data were obtained with the use of equipment purchased through a DOD instrumentation grant provided by the U.S. Army Research Office through Grant No. DAAG29-83-G0101.

Registry No. I, 311-03-5; II, 99476-97-8; hexachlorocyclotriphosphazene, 940-71-6; catechol, 120-80-9.

Supplementary Material Available: Tables of thermal parameters, root-mean-square displacements, and observed and calculated structure factor amplitudes for both structures (15 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
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Preparation of Six- and Eight-Membered Mixed Cyanuric–Thiazyl Rings, $(R_2NCN)_x(NSCl)_2$ ($x = 1, 2$), and the X-ray Crystal Structure of $(Et_2NCN)(NSCl)_2$

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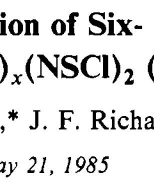
The reaction of dialkylcyanamides with NSCl units generated from $(NSCl)_3$ in CCl_4 at ca. 60 °C produces either the six-membered rings $(R_2NCN)(NSCl)_2$ (R = Me, Et, *i*-Pr) or, in the presence of a large excess of Me_2NCN, the eight-membered ring 1,3-$(Me_2NCN)_2(NSCl)_2$. In contrast, the addition of $(C_6H_{11})_2NCN$ to a warm solution of $(NSCl)_3$ in CCl_4 yields $(C_6H_{11})_2NC(Cl)NS_3N_2^+Cl^-$, a derivative of a five-membered S_3N_2 ring, which can also be prepared by the reaction of $(C_6H_{11})_2NCN$ with $S_3N_2Cl_2$ in CH_2Cl_2 at 23 °C. Oxidative addition of Cl_2 (as SO_2Cl_2) to 1,5-$(Me_2NCN)_2(SN)_2$ gives 1,5-$(Me_2NCN)_2(NSCl)_2$. The latter is thermally more stable than the structural isomer, 1,3-$(Me_2NCN)_2(NSCl)_2$, which undergoes ring contraction, with loss of Me_2NCN, in acetonitrile at 25 °C. The mechanism of the cycloaddition reaction of R_2NCN with NSCl units is discussed. The crystal structure of $(Et_2NCN)(NSCl)_2$, determined by X-ray crystallography, shows that the exocyclic chlorine substituents adopt a cis configuration with respect to the almost planar CN_3S_2 ring. Crystal data: monoclinic, space group $P2_1/n$, $a = 9.464$ (3) Å, $b = 8.921$ (1) Å, $c = 13.421$ (4) Å, $\beta = 108.29$ (1)°, $V = 1075.9$ (5) Å^3, $Z = 4$. The final R and R_w values were 0.043 and 0.044, respectively.

Introduction

The preparation and X-ray structure of the six-membered mixed thiazyl–cyanuric ring **1** ($R = Me_2N$) via the cyclocondensation reaction between an amidine and $S_3N_2Cl_2$ was reported recently by Roesky et al., but the yield of **1** was only 7% (based on $S_3N_2Cl_2$).[1] During the course of the present study,[2] Mews et al. isolated **1** ($R = CF_3$) in 21% yield from the reaction of CF_3CN with $(NSCl)_3$ in an autoclave at 50 °C.[3] The five-membered ring **2**, $RCN_2S_2^+$ ($R = CF_3$), which is normally obtained in the reactions of organic nitriles with $(NSCl)_3$ at reflux,[4] was the major product (45%).[3]



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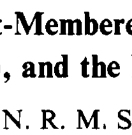

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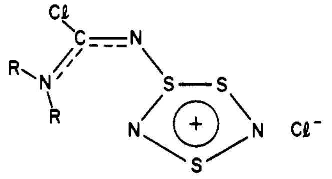

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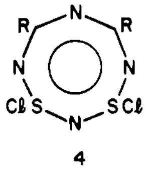

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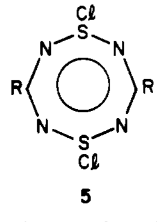

5

We describe here a convenient, high-yield synthesis of **1** ($R = Me_2N$, Et_2N, *i*-Pr_2N) by the cycloaddition reaction of dialkylcyanamides with NSCl units generated from $(NSCl)_3$ in CCl_4 at ca. 60 °C. With $(C_6H_{11})_2NCN$, however, the same procedure gives **3** ($R = C_6H_{11}$), a derivative of a five-membered S_3N_2 ring, which is formally related to **2** by the addition of one NSCl unit.

In the presence of excess Me_2NCN the cycloaddition reaction produces the heterocycle **4** ($R = Me_2N$), the first example of an eight-membered mixed thiazyl–cyanuric ring. The structural isomer **5** is obtained by the oxidative addition of Cl_2 across the S–S bond of 1,5-$Me_2NC(NSN)_2CNMe_2$. The possible involvement of the dimeric species $(NSCl)_2$ in the cycloaddition reaction, as speculated by Mews et al.,[3] is discussed. The X-ray crystal structure of **1** ($R = Et_2N$) is also described.

Experimental Section

Reagents and General Procedures. Solvents were dried (carbon tetrachloride and methylene dichloride (P_2O_5), *n*-pentane (CaH_2), and acetonitrile (CaH_2 and P_2O_5)) and freshly distilled before use. All reactions and the manipulation of moisture-sensitive products were carried out under an atmosphere of dry nitrogen (99.99%). Chemical analyses were performed by the Analytical Services of the Department of Chemistry, University of Calgary, and by MHW Laboratories, Phoenix, AZ.

