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THE CRYSTAL STRUCTURE OF CHLOROTHIODIAZYL CHLORIDE, $S_3N_2Cl_2$

Allan Zalkin, Ted E. Hopkins, and David H. Templeton

April 1966

CONTRIBUTION FROM THE LAWRENCE RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY,
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The Crystal Structure of Chlorothiodiazyl Chloride, $S_3N_2Cl_2$ ¹

BY ALLAN ZALKIN, TED E. HOPKINS, AND DAVID H. TEMPLETON

$S_3N_2Cl_2$ crystallizes in the monoclinic space group $P2_1$ with cell dimensions $a = 6.546 \text{ \AA}$, $b = 8.600 \text{ \AA}$, $c = 5.508 \text{ \AA}$, and $\beta = 102.37^\circ$; there are two formula units per unit cell. The material is a salt consisting of a chloride anion, and a $S-N-S-N-S-Cl^+$ cation. The sulfur and nitrogen atoms form a puckered five membered ring.

Introduction

$S_3N_2Cl_2$ was first identified by E. Demarcay² who prepared it by reacting S_2Cl_2 or S_2Cl_2 with S_4N_4 . A. Meuwesen³ prepared $S_3N_2Cl_2$ by reacting $(NSCl)_3$ with S_2Cl_2 . More recently Jolly, Maguire and Rabinovich⁴ produced the material by refluxing a suspension of ammonium chloride in S_2Cl_2 . An X-ray crystal structure analysis was undertaken to determine the molecular structure of this compound.

Experimental

$S_3N_2Cl_2$ is a yellow crystalline salt which decomposes in the air. The salt was removed from its container in a nitrogen filled dry box, crushed, and sieved. Several crystal fragments of about 0.3 mm were introduced into tapered quartz capillaries of about the same size and sealed. With patient use of a microscope and a file, a single crystal fragment was isolated and wedged in the capillary; the capillary was fire sealed to a final length of about one cm. The crystal fragment

was an irregular plate with dimensions approximately 0.3 x 0.4 x 0.2 mm. Some decomposition of the crystal surface did occur as the crystal lost its yellow color and took on a blackish tinge; however, the crystal diffracted X-rays well and no further decomposition was encountered. The crystal was oriented with the monoclinic b axis parallel to the length of the capillary.

A General Electric XRD-5 apparatus equipped with a quarter circle Eulerian cradle type goniostat, a scintillation counter, a pulse height discriminator, and a molybdenum X-ray tube was used to measure the cell dimensions and the intensities. The X-ray tube was operated at 20 ma and 40 kv. The primary X-ray beam was filtered with a Zr filter.

The measured monoclinic cell dimensions based on $\lambda_{\text{K}\alpha 1} = 0.70926 \text{ \AA}$ are: $a = 6.546 \pm 0.007 \text{ \AA}$, $b = 8.600 \pm 0.004 \text{ \AA}$, $c = 5.508 \pm 0.005 \text{ \AA}$, and $\beta = 102.37 \pm 0.03^\circ$. The observed density was 2.0 g/ml, suggesting two formula units per unit cell; the calculated X-ray density is $2.14 \pm 0.01 \text{ g/ml}$. The observed extinctions are $0k0$, $k = 2n + 1$, and the space group is $P2_1$.

1022 independent reflections were each counted for 10 seconds using a stationary-crystal-stationary-counter technique. These are all of the data in a quarter of the sphere of reflection where $2\theta < 62^\circ$, or $\sin\theta / \lambda < 0.726$. Background was plotted as a function of 2θ and applied routinely to the reflections with the exception of a minority of intensities where very intense reflections would spill over on weaker ones in the same row; these backgrounds were then measured individually. Typical background counts were 20, 10, and 6 counts per second at 20° , 40° and 60° of 2θ respectively. The most intense reflection ($10\bar{2}$) was about 56,000 counts per second.

All of the computations were performed with an IBM 7044 computer with a 32K memory. The least squares program used minimizes the function $\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2$, where w is the weighting factor, F_o and F_c are the observed and calculated structure factors. All of the reflections were given unit weights with the exception of the six most intense reflections which toward the end of the computations were given zero weight.

