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THE CRYSTAL STRUCTURE OF CHLOROTHIODIAZYL CHLORIDE, $S_3N_2Cl_2$

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The Crystal Structure of Chlorothiodiazyl Chloride, $S_3N_2C\ell_2$[1]

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

$S_3N_2C\ell_2$ crystallizes in the monoclinic space group $P2_1$ with cell dimensions $\underline{a}$ = 6.546 Å, $\underline{b}$ = 8.600 Å, $\underline{c}$ = 5.508 Å, and β = 102.37°; there are two formula units per unit cell. The material is a salt consisting of a chloride anion, and a $\underbrace{S\text{-}N\text{-}S\text{-}N\text{-}S}\text{-}C\ell^+$ cation. The sulfur and nitrogen atoms form a puckered five membered ring.

Introduction

$S_3N_2C\ell_2$ was first identified by E. Demarcay[2] who prepared it by reacting $SC\ell_2$ or $S_2C\ell_2$ with S_4N_4. A. Meuwsen[3] prepared $S_3N_2C\ell_2$ by reacting $(NSC\ell)_3$ with $S_2C\ell_2$. More recently Jolly, Maguire and Rabinovich[4] produced the material by refluxing a suspension of ammonium chloride in $S_2C\ell_2$. An X-ray crystal structure analysis was undertaken to determine the molecular structure of this compound.

Experimental

$S_3N_2C\ell_2$ 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 $\lambda_{K\alpha 1}$=0.70926 Å are: $a = 6.546 \pm 0.007$ Å, $b = 8.600 \pm 0.004$ Å, $c = 5.508 \pm 0.005$ Å, 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 ± 0.01 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 $\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2$, 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 $\exp-(\underline{h}^2\beta_{11} + \underline{k}^2\beta_{22} + \underline{\ell}^2\beta_{33} + 2\underline{hk}\beta_{12} + 2\underline{h\ell}\beta_{13} + 2\underline{k\ell}\beta_{23})$, however, for our convenience the program converts these thermal parameters to $B_{\underline{ij}}$ in $Å^2$ where $B_{\underline{ij}} = 4\beta_{\underline{ij}}/\underline{a_i^*}\underline{a_j^*}$ and $\underline{a_i^*}$ is the $\underline{i}$th reciprocal axis length.

Atomic scattering factors[5] 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 $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.

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 pentahydrate[7] and in a diiodocyclobutene[8] 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 $S_3N_2C\ell_2$ is shown in the following Table I.

TABLE I.

POSITIONAL[a] AND THERMAL[b] PARAMETERS IN $S_3N_2C\ell_2$.

Atom	x	y	z	B11	B22	B33	B12	B13	B23
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	0.1148	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

[a]Estimated standard deviations of the positional parameters for S and Cℓ are less than 0.0003, and for N are less than 0.0008.

[b]Estimated standard deviations of the thermal parameters for S and Cℓ are about 0.05, and for N they are about 0.2.

Units of Bij are $Å^2$.

[c]Polar 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,K= 0, 0

L	FOBS	FCAL
1	191	188
2	75	71
3	240	281
4	145	144
5	247	247
6	65	61
7	12	8

H,K= 0, 1

L	FOBS	FCAL
1	476	510*
2	118	117
3	104	106
4	122	123
5	87	86
6	43	42
7	80	78

H,K= 0, 2

L	FOBS	FCAL
-0	434	466*
1	293	302
2	129	129
3	253	258
4	187	186
5	125	122
6	87	87
7	12	5

H,K= 0, 3

L	FOBS	FCAL
1	331	348
2	454	480
3	203	205
4	146	147
5	35	33
6	87	82
7	64	64

H,K= 0, 4

L	FOBS	FCAL
-0	307	308
1	128	132
2	55	55
3	309	313
4	57	53
5	46	45
6	46	47
7	27	28

H,K= 0, 5

L	FOBS	FCAL
1	174	178
2	373	389
3	162	165
4	54	47
5	52	50
6	46	47
7	75	71

H,K= 0, 6

L	FOBS	FCAL
-0	345	346
1	115	116
2	58	58
3	37	36
4	50	50
5	97	96
6	80	81

H,K= 0, 7

L	FOBS	FCAL
1	179	182
2	20	22
3	78	79
4	25	25
5	60	60
6	29	24

H,K= 0, 8

L	FOBS	FCAL
-0	340	348
1	143	144
2	84	67
3	123	126
4	112	115
5	85	87

H,K= 0, 9

L	FOBS	FCAL
1	63	65
2	34	35
3	26	25
4	61	60
5	57	59

H,K= 0, 10

L	FOBS	FCAL
-0	35	37
1	60	62
2	15	15
3	50	57
4	60	61

H,K= 0, 11

L	FOBS	FCAL
1	73	75
2	90	95
3	47	53

H,K= 0, 12

L	FOBS	FCAL
-0	43	46
1	38	39
2	15	14

H,K= 1, 0

L	FOBS	FCAL
-7	65	66
-6	99	97
-5	104	101
-4	114	112
-3	22	21
-2	977	1140*
-1	468	473*
-0	26	24
1	428	440
2	212	217
3	513	538
4	63	56
5	12	15
6	93	89
7	49	44

H,K= 1, 1

L	FOBS	FCAL
-7	33	36
-6	104	101
-5	33	31
-4	169	166
-3	349	352
-2	106	107
-1	364	375
-0	175	162
1	319	312
2	123	124
3	182	183
4	89	92
5	80	81
6	61	63
7	24	30