The following reagents were prepared by literature procedures: $(NSCl)_3$,[5] $(C_6H_{11})_2NCN$,[6] 1,5-$Me_2NC(NSN)_2CNMe_2$.[7] Other chemicals were commercial products used as received: Me_2NCN, Et_2NCN, and *i*-Pr_2NCN (Aldrich). Sulfuryl chloride (Aldrich) was distilled before use.

Instrumentation. Infrared spectra were recorded as Nujol mulls (CsI windows) on a Nicolet 5DX FT-IR spectrometer. NMR spectra were

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recorded on Hitachi Perkin-Elmer R-24B (routine ^{1}H) or Bruker WH-90 or Varian XL-200 (^{1}H and ^{13}C) instruments. It was necessary to use T_1 delay times of 20 s in order to observe the signal for the ring C atoms in **1** (R = Me_2N, Et_2N, *i*-Pr_2N). Chemical shifts are reported in ppm downfield from Me_4Si. Mass spectra were obtained on a Kratos MS80RFA instrument (EI, 70 eV).

Preparation of $(Me_2NCN)(NSCl)_2$. A solution of (dimethylamino)cyanamide (0.27 g, 3.86 mmol) in CCl_4 (30 mL) was added slowly (ca. 30 min), with vigorous stirring, to a solution of $(NSCl)_3$ (1.42 g, 5.80 mmol) in CCl_4 (50 mL) at ca. 65 °C. After the addition was complete, the reaction mixture was heated at reflux for ca. 3 h, until the solution had become orange, and then cooled at 23 °C. The volume of the solution was reduced to half, and *n*-pentane (30 mL) was added. After 4 days at −20 °C, yellow crystals were filtered off and identified as $(Me_2NCN)(NSCl)_2$ (0.53 g, 2.26 mmol) by comparison of the infrared, NMR, and mass spectra[8] with the literature data (^{1}H (in $CDCl_3$) δ 3.24; ^{13}C δ 36.65 (CH_3) and 152.25 (NCN_2); cf. lit.[1] 3.2, 36.7, and 152.5, respectively). Removal of the solvent from the filtrate *in vacuo* gave a further 0.31 g (1.32 mmol) of essentially pure $(Me_2NCN)(NSCl)_2$, which can be recrystallized from CCl_4/*n*-pentane (1:1). The total yield of $(Me_2NCN)(NSCl)_2$ before recrystallization is 93% based on Me_2NCN.

Preparation of $(R_2NCN)(NSCl)_2$ (R = Et, *i*-Pr). The method used for the preparation of other derivatives of **1** was similar to that described above for **1** (R = Me_2N). In order to obtain crystalline products, however, different workup procedures, described below, were developed for each compound.

(a) $(Et_2NCN)(NSCl)_2$. The carbon tetrachloride solution (135 mL) obtained from the reaction of Et_2NCN (0.57 g, 5.8 mmol) and $(NSCl)_3$ (2.13 g, 8.7 mmol) at ca. 60 °C for 3 h was reduced to one-fourth volume, and *n*-pentane (50 mL) was added. After 1 day at −20 °C, this solution was filtered quickly through a medium-porosity frit to give opaque yellow needles of $(Et_2NCN)(NSCl)_2$ (1.20 g, 4.6 mmol). Anal. Calcd for $C_5H_{10}Cl_2N_4S_2$: C, 22.96; H, 3.83; Cl, 27.17; N, 21.44; S, 24.54. Found: C, 22.89; H, 4.08; Cl, 26.98; N, 21.28; S, 24.54. IR (cm^{-1}): 1548 vs, 1308 vs, 1214 vs, 1128 m, 1087 s, 999 s, 972 s, 921 s, 861 s, 798 m, 782 s, 723 s, 613 m, 507 m, 472 s, 455 m, 425 s. ^{1}H NMR (in $CDCl_3$): δ 1.28 (3 H, t, $J_{CH_3-CH_2}$ = 7.2 Hz, CH_3), 3.63 (2 H, quart, $J_{CH_2-CH_3}$ = 7.3 Hz, CH_2). ^{13}C NMR (in $CDCl_3$): δ 13.31 (CH_3), 42.76 (CH_2), and 151.49 (NCN_2). EI mass spectrum (*m*/*e* (relative intensity)): 225 (3, M − Cl^+), 190 (89, M − Cl_2^+), 144 (46), 119 (48), 98 (73), 97 (81), 83 (89), 78 (87), 72 (92), 56 (74), 46 (100).