Anisotropic temperature factors have the form $\exp(-h^2 \beta_{11} + k^2 \beta_{22} + l^2 \beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$, however, for our convenience the program converts these thermal parameters to B_{ij} in $\text{\AA}^2$ where $B_{ij} = 4\beta_{ij} / a_i^* a_j^*$ and a_i^* is the i th reciprocal axis length.

Atomic scattering factors⁵ for neutral S, Cl, and N were used. S and Cl were both corrected for the anomalous dispersion effect, with $\Delta f' = 0.1$ and $\Delta f'' = 0.2$ electrons.⁶ The real component $\Delta f'$ was added to the scattering factors, the imaginary component $\Delta f''$ was incorporated into the actual least squares calculation.

The "unreliability index" reported throughout this paper is $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.

Determination of Structure

The structure was deduced from the three-dimensional Patterson function. A careful investigation of the function gave us trial positions for the three sulfur, two chlorine and one nitrogen atoms; a Fourier based on the phases of the six atom structure then gave the last nitrogen atom. As the atomic positions were deduced their parameters were introduced into a least-squares refinement using isotropic temperature factors. Starting with three atoms (Cl, S, N) the structure refined to $R = 0.47$, with four atoms (2Cl, S, N) $R = 0.37$, with five atoms (2Cl, 2S, N) $R = 0.29$, with six atoms (2Cl, 3S, N) $R = 0.13$, and finally all seven

atoms $R = 0.09$. At the five-atom stage a non-existent atom was introduced, but was rejected by the least squares via a large temperature parameter. The final identification of the sulfur and chlorine atoms was determined by studying the structure geometry and the interatomic distances. Anisotropic temperature factors were applied to all of the atoms and R reduced to 0.048. A few blunders in the data were detected, and these reflections were remeasured and corrected. Large discrepancies were present in the six most intense reflections which could be attributed to extinction effects and to the non-linearity of the scintillation counter at high counting rates. These six reflections, all those with counting rates greater than 20,000 counts per second, were assigned zero weight. The R decreased to 0.0292. The introduction of the imaginary dispersion correction increased R to 0.0293; the y parameters were all reversed and R became 0.0291. This difference is so small that there may be some doubt concerning which structure is correct, but we report the one which gave the best agreement. The other structure is almost identical except that the two nitrogen atoms are shifted 0.014 Å toward zero along the y axis. The only bond lengths which are significantly different are S(1)-N(1) and S(1)-N(2), which are respectively longer and shorter by about 0.010 Å in the other structure. This relative shift of light and heavy atoms along a polar direction when refined in this manner, or "polar dispersion shift", is an effect which has also been observed in thorium nitrate pentahydrate⁷ and in a diiodocyclobutene⁸ and which is explained in more detail elsewhere.⁷ In the present case the ambiguity is of trivial importance to the chemical interpretation.

Results

A list of the atomic and thermal parameters of $S_3N_2Cl_2$ is shown in the following Table I.

TABLE I.

POSITIONAL^a AND THERMAL^b PARAMETERS IN $S_3N_2Cl_2$.

Atom	<u>x</u>	<u>y</u>	<u>z</u>	<u>B</u> ₁₁	<u>B</u> ₂₂	<u>B</u> ₃₃	<u>B</u> ₁₂	<u>B</u> ₁₃	<u>B</u> ₂₃
Cl(1)	0.1017	0.0 ^c	0.4844	3.32	5.33	3.63	1.18	1.51	1.24
Cl(2)	0.1975	-0.3541	0.1028	2.86	2.83	3.08	0.11	0.50	-0.09
S(1)	0.6099	0.1671	0.3235	2.37	3.48	2.81	0.37	0.37	-0.11
S(2)	0.2303	0.0264	0.1552	2.69	2.14	2.82	0.13	0.88	0.11
S(3)	0.2161	0.2734	0.11148	2.56	2.10	3.61	0.11	0.06	0.13
N(1)	0.4756	0.0105	0.2436	2.54	2.88	3.60	0.85	1.02	0.46
N(2)	0.4558	0.3039	0.2549	2.98	2.68	3.55	-0.10	0.30	-0.89

^aEstimated standard deviations of the positional parameters for S and Cl are less than 0.0003, and for N are less than 0.0008.

