-S. *J. Chem. Phys.* **1966**, *44*, 3638.

(32) Nakamoto, K. "Infrared Spectra of Inorganic and Coordination Compounds", 2nd ed.; Wiley-Interscience: New York, 1970; p 84.

(33) Ault, B. S.; Andrews, L. *J. Am. Chem. Soc.* **1975**, *97*, 3824. In contrast to the data reported for n-$Pr_4N^+Cl_3^-$ (Table IV), these authors have attributed infrared bands at 375 and 327 cm^{-1} to the ν_3 vibrations of $NaCl_3$ and $CsCl_3$, respectively, in an argon matrix at 17 K.

(34) Reference 32, p 123.

(35) Spectroscopic evidence (Raman and NMR) for the formation of $(Me_2N)_2S^{2+}$ in solution has been presented: Cowley, A. H.; Pagel, D. J.; Walker, M. L. *J. Chem. Soc., Chem. Commun.* **1979**, 965.

(36) A report of the vibrational spectra of $Ph_4E^+Cl_3^-$ (E = P, As) has appeared since the submission of this paper.[37] The Raman spectra of solid samples show a strong band at ca. 270 cm^{-1} attributed to ν_1 of the Cl_3^- ion. The ν_3 vibration is reported to occur as a *broad* band at ca. 230 cm^{-1} in the infrared spectrum.

(37) Bouchē, R.; Vanclef, A.; De Meyer, M.; Levert, J. M. *Spectrosc. Lett.* **1984**, *17*, 409.