(b) (*i*-$Pr_2NCN)(NSCl)_2$. The carbon tetrachloride solution (105 mL) obtained from the reaction of *i*-Pr_2NCN (0.64 g, 5.04 mmol) and $(NSCl)_3$ (1.85 g, 7.56 mmol) at ca. 60 °C for 2 h was filtered and then reduced in volume to ca. 10 mL before addition of *n*-pentane. After 1 day at −20 °C, yellow crystals of (*i*-$Pr_2NCN)(NSCl)_2$ (0.53 g, 1.83 mmol) were isolated by filtration. Anal. Calcd for $C_7H_{14}Cl_2N_4S_2$: C, 29.05; H, 4.85; N, 19.38. Found: C, 29.34; H, 5.20; N, 19.43. IR (cm^{-1}): 1536 vs, 1377 vs, 1369 vs, 1226 s, 1187 s, 1145 s, 1099 s, 1039 s, 940 s, 916 s, 873 m, 845 m, 825 s, 798 m, 726 s, 706 m, 554 m, 516 m, 481 m, 446 vs, 416 s. ^{1}H NMR (in $CDCl_3$) δ 1.39 (6 H, d, $J_{(CH_3)_2-CH}$ = 7.2 Hz, $(CH_3)_2$), 4.41 (1 H, sept, $J_{CH-(CH_3)_2}$ = 6.8 Hz, CH). ^{13}C NMR (in $CDCl_3$): δ 20.51 ($(CH_3)_2$), 48.46 (CH), 151.67 (NCN_2). EI mass spectrum (*m*/*e* (relative intensity)): 253 (0.5, M − Cl^+), 218 (41, M − Cl_2^+), 172 (14), 100 (28), 88 (88), 78 (20), 69 (67), 58 (36), 46 (100).

Reaction of $(C_6H_{11})_2NCN$ with $(NSCl)_3$. The carbon tetrachloride solution (185 mL) obtained from the reaction of $(C_6H_{11})_2NCN$ (1.59 g, 7.63 mmol) with $(NSCl)_3$ (2.80 g, 11.4 mmol) was filtered to give orange-brown needles of $(C_6H_{11})_2NC(Cl)NS_3N_2{}^+Cl^-$ (0.95 g, 2.37 mmol). Recrystallization from toluene (0.2 g in 30 mL) and cooling to −20 °C produced orange needles. Anal. Calcd for $C_{13}H_{22}Cl_2N_4S_3$: C, 38.88; H, 5.48; Cl, 17.69; N, 13.96; S, 23.97. Found: C, 39.38; H, 5.97; Cl, 16.59; N, 13.64; S, 22.34. IR (cm^{-1}): 1575 vs, 1353 m, 1336 s, 1326 m, 1278 m, 1261 w, 1208 w, 1165 w, 1108 w, 999 s, 958 m, 915 w, 892 m, 887 w, 769 s, 698 w, 649 m, 628 m, 578 w, 558 w, 398 s. ^{1}H NMR (in $CDCl_3$): δ 1.30 (m, 6 H), 1.71 (m, 6 H), 1.96 (m, 6 H), 2.37 (d, 2 H), 3.38 (s, 1 H), 3.74 (s, 1 H). ^{13}C NMR (in $CDCl_3$): δ 24.61 (C_4 and $C_{4'}$), 25.28 (C_3), 25.53 ($C_{3'}$), 28.78 (C_2), 29.23 ($C_{2'}$), 62.63 (C_1), 70.70 ($C_{1'}$), 187.81 (NC(Cl)N). EI mass spectrum (*m*/*e* (relative intensity)): 206 (3), 156 (5), 117 (34), 92 (59), 81 (29), 46 (100).

Preparation of $(C_6H_{11})_2NC(Cl)NS_3N_2{}^+Cl^-$ from $(C_6H_{11})_2NCN$ and $S_3N_2Cl_2$. A solution of $(C_6H_{11})_2NCN$ (1.40 g, 6.81 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a suspension of $S_3N_2Cl_2$ (1.33 g, 6.81 mmol) in CH_2Cl_2 (60 mL). The reaction mixture was stirred at 23 °C for 16 h. Filtration of the dark brown-orange solution gave S_4N_3Cl (0.10 g), identified by IR spectrum. Removal of the solvent in vacuo gave an orange solid (1.95 g), which showed a strong IR band at 2204 cm^{-1} ($\nu_s(C{\equiv}N)$) due to unreacted $(C_6H_{11})_2NCN$. About 1.4 g of this crude product was slurried with warm *n*-pentane (30 mL) to give $(C_6H_{11})_2NC(Cl)NS_3N_2{}^+Cl^-$ (0.85 g, 2.12 mmol) with an IR spectrum identical with that of the product obtained from $(C_6H_{11})_2NCN$ and $(NSCl)_3$ in warm CCl_4 (vide supra).