^bEstimated standard deviations of the thermal parameters for S and Cl are about 0.05, and for N they are about 0.2.

Units of B_{ij} are $\text{\AA}^2$.

^cPolar space group $P2_1$ requires one y parameter to be fixed.

Table II presents a list of the observed and calculated structure factors.

TABLE II.

OBSERVED AND CALCULATED STRUCTURE FACTORS (X10) OF $S_3N_2Cl_2$.

ASTERISK INDICATES ZERO WEIGHT.

H ₁ 0 0	-5 104 101	-5 51 54	6 71 70	1 84 82	L FOMS FCAL	4 50 49	H ₁ 5 0	-1 47 50	H ₁ 7 7
L FOMS FCAL	-4 114 112	-4 62 64	7 35 33	2 21 19	-4 65 63	5 37 37	L FOMS FCAL	-0 52 51	L FOMS FCAL
1 191 188	-3 22 21	-3 167 163	H ₁ 2 3	3 25 25	-5 85 85	6 41 40	-7 51 50	-4 112 112	2 60 60
2 75 71	-2 937 1140	-1 67 65	H ₁ 2 3	4 23 22	-6 77 77	-3 98 98	H ₁ 3 5	-3 14 16	3 62 62
3 240 241	-1 406 473*	-1 127 122	L FOMS FCAL	H ₁ 2 11	-7 31 31	H ₁ 3 5	-6 30 30	-2 53 49	-1 140 131
4 145 144	-0 78 78	-0 69 66	-7 39 39	H ₁ 2 11	-7 41 38	L FOMS FCAL	-5 126 122	-3 14 16	3 62 62
5 247 247	1 476 440	1 99 100	-6 70 70	H ₁ 2 11	-7 41 38	L FOMS FCAL	-5 101 157	-2 24 27	1 70 69
6 65 61	2 712 717	2 29 34	-5 106 183	-3 31 31	-0 96 89	-6 68 66	-3 51 51	-0 144 141	L FOMS FCAL
7 12 8	3 513 516	3 91 91	-4 30 31	-2 90 92	1 101 101	-6 68 66	-2 24 27	1 70 69	-5 5 12
H ₁ 0 1	4 63 36	4 41 38	-3 130 129	-1 76 77	2 3 3	-3 72 72	-3 31 31	-0 250 240	3 33 37
L FOMS FCAL	0 93 89	6 39 41	-1 242 236	1 10 23	4 95 96	-2 53 51	1 54 48	-2 35 24	-7 21 23
1 476 510*	7 48 44	-0 146 142	2 49 48	5 67 62	-1 451 451	2 152 154	-1 45 40	-1 45 40	-0 71 73
2 118 117	H ₁ 1 4	2 72 71	H ₁ 2 12	H ₁ 3 7	1 49 100	4 153 154	-4 31 31	1 21 17	H ₁ 0 0
3 104 100	L FOMS FCAL	-6 54 40	3 415 418	L FOMS FCAL	2 146 143	5 42 42	-5 25 27	2 19 22	L FOMS FCAL
4 122 123	L FOMS FCAL	-5 73 74	4 105 103	-1 28 26	-6 47 48	3 51 52	-2 12 16	-3 34 30	-5 28 27
5 87 86	-7 33 36	-5 73 74	5 70 70	-0 55 55	-6 47 48	3 51 52	-2 12 16	-3 34 30	-5 28 27
6 43 42	-6 104 101	-4 51 51	6 35 36	-4 27 44	5 47 49	L FOMS FCAL	-0 32 32	H ₁ 0 2	-5 20 19
7 80 78	-5 33 33	-3 61 61	6 35 36	H ₁ 3 0	-3 67 68	6 9 13	-6 21 21	7 12 10	-4 15 17
H ₁ 0 2	-4 169 168	-2 286 287	7 30 32	H ₁ 3 0	-3 67 68	6 9 13	-6 21 21	7 12 10	-4 15 17
L FOMS FCAL	-2 106 107	-0 94 92	H ₁ 2 4	-7 11 5	-1 50 49	H ₁ 4 4	-5 107 103	H ₁ 5 10	-3 86 85