Preparation of 1,3-$(Me_2NCN)_2(NSCl)_2$. A solution of dimethylcyanamide (15.4 g, 220 mmol) in CCl_4 (25 mL) was added quickly (ca. 10 min) to a solution of $(NSCl)_3$ (4.25 g, 17.4 mmol) in CCl_4 (50 mL) at ca. 65 °C. The yellow solution became dark red-brown, and an immiscible red oil was formed. The reaction mixture was heated at reflux for ca. 3 h and then cooled to 23 °C before removal of solvent in vacuo. The sticky yellow-brown residue was extracted with CCl_4 (40 mL) at 23 °C to leave a yellow-brown solid (4.8 g, 15.9 mmol), which was recrystallized from CH_3NO_2/diethyl ether (1:2) to give 1,3-$(Me_2NCN)_2(NSCl)_2$. Anal. Calcd for $C_6H_{12}Cl_2N_6S_2$: C, 23.75; H, 3.96; N, 27.72. Found: C, 23.59; H, 4.38; N, 26.93. The red-brown CCl_4 extract produced a brown solid (2.0 g, 6.6 mmol) with an identical infrared spectrum after 7 days at −30 °C. IR (cm^{-1}): 1591 vs, 1558 vs, 1419 s, 1400 vs, 1254 vs, 1232 vs, 1147 m, 1131 s, 1114 m, 1060 m, 948 vs, 926 s, 918 s, 918 s, 884 m, 807 s, 720 s, 661 m, 621 m, 588 m, 516 m, 504 m, 482 m, 458 m, 436 s, 422 m. EI mass spectrum (*m*/*e* (relative intensity)): 232 (2, M − Cl_2^+), 186 (4), 162 (56), 116 (37), 78 (27), 70 (89), 69 (100), 46 (86). ^{1}H NMR (in $CDCl_3$): δ 2.88 (s, 6 H), 3.26 (s, 6 H); cf. Me_2NCN (δ 2.81) and $(Me_2NCN)(NSCl)_2$ (δ 3.24). ^{13}C NMR (in $CDCl_3$): δ 40.46 (s), 36.65 (s); cf. Me_2NCN (δ 40.02) and $(Me_2NCN)(NSCl)_2$ (δ 36.70).

Preparation of 1,5-$(Me_2NCN)_2(NSCl)_2$. Sulfuryl chloride (0.36 g, 2.58 mmol) was added by syringe to a solution of 1,5-$Me_2NC(NSN)_2CNMe_2$ (0.30 g, 1.3 mmol) in carbon tetrachloride (20 mL) at 23 °C. The solution changed color quickly from yellow to dark red-orange to give an orange precipitate (0.40 g, 1.3 mmol), after ca. 5 min, which was isolated by filtration. Recrystallization from carbon tetrachloride (20 mL) at −5 °C for 2 days gave orange microcrystals of 1,5-$(Me_2NCN)_2(NSCl)_2$ (0.07 g, 0.23 mmol). Anal. Calcd for $C_6H_{12}Cl_2N_6S_2$: C, 23.75; H, 3.96; N, 27.72. Found: C, 23.23; H, 4.68; N, 28.14. IR: 1571 s, 1312 vs, 1298 vs, 1286 vs, 947 ms, 893 s, 780 mw, 739 ms, 722 ms, 653 ms, 564 mw, 542 ms cm^{-1}. ^{1}H NMR (in $CDCl_3$): δ 3.13. ^{13}C NMR (in $CDCl_3$): δ 41.03 (CH_3), 154.01 (NCN_2). EI mass spectrum (*m*/*e* (relative intensity)): 232 (7, M − Cl_2^+), 186 (41), 148 (9), 116 (13), 70 (13), 69 (28), 46 (22), 44 (100), 42 (40). Approximately 0.15 g of the crude product did not dissolve in CCl_4. This material had an infrared spectrum very similar to that of 1,5-$(Me_2NCN)_2(NSCl)_2$ except that the 1286-cm^{-1} band is stronger relative to the bands at 1312 and 1298 cm^{-1} in the former.

X-ray Analysis of $(Et_2NCN)(NSCl)_2$. Crystal data: $C_5H_{10}Cl_2N_4S_2$, fw 261.20, monoclinic, $P2_1/n$ (alternate setting of $P2_1/c$), a = 9.464 (3) Å, b 8.921 (1) Å, c = 13.421 (4) Å, β = 108.29 (1)°, V = 1075.9 (5) Å^3, Z = 4, D_{calcd} = 1.612 g cm^{-3}, $F(000)$ = 536.0, μ(Mo Kα) = 9.35 cm^{-1}, Mo Kα radiation (λ = 0.709 26 Å, graphite monochromator), T = 21 (1) °C, θ_{max} = 27.5°, scan range 1.5 (0.76 + 0.347 tan θ), scan speed 3.5 ranging to 0.7° min^{-1}, data collected $\pm h,+k,+l$, 2459 unique reflections of which 1615 considered observed ($I > 3\sigma(I)$, where $\sigma(I)$ was derived from counting statistics). Space group determination and data collection procedures were as described previously.[9] The intensities of three standard reflections (060, 4,2,−7, −4,2,7), which were measured every 1500 s of X-ray exposure time, showed a slight decrease of 6%. The data were corrected for this decrease with use of a smoothing function.[10] Lorentz and polarization corrections were applied, and the data were corrected for absorption with use of Gaussian techniques.[11] The eight crystal faces were identified as {010}, {101}, (1,1,−1), and (−1,−1,1). The grid used was 10 × 10 × 14, and the minimum and maximum transmission factors were 0.58 and 0.77, respectively.

The structure was solved by MULTAN 78[12] followed by Fourier and least-squares techniques. The final full-matrix least-squares cycle was based on F and minimized the function $\sum w(|F_o| - |F_c|)^2$, where the weight w was defined as $[\sigma^2(F_o) + 0.00005(F_o{}^2)]^{-1}$. H atoms were readily located on a difference Fourier map, and H positional parameters were

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[8] The value of m/e = 175 given in ref 1 for the base peak in the mass spectrum of **1** (R=Me_2N) is incorrect. The base peak has m/e = 162 corresponding to $[(CH_3)_2NCN][SN]_2{}^+$.

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Table I. Positional (Non-H $\times 10^4$, H $\times 10^3$) and Isotropic Thermal Parameters ($\times 10$) for Refined Atoms of $(Et_2NCN)(NSCl)_2$

atom	x/a	y/b	z/c	B_{eq} or B_{iso}[a]
Cl1	4865 (1)	8157 (1)	2377 (1)	49.9 (5)
Cl2	8320 (1)	8172 (1)	4439 (1)	51.6 (6)
S1	5889 (1)	6026 (1)	2080 (1)	34.8 (4)
S2	8564 (1)	6064 (1)	3654 (1)	37.6 (4)
N1	5437 (3)	4892 (3)	2817 (2)	36 (1)
N2	7617 (4)	6414 (3)	2462 (2)	39 (1)
N3	7811 (3)	4879 (4)	4184 (2)	38 (1)
N4	5801 (4)	3631 (3)	4353 (2)	41 (2)
C1	6355 (4)	4503 (4)	3768 (3)	33 (2)
C2	6728 (6)	3140 (6)	5404 (4)	59 (3)
C3	7568 (7)	1770 (7)	5379 (5)	63 (3)
C4	4259 (5)	3081 (5)	3955 (4)	55 (2)
C5	4093 (6)	1623 (6)	3397 (6)	64 (3)
H2A	740 (5)	396 (5)	581 (3)	65
H2B	607 (4)	294 (5)	584 (3)	65
H3A	806 (5)	158 (5)	613 (4)	69
H3B	701 (5)	103 (5)	512 (4)	69
H3C	826 (5)	188 (5)	495 (4)	69
H4A	392 (4)	302 (5)	457 (3)	60
H4B	356 (4)	392 (5)	345 (3)	60
H5A	464 (5)	100 (5)	385 (4)	70
H5B	321 (5)	133 (5)	319 (4)	70
H5C	477 (5)	153 (5)	287 (3)	70

[a] B_{eq} is calculated from $^1/_3$ the trace of the $\mathbf{B}_{ij}$ matrix. H atoms are labeled according to the atom to which they are bonded, and B_{iso} is set to 1.1 B_{eq} of that atom.

refined with thermal parameters set to $1.1B_{eq}$ of the C atom to which they are bonded. The model converged for 1615 reflections and 148 variables with the agreement factors $R = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.043$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.044$. The maximum shift/error was 0.2 (associated with an H atom), the average shift/error was 0.04, and the goodness of fit value was 0.85, but the isotropic extinction parameter could not be refined. The highest peak in the final difference Fourier synthesis is 0.6 e Å^{-3} and is associated with S(1).

All computations were done with use of the XRAY-76 system of programs[10] implemented on the Honeywell computer at the University of Calgary. Atomic scattering factors used for non-hydrogen atoms were those of Cromer and Mann[13] and those for H atoms were from ref 14. Real and anomalous dispersion corrections were applied to all non-hydrogen atoms.[15] The final atomic coordinates of the non-hydrogen atoms are given in Table I.

Results and Discussion

Preparation of Mixed Cyanuric–Thiazyl Rings, $(R_2NCN)_x(NSCl)_2$ (x = 1, 2). The cycloaddition reaction of an organic nitrile with thiazyl units potentially represents a versatile synthesis of mixed cyanuric–thiazyl rings:

$$x\mathrm{RCN} + y\mathrm{NSCl} \rightarrow (\mathrm{RCN})_x(\mathrm{NSCl})_y \qquad (1)$$

This approach, however, usually gives the five-membered 1,2,3,5-dithiadiazolium cation **2** as the major product.[3,4] In an extension of our investigations of the reactions of dialkylcyanamides with sulfur–halogen compounds,[16] we have found that reaction 1 provides a convenient route to mixed cyanuric–thiazyl heterocycles where R = Me_2N, Et_2N, i-Pr_2N. The successful procedure involves the slow addition of the nitrile to a solution of $(NSCl)_3$ in CCl_4 at ca. 60 °C. By the appropriate choice of reaction conditions either the six-membered ring **1** or the eight-membered ring **4** (R = Me_2N) can be prepared.

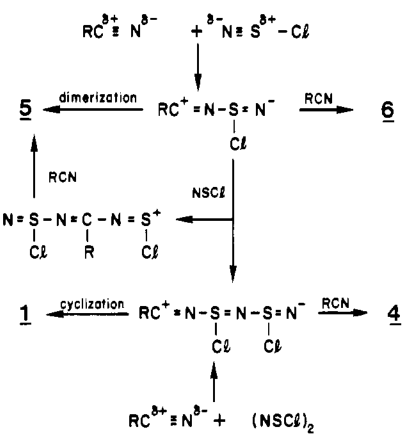

Figure 1. Scheme for the formation of mixed cyanuric–thiazyl rings from the cycloaddition reaction of an organic nitrile with NSCl monomer or the dimer $(NSCl)_2$.

The yields of the six-membered ring range from ca. 65% (R = i-Pr_2N) to ca. 90% (R = Me_2N or Et_2N). Optimum yields of **1** were achieved by *slow* addition of the nitrile, *dilute* solutions of reagents (ca. 0.1 M), and *careful purification* of $(NSCl)_3$ (prepared from S_4N_4 and SO_2Cl_2).[5] The use of slightly more concentrated solutions of the nitrile (0.5–1.0 M) caused the formation of a red oil in addition to **1**. The structure of **1** (R = Et_2N) was ascertained by X-ray crystallography (vide infra).