-0 434 406*	-1 364 375	1 134 131	L FOMS FCAL	-6 106 108	-0 83 79	L FOMS FCAL	-7 87 87	L FOMS FCAL	-1 47 48
1 273 302	-0 125 142	2 163 183	-7 50 50	-5 285 287	1 45 45	-7 27 29	-3 9 9	L FOMS FCAL	-1 47 48
2 729 124	1 319 312	3 170 173	-6 74 75	-4 43 44	2 50 58	-6 59 59	-2 26 27	-3 36 34	-0 36 37
3 253 258	2 173 174	4 15 15	-5 7 3	-3 76 74	3 27 26	-6 67 66	-1 56 59	-2 28 28	1 54 52
4 167 166	3 182 183	5 46 47	-2 23 13	-2 311 307	4 104 104	-0 165 163	-0 118 117	-1 9 11	2 72 72
5 174 178	5 80 81	-2 130 127	-0 429 416	H ₁ 3 8	-1 87 88	3 42 42	4 20 21	H ₁ 0 0	-3 43 40
6 87 87	5 80 81	-2 130 127	-0 429 416	H ₁ 3 8	-1 87 88	3 42 42	4 20 21	H ₁ 0 0	-3 43 40
7 12 5	6 61 63	L FOMS FCAL	-1 251 235	1 110 107	H ₁ 3 8	-1 87 88	3 42 42	4 20 21	H ₁ 0 0
H ₁ 0 3	-4 16 13	1 102 93	3 314 313	4 141 140	-4 50 50	2 136 138	H ₁ 5 2	-5 26 22	1 20 14
L FOMS FCAL	-3 33 34	2 101 101	4 141 140	-4 50 50	2 136 138	H ₁ 5 2	-5 26 22	1 20 14	H ₁ 0 0
1 331 348	L FOMS FCAL	-2 49 33	3 62 62	4 213 212	6 12 10	-2 144 142	4 89 89	-7 56 57	-4 76 75
2 454 460	-7 72 72	-1 84 85	4 213 212	6 12 10	-2 144 142	4 89 89	-7 56 57	-4 76 75	-4 76 75
3 203 205	-6 42 41	-0 43 43	5 33 38	6 61 64	L FOMS FCAL	-0 152 149	-5 135 137	-2 243 243	L FOMS FCAL
4 146 147	-5 106 107	1 45 42	6 61 64	H ₁ 2 5	-7 42 44	3 134 136	-7 26 28	-3 44 44	-0 145 145
5 35 33	2 20 54	-5 20 18	-6 115 113	-3 183 175	-2 263 253	L FOMS FCAL	-2 80 77	2 40 40	H ₁ 0 1
6 87 82	-3 152 131	3 75 74	L FOMS FCAL	-6 62 62	3 134 136	-7 26 28	-3 44 44	-0 145 145	-5 94 94
7 64 64	-2 321 320	4 50 52	-5 20 18	-6 115 113	-3 183 175	-2 263 253	L FOMS FCAL	-2 80 77	2 40 40
H ₁ 0 4	-0 243 238	H ₁ 1 10	-5 127 127	-4 44 45	-2 263 253	L FOMS FCAL	-2 80 77	2 40 40	H ₁ 0 1
L FOMS FCAL	1 324 324	L FOMS FCAL	-4 44 45	-2 263 253	L FOMS FCAL	-2 80 77	2 40 40	H ₁ 0 1	H ₁ 0 1
-0 107 108	2 201 274	-4 44 45	-2 263 253	L FOMS FCAL	-2 80 77	2 40 40	H ₁ 0 1	H ₁ 0 1	H ₁ 0 1
1 128 132	3 218 217	-4 44 45	-2 263 253	L FOMS FCAL	-2 80 77	2 40 40	H ₁ 0 1	H ₁ 0 1	H ₁ 0 1
2 55 55	4 156 154	-3 34 37	-2 314 310	-0 184 178	-4 0 4	-1 240 203	3 49 48	H ₁ 0 1	1 150 152
3 304 313	5 18 17	-2 36 38	-1 374 362	1 133 128	-3 33 33	-0 240 234	4 66 66	H ₁ 0 1	1 150 152