The *rapid* addition of a *10-fold* excess of dimethylcyanamide in CCl_4 (ca. 8 M) to a solution of $(NSCl)_3$ in CCl_4 (ca. 0.3 M) at 65 °C produces the eight-membered ring **4** (R = Me_2N) in ca. 85% yield (based on $(NSCl)_3$). The preparation of other derivatives of **4** was thwarted by the difficulty of separating large amounts of excess dialkylcyanamide from the product.

Heterocycle **4** (R = Me_2N) is thermally unstable and undergoes a quantitative ring contraction reaction in $CDCl_3$ or CH_3CN at 23 °C to give **1** and Me_2NCN as determined by ^1H NMR spectroscopy:

$$1,3\text{-}(\mathrm{Me_2NCN})_2(\mathrm{NSCl})_2 \rightarrow (\mathrm{Me_2NCN})(\mathrm{NSCl})_2 + \mathrm{Me_2NCN} \qquad (2)$$

It can, however, be recrystallized from nitromethane–diethyl ether at −20 °C without decomposition. The characterization of **4** is based on elemental analysis, the appearance of a peak at m/e 232 ($(Me_2NCN)_2(SN)_2^+$) in the mass spectrum, and the quantitative decomposition represented in eq 2. This behavior is in contrast to that of the related phosphazene–thiazyl ring system 1,3-$(Ph_2PN)_2(NSCl)_2$, which undergoes ring contraction via loss of NSCl.[17]

The heterocycle **5** (R = Me_2N), a structural isomer of **4**, was obtained as thermally stable orange crystals by the oxidative addition of Cl_2 (as SO_2Cl_2) across the S–S bond of 1,5-$Me_2NC(NSN)_2CNMe_2$[7] (cf. preparation of 1,5-$(Ph_2PN)_2(NSX)_2$ (X = Cl, Br)).[17]

Mechanism of the Cycloaddition Reaction. The high yields of **1** and **4** in the cycloaddition reaction (1) are remarkable in view of the lack of success reported in other investigations of the reactions of $(NSCl)_3$ with electron-rich organic substrates.[18] The reaction was deliberately conducted under conditions that are thought to favor the formation of NSCl monomer.[19-23] Mews

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(19) Although the species responsible for the green color of warm solutions of $(NSCl)_3$ has not been conclusively identified, it is generally assumed that NSCl monomer, a green gas, is a leading candidate (see, for example, ref 20–23).

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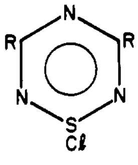
et al. have speculated, however, that the *dimeric species* $(NSCl)_2$ is involved in the formation of **1** (R = CF_3) from CF_3CN and $(NSCl)_3$ at 50 °C.[3] We arrived at a similar conclusion independently.[2]

The $R_2NCN/(NSCl)_3$ reaction was carried out in CCl_4 at 60 °C with use of a wide range of reagent stoichiometries and concentrations. Except in the case of R = C_6H_{11} (vide infra), the only products isolated were **1** or **4** and no evidence was obtained for the formation of significant amounts of **5** or **6**.[24-26] As indicated in Figure 1, the interaction of the nitrile with NSCl monomer is expected to give rise to the last two ring systems, in addition to the observed products **1** and **4**. The predominant formation of **1** and **4** strongly suggests the involvement of the linear intermediate $(R_2NCN)(NSCl)_2$ *in which the thiazyl groups are juxtaposed.* We believe, therefore, that our results are best explained by the interaction of the nitrile with the dimeric species $(NSCl)_2$, rather than NSCl monomer, to give this intermediate, which cyclizes or reacts with excess nitrile to give **1** or **4**, respectively.



6

Finally, it should be pointed out that the above procedure for the preparation of **1** appears to be limited to derivatives in which R is a dialkylamino group. The method was not successful for the preparation of **1** from other nitriles (R = *t*-Bu, Me_3Si, 4-$Me_2NC_6H_4$).

Formation and Characterization of $(C_6H_{11})_2NC(Cl)NS_3N_2^+Cl^-$. Unlike the other dialkylcyanamides, R_2NCN (R = Me, Et, *i*-Pr), the reaction of $(C_6H_{11})_2NCN$ with $(NSCl)_3$ in warm CCl_4 produced an insoluble product. The IR and mass spectra of this product were not consistent with those expected for a ring system of type **1** (R = C_6H_{11}). For example, the mass spectrum showed no peaks corresponding to $(\mathbf{1} - Cl)^+$ or $(\mathbf{1} - Cl_2)^+$, and the base peak was at *m/e* 92 ($S_2N_2^+$). Complete elemental analyses suggested the formula $(C_6H_{11})_2NCNS_3N_2Cl_2$. Indeed the same product was obtained from the reaction of $(C_6H_{11})_2NCN$ with $S_3N_2Cl_2$ in CH_2Cl_2. We suggest, therefore, that this product can be represented by structure **3**, the result of the addition of an S–Cl unit (of $S_3N_2Cl^+$) across the –C≡N bond of the nitrile (cf. ref 16). Attempts to grow single crystals of **3** suitable for X-ray crystallography from toluene or CCl_4–CH_2Cl_2 mixtures have yielded only thin needles. It should be noted, however, that the ^1H and ^{13}C NMR data indicate nonequivalent cyclohexyl groups with the nonequivalence being most pronounced for the carbon atoms attached to nitrogen.[27] The ^{13}C NMR signals of the cyclohexyl groups of **3** occur at δ 24.61 (C_4 and $C_{4'}$), 25.28 (C_3), 25.53 ($C_{3'}$), 28.78 (C_2), 29.23 ($C_{2'}$), 62.63 (C_1), and 70.70 ($C_{1'}$). For comparison the NMR spectrum of $(C_6H_{11})_2NCN$ shows signals at 25.08 (C_3 and C_4), 31.71 (C_2), and 57.96 (C_1). Thus the NMR data are consistent with structure **3** (R = C_6H_{11}), in which there is restricted rotation about the $(C_6H_{11})_2N{=\!\!-}C$ bond, with the result that one C_6H_{11} group will be in closer proximity to the Cl atom attached to carbon than the other. By contrast, ring systems of type **1** (R = Me_2N, Et_2N, *i*-Pr_2N) all show equivalent alkyl groups in their ^1H and ^{13}C NMR spectra and the signal for the ring carbon atom occurs at ca. 152 ppm (cf. 187.81 and 115.41 ppm for the nitrile carbon atoms of **3** (R = C_6H_{11} and $(C_6H_{11})_2NCN$, respectively)).

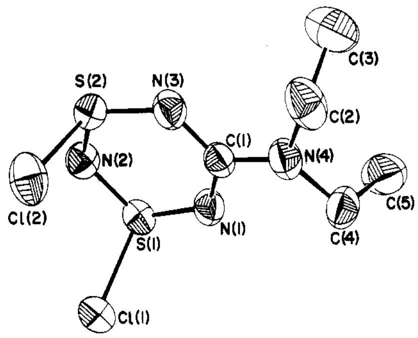


Figure 2. ORTEP plot (50% probability ellipsoids) for $(Et_2NCN)(NSCl)_2$ showing the atomic numbering scheme.

Table II. Bond Lengths (Å) and Angles (deg) for $(Et_2NCN)(NSCl)_2$

N1–S1	1.566 (3)	C1–N1	1.345 (4)
S1–Cl1	2.226 (1)	C1–N4	1.324 (5)
S1–N2	1.591 (3)	N4–C2	1.475 (5)
N2–S2	1.600 (3)	N4–C4	1.472 (5)
S2–Cl2	2.203 (2)	C2–C3	1.464 (8)
S2–N3	1.565 (4)	C4–C5	1.484 (8)
N3–C1	1.357 (4)		
C1–N1–S1	122.9 (2)	N3–C1–N1	126.6 (4)
N1–S1–N2	113.2 (1)	N3–C1–N4	116.2 (3)
N1–S1–Cl1	102.6 (1)	N1–C1–N4	117.1 (3)
N2–S1–Cl1	102.5 (1)	C1–N4–C2	121.0 (3)
S1–N2–S2	118.5 (2)	C1–N4–C4	120.8 (3)
N2–S2–N3	113.2 (2)	C2–N4–C4	118.1 (4)
N2–S2–Cl2	101.6 (1)	N4–C2–C3	113.0 (4)
N3–S2–Cl2	103.2 (1)	N4–C4–C5	114.2 (4)
S2–N3–C1	121.9 (2)		

Although the reason for the different reaction pathway in the case of $(C_6H_{11})_2NCN$ is not obvious, we point out that compound **3** is formally related to the dithiazolium salts **2** by the addition of one NSCl unit. Banister et al. have envisaged the formation of **2** to involve the cycloaddition of RCN with NSCl and a sulfur atom.[4] In the light of our discussion of the mechanism of the $R_2NCN/(NSCl)_3$ reaction (vide supra) it seems reasonable to propose that **3** is formed by a similar cycloaddition with the dimer $(NSCl)_2$ rather than NSCl monomer. The source of the additional sulfur atom in these cycloaddition reactions is, however, uncertain.

Crystal and Molecular Structure of $(Et_2NCN)(NSCl)_2$. An ORTEP drawing the molecule is shown in Figure 2. Table I gives the positional parameters, and Table II contains the bond lengths and bond angles for non-hydrogen atoms in $(Et_2NCN)(NSCl)_2$. The molecule consists of an almost planar six-membered ring (maximum deviation is 0.11 Å for N(2)) with the two chlorine substituents in a cis conformation (*d*(S–Cl) = 2.203 (2) and 2.226 (1) Å). The planar geometry at the exocyclic N(4) atom and the short C(1)–N(4) distance of 1.324 (5) Å are indicative of sp^2 hybridization. These structural features and the endocyclic bond lengths and bond angles are essentially similar to those reported by Roesky et al. for the Me_2N derivative of **1**,[1] and further discussion is unnecessary.