4 57 53	1 37 63	-0 16 16	1 148 147	3 0 8	-1 15 15	2 44 43	3 49 48	H ₁ 0 1	1 150 152
5 46 45	7 40 78	1 49 53	2 141 141	4 193 189	-0 121 119	3 91 89	H ₁ 5 3	-5 41 43	H ₁ 0 1
6 40 47	2 79 61	3 25 28	5 59 60	6 8 8	-2 46 46	5 38 38	H ₁ 5 3	-5 41 43	H ₁ 0 1
7 27 28	H ₁ 1 3	3 49 50	4 84 87	5 60 64	7 46 46	5 38 38	H ₁ 5 3	-5 41 43	H ₁ 0 1
H ₁ 0 5	-6 111 112	H ₁ 1 11	-7 20 18	H ₁ 2 0	-0 172 121	L FOMS FCAL	-6 40 43	-3 33 33	H ₁ 0 1
L FOMS FCAL	-6 111 112	H ₁ 1 11	-7 20 18	H ₁ 2 0	-0 172 121	L FOMS FCAL	-6 40 43	-3 33 33	H ₁ 0 1
1 174 178	-4 204 204	-3 67 69	-7 14 16	-5 86 84	-6 64 67	-1 103 105	-4 11 12	-2 71 69	-4 37 43
2 173 149	-5 317 320	-3 67 69	-7 14 16	-5 86 84	-6 64 67	-1 103 105	-4 11 12	-2 71 69	-4 37 43
3 162 165	-5 317 320	-3 67 69	-7 14 16	-5 86 84	-6 64 67	-1 103 105	-4 11 12	-2 71 69	-4 37 43
4 54 47	-2 55 56	-2 22 22	-7 14 16	-5 86 84	-6 64 67	-1 103 105	-4 11 12	-2 71 69	-4 37 43
5 54 47	-2 55 56	-2 22 22	-7 14 16	-5 86 84	-6 64 67	-1 103 105	-4 11 12	-2 71 69	-4 37 43
6 40 47	-0 691 776*	-0 113 113	-5 79 77	-3 124 127	-2 32 33	-2 117 115	1 76 77	H ₁ 0 2	-2 79 78
7 75 71	1 252 254	1 65 67	-4 121 117	-1 40 43	-1 91 91	-1 90 90	3 66 64	4 46 45	-6 57 57
H ₁ 0 6	2 2 2	2 2 2	2 2 2	2 2 2	2 2 2	2 2 2	2 2 2	2 2 2	2 2 2
L FOMS FCAL	4 101 100	H ₁ 1 12	-0 117 175	3 123 118	4 156 153	H ₁ 3 11	5 50 54	L FOMS FCAL	-2 103 109
-0 145 146	5 195 194	H ₁ 1 12	-0 117 175	3 123 118	4 156 153	H ₁ 3 11	5 50 54	L FOMS FCAL	-2 103 109
1 115 116	6 204 204	-2 34 37	2 109 109	3 83 82	5 49 46	L FOMS FCAL	-2 103 109	-1 40 40	-3 33 39
2 54 58	7 47 45	-2 34 37	2 109 109	3 83 82	5 49 46	L FOMS FCAL	-2 103 109	-1 40 40	-3 33 39
3 37 38	H ₁ 1 4	-0 17 13	4 30 29	6 8 8	-2 52 52	-6 12 12	-5 53 55	-2 23 23	-4 38 34
4 50 50	H ₁ 1 4	-0 17 13	4 30 29	6 8 8	-2 52 52	-6 12 12	-5 53 55	-2 23 23	-4 38 34
5 97 96	L FOMS FCAL	1 40 40	5 49 49	H ₁ 2 0	-7 13 11	2 45 45	-3 42 42	-2 124 125	4 12 17
6 80 81	-7 33 34	H ₁ 2 0	6 59 54	H ₁ 2 0	-7 13 11	2 45 45	-3 42 42	-2 124 125	4 12 17
H ₁ 0 7	-6 41 41	L FOMS FCAL	-6 13 11	2 45 45	-3 42 42	-2 124 125	4 12 17	H ₁ 0 3	-6 14 21
L FOMS FCAL	-6 41 41	L FOMS FCAL	-6 13 11	2 45 45	-3 42 42	-2 124 125	4 12 17	H ₁ 0 3	-6 14 21
1 179 182	-5 53 53	-6 103 101	-6 50 59	-5 86 84	-6 64 67	-1 103 105	-4 11 12	-2 71 69	-4 37 43