Since the original submission of this manuscript, the reaction of 1,5-$Me_2NC(NSN)_2CNMe_2$ with 2 mol of Cl_2 (as Cl_2 gas) to give the *S*-chloro salt $[1,5\text{-}(Me_2NCN)_2(NSCl)(NS)]^+[Cl_3]^-$, which was structurally characterized by X-ray crystallography, has been reported in a preliminary communication.[28] We have prepared the bromo analogue of this salt $[1,5\text{-}(Me_2NCN)_2(NSBr)(NS)]^+[Br_3]^-$ as purple-black microcrystals by the reaction of 1,5-$Me_2NC(NSN)_2CNMe_2$ with Br_2 in CCl_4 or CH_3CN.[2] Anal. Calcd for $C_6H_{12}Br_4N_4S_2$: C, 13.05; H, 2.17; N, 15.23. Found: C, 13.36; H, 2.32; N, 15.26. Raman (cm^{-1}): $\nu_s(Br_3^-)$ 162.

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Conclusion

The cycloaddition reaction between dialkylcyanamides and NSCl units generated from $(NSCl)_3$ in warm carbon tetrachloride represents a much improved synthesis of the six-membered rings $(R_2NCN)(NSCl)_2$ and provides a route to the first example of an eight-membered mixed cyanuric–thiazyl ring, 1,3-$(R_2NCN)_2(NSCl)_2$. Easier access to these bifunctional heterocycles should facilitate investigations of their chemical reactions. This study also draws attention to the need for a better understanding of the species formed from $(NSCl)_3$ in warm solvents. A ^{15}N NMR study of ^{15}N-enriched $(NSCl)_3$ in various solvents at different temperatures should be informative.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Supplementary Material Available: Listings of anisotropic thermal parameters, bond distances and angles involving H atoms, and structure factors for $(Et_2NCN)(NSCl)_2$ (14 pages). Ordering information is given on any current masthead page.

Contribution from the Central Leather Research Institute,
Adyar, Madras 600 020, India

Synthesis and Characterization of New Chromium(III) Complexes of Macrocyclic Ligands

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Synthesis of new chromium(III) complexes of tetraaza macrocyclic ligands having 13-membered or symmetrical 14-membered intraligand ring sizes is reported here. The complexes of the formulation *trans*-$\mathrm{Cr(macrocycle)(X)(H_2O)^{(3-n)+}}$, where macrocycle = Me_6[14]ane, Me_6[14]diene, Me_4[14]tetraene, or Me_2[13]diene, X = OH_2, NCS^-, or $CHCl_2^-$, and n = 0 or 1, have been prepared and characterized by means of elemental analysis, paramolybdate titrations, conductance measurements, and electronic as well as infrared spectra. Considerable steric strain in the cases of macrocycles with imine bonds as in Me_4[14]tetraene and Me_6[14]diene has been inferred from electronic spectral data. Firm experimental evidence for ring opening and breakdown of the macrocyclic ligands investigated under synthetic conditions is also presented. The possible steric advantages of symmetrical 14-membered macrocycles in stabilizing unusual oxidation states of chromium are also highlighted.

Introduction

Whereas many complexes of cobalt(III) with macrocyclic ligands of various structure have been reported,[1-3] the analogous chromium(III) derivatives have been rather few. Until 1982, the only macrocyclic complexes of chromium(III) which had been investigated systematically were those with 1,4,8,11-tetraazacyclotetradecane (cyclam) and 1,5,9,12-tetraazacyclopentadecane ([15]ane).[4-6] Although macrocyclic complexes of Cr(III) were relatively few, the preparation and reactivities of many complexes of the metal ion with pseudomacrocyclic ligands had been reported.[7,8] Recently, House et al.[9] reported the synthesis of a dichloro derivative of a Cr(III) macrocycle. While our work was in progress, Swisher et al.[10] reported also an elegant study in which ligand field effects and the importance of intraligand ring size of the macrocyclic ligands in influencing the cis and trans structures of octahedral complexes were considered. Their study[10] indicated that, in the formation of complexes having equatorially coordinated macrocyclic ligands, the Cr(III) ion shows preference to ligands having either unsymmetrical [14]-membered or [15]-membered intraligand ring sizes. At the time of our study, there were only a few examples for *trans*-$\mathrm{Cr(macrocycle)(X)_2^{n+}}$, where macrocycle is a symmetrical [14]-membered ligand with the exception of cyclam.

As a part of our efforts[11] to stabilize an unusual oxidation state like Cr(IV) by taking advantage of suspected Franck–Condon barriers for the conversion of octahedral Cr(IV) to tetrahedral Cr(V), we investigated the synthesis of a few Cr(III) macrocyclic complexes. Some of the difficulties in the synthesis of Cr(III) macrocyclic complexes with symmetrical [14]-membered ligands have been often attributed to the relatively smaller intraligand ring size of the macrocycles compared to the size of the Cr(III)[6,10] ion. Since Cr(IV), by virtue of its higher positive charge, is believed to be of smaller size than Cr(III), it may be expected that macrocyclic ligands having smaller intraligand ring size than needed for Cr(III) may minimize the Franck–Condon barriers for the conversion of Cr(III) to Cr(IV). Therefore, we report here the synthesis of a series of complexes of Cr(III) with macrocyclic ligands of structures shown in Figure 1 and with either symmetrical [14]-membered or unsymmetrical [13]-membered intraligand ring sizes.

Experimental Section

Materials. The free lgiands 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (Me_6[14]ane), 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (Me_6[14]diene), and 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene (Me_4[14]tetraene) were prepared by using known procedures.[12-14] Although the solvents used in this study were generally of reagent grade, most solvents like acetonitrile, methanol, tetrahydrofuran, and di-

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