2 20 22	-0 145 146	-1 40 43	-2 34 37	2 109 109	3 83 82	5 49 46	L FOMS FCAL	-2 103 109	-1 40 40
3 74 79	-1 158 151	-4 403 407	-4 74 74	-3 211 205	L FOMS FCAL	-0 27 29	1 13 14	L FOMS FCAL	-2 122 121
4 25 25	-0 119 116	-1 427 432	-3 46 45	-2 144 144	1 16 16	3 99 87	-5 57 54	L FOMS FCAL	-2 122 121
5 60 60	1 188 187	-2 53 53	-7 87 86	-1 81 81	-6 22 24	2 127 125	4 24 27	-4 25 23	-6 117 116
6 29 24	2 65 65	-1 104 178	-1 102 103	-0 83 74	-5 107 107	3 17 21	5 50 54	-5 14 15	-3 12 16
H ₁ 0 8	3 84 87	-0 349 349	-0 41 88	1 562 560	-4 169 165	4 76 76	H ₁ 5 5	-0 151 145	-2 48 45
L FOMS FCAL	4 80 80	1 726 776*	1 84 84	2 166 162	-3 273 268	-2 450 444	H ₁ 5 5	-0 151 145	-2 48 45
1 115 116	5 53 51	2 131 122	2 63 63	3 80 86	-2 450 444	-4 64 72	-4 40 41	3 27 27	-1 107 108
2 54 58	7 47 45	-2 34 37	2 109 109	3 83 82	5 49 46	L FOMS FCAL	-2 103 109	-1 40 40	-3 33 39
3 37 38	H ₁ 1 4	-0 17 13	4 30 29	6 8 8	-2 52 52	-6 12 12	-5 53 55	-2 23 23	-4 38 34
4 50 50	H ₁ 1 4	-0 17 13	4 30 29	6 8 8	-2 52 52	-6 12 12	-5 53 55	-2 23 23	-4 38 34
5 97 96	L FOMS FCAL	1 40 40	5 49 49	H ₁ 2 0	-7 13 11	2 45 45	-3 42 42	-2 124 125	4 12 17
6 80 81	-7 33 34	H ₁ 2 0	6 59 54	H ₁ 2 0	-7 13 11	2 45 45	-3 42 42	-2 124 125	4 12 17
H ₁ 0 9	-6 41 41	L FOMS FCAL	-6 13 11	2 45 45	-3 42 42	-2 124 125	4 12 17	H ₁ 0 3	-6 14 21
L FOMS FCAL	-6 41 41	L FOMS FCAL	-6 13 11	2 45 45	-3 42 42	-2 124 125	4 12 17	H ₁ 0 3	-6 14 21
1 179 182	-5 53 53	-6 103 101	-6 50 59	-5 86 84	-6 64 67	-1 103 105	-4 11 12	-2 71 69	-4 37 43
2 20 22	-0 145 146	-1 40 43	-2 34 37	2 109 109	3 83 82	5 49 46	L FOMS FCAL	-2 103 109	-1 40 40
3 74 79	-1 158 151	-4 403 407	-4 74 74	-3 211 205	L FOMS FCAL	-0 27 29	1 13 14	L FOMS FCAL	-2 122 121
4 25 25	-0 119 116	-1 427 432	-3 46 45	-2 144 144	1 16 16	3 99 87	-5 57 54	L FOMS FCAL	-2 122 121
5 60 60	1 188 187	-2 53 53	-7 87 86	-1 81 81	-6 22 24	2 127 125	4 24 27	-4 25 23	-6 117 116
6 29 24	2 65 65	-1 104 178	-1 102 103	-0 83 74	-5 107 107	3 17 21	5 50 54	-5 14 15	-3 12 16
H ₁ 0 10	3 84 87	-0 349 349	-0 41 88	1 562 560	-4 169 165	4 76 76	H ₁ 5 5	-0 151 145	-2 48 45
L FOMS FCAL	4 80 80	1 726 776*	1 84 84	2 166 162	-3 273 268	-2 450 444	H ₁ 5 5	-0 151 145	-2 48 45
1 115 116	5 53 51	2 131 122	2 63 63	3 80 86	-2 450				

The most interesting result of this work is the apparent ionic nature of the material. The material consists of a $S_3N_2Cl^+$ ion and a Cl^- ion. The chloride ion is $Cl(2)$ and its closest approaches are to $S(1)$ at 2.90 Å, $S(3)$ at 2.93 Å, and $S(2)$ at 3.04 Å. Figure 1 shows a sketch of the $S_3N_2Cl^+$ ion labelled with distances and angles.

The three sulfurs and two nitrogens form a slightly puckered five membered ring with a Cl atom, $Cl(1)$ attached to the thio sulfur, i.e. $Cl-S-N-S-N-S$. The puckering can be described as a chair form in the following sense. If a plane is drawn through the three sulfur atoms, the $Cl(1)$ atom is 2.09 Å above the plane, $N(1)$ is 0.188 Å below the plane, and the opposing $N(2)$ atom is 0.140 Å above the plane.

The five membered ring in $S_3N_2Cl_2$ is the smallest such ring system in a series of cyclic azyl systems. Six membered rings are present in $(NSOCl)_3$,⁹ $(NSCl)_3$,¹⁰ and $(NSF)_3$,¹¹ a seven membered ring is present in $S_4N_3NO_3$,¹² and an eight membered ring in $N_4S_4H_4$.¹³ In all these cases the nitrogens are separated by sulfur; and halogen, when present, is bonded to sulfur. Table III shows a comparison of the common bonds in these compounds.

TABLE III

SELECTED BOND LENGTHS IN SOME AZYL RING SYSTEMS

Formula	S-S	S-N	S-Cl	Reference
$\text{Cl-S-N-S-N-S}^+\text{Cl}^-$	2.136 Å	1.543-1.617 Å	2.168 Å	This work
$\begin{array}{c} \text{Cl} \quad \text{Cl} \quad \text{Cl} \\ \text{S-N-S-N-S-N} \end{array}$		1.600-1.614 Å	2.084-2.150 Å	(10)
$\begin{array}{c} \text{Cl} \quad \text{Cl} \quad \text{Cl} \\ \text{S-N-S-N-S-N} \\ \text{O} \quad \text{O} \quad \text{O} \end{array}$		1.546-1.578 Å	1.991-1.999 Å	(9)
$\begin{array}{c} \text{F} \quad \text{F} \quad \text{F} \\ \text{S-N-S-N-S-N} \end{array}$		1.540-1.660 Å		(11)
$\text{S-N-S-N-S-N-S}^+\text{NO}_3^-$	2.064 Å	1.493-1.582 Å		(12)
$\text{N}_4\text{S}_4\text{H}_4$		1.65		(13)

Figure 2 shows the packing in the crystal as seen in projection down the c axis.

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Captions

Figure 1.- Distances and angles in $S_3N_2Cl^+$. The estimated standard deviations are about 0.005 Å on the distances, and about 0.3° on the angles.

Figure 2.- Projection of $S_3N_2Cl_2$ down the c axis.

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Figure 1.

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Figure 2.

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