H,K= 1, 2

L	FOBS	FCAL
-7	72	72
-6	92	91
-5	106	107
-4	33	33
-3	132	131
-2	321	320
-1	263	250
-0	243	238
1	328	342
2	281	278
3	218	217
4	156	154
5	18	17
6	59	56
7	80	78

H,K= 1, 3

L	FOBS	FCAL
-7	27	31
-6	111	112
-5	116	116
-4	206	204
-3	317	320
-2	55	54
-1	153	148
-0	691	776*
1	252	258
2	94	95
3	55	56
4	101	100
5	195	194
6	60	62
7	47	45

H,K= 1, 4

L	FOBS	FCAL
-7	33	34
-6	41	41
-5	160	159
-4	56	60
-3	55	53
-2	183	177
-1	158	151
-0	119	116
1	388	392
2	65	65
3	84	87
4	80	80
5	53	51
6	111	109
7	44	43

H,K= 1, 5

L	FOBS	FCAL
-7	15	11
-6	60	57
-5	54	59
-4	250	249
-3	192	194
-2	56	59
-1	99	95
-0	431	433
1	312	322
2	54	58
3	112	113
4	91	92
5	155	154
6	20	22

H,K= 1, 6

L	FOBS	FCAL
-6	47	45
-5	21	23
-4	66	65
-3	111	114
-2	262	259
-1	76	68
-0	48	47
1	43	29
2	54	54
3	168	166
4	120	123
5	45	46
6	25	21

H,K= 1, 7

L	FOBS	FCAL
-6	33	33
-5	51	54
-4	62	64
-3	167	163
-2	66	65
-1	127	122
-0	69	66
1	96	100
2	29	34
3	91	91
4	41	38
5	34	36
6	39	41

H,K= 1, 8

L	FOBS	FCAL
-6	54	49
-5	73	74
-4	53	51
-3	61	61
-2	284	287
-1	205	199
-0	94	92
1	134	131
2	163	163
3	170	173
4	15	13
5	46	47

H,K= 1, 9

L	FOBS	FCAL
-5	31	27
-4	16	13
-3	33	34
-2	49	50
-1	84	85
-0	43	39
1	45	42
2	56	54
3	75	74
4	50	52
5	20	18

H,K= 1, 10

L	FOBS	FCAL
-4	24	25
-3	34	37
-2	36	38
-1	67	63
-0	18	16
1	49	53
2	79	81
3	59	60
4	12	14

H,K= 1, 11

L	FOBS	FCAL
-3	67	69
-2	22	23
-1	54	54
-0	113	113
1	65	67
2	52	55
3	29	24

H,K= 1, 12

L	FOBS	FCAL
-2	34	37
-1	45	48
-0	17	13
1	40	40

H,K= 2, 0

L	FOBS	FCAL
-7	8	8
-6	103	101
-5	0	1
-4	403	407
-3	427	432
-2	53	43
-1	194	178
-0	349	349
1	726	776*
2	131	122
3	44	44
4	172	171
5	134	133
6	71	70
7	53	53

H,K= 2, 1

L	FOBS	FCAL
-7	23	21
-6	121	120
-5	174	172
-4	84	83
-3	197	196
-2	192	180
-1	368	355
-0	312	309
1	285	287
2	157	155
3	34	35
4	147	147
5	23	26
6	92	90
7	33	33

H,K= 2, 2

L	FOBS	FCAL
-7	14	17
-6	74	72
-5	41	39
-4	199	194
-3	120	112
-2	107	107
-1	141	138
-0	231	213
1	360	359
2	133	128
3	54	53
4	110	108
5	127	127
6	71	70
7	35	33

H,K= 2, 3

L	FOBS	FCAL
-7	39	39
-6	86	84
-5	166	183
-4	30	31
-3	130	129
-2	561	581
-1	242	236
-0	146	140
1	117	118
2	72	71
3	415	418
4	109	108
5	70	70
6	35	26
7	30	32

H,K= 2, 4

L	FOBS	FCAL
-7	50	50
-6	74	75
-5	7	3
-4	23	13
-3	134	130
-2	130	127
-1	251	235
-0	99	96
1	102	93
2	101	101
3	62	62
4	213	212
5	33	28
6	64	64

H,K= 2, 5

L	FOBS	FCAL
-7	12	13
-6	115	113
-5	127	127
-4	44	45
-3	62	60
-2	314	310
-1	384	382
-0	165	179
1	146	147
2	141	141
3	257	257
4	88	87
5	41	43
6	31	32

H,K= 2, 6

L	FOBS	FCAL
-7	18	19
-6	53	52
-5	79	77
-4	121	117
-3	86	83
-2	73	72
-1	59	57
-0	41	35
1	187	175
2	109	109
3	83	82
4	30	29
5	49	49
6	59	58

H,K= 2, 7

L	FOBS	FCAL
-6	58	59
-5	94	91
-4	74	74
-3	46	45
-2	87	86
-1	102	103
-0	91	88
1	88	86
2	63	63
3	57	58
4	62	64
5	22	25

H,K= 2, 8

L	FOBS	FCAL
-6	28	26
-5	36	38
-4	162	161
-3	173	175
-2	66	68
-1	76	72
-0	200	195
1	241	239
2	79	80
3	77	75
4	79	80
5	69	70

H,K= 2, 9

L	FOBS	FCAL
-5	15	16
-4	51	53
-3	70	71
-2	24	23
-1	59	55
-0	39	36
1	54	55
2	101	104
3	26	28
4	54	53

H,K= 2, 10

L	FOBS	FCAL
-4	32	34
-3	36	38
-2	46	44
-1	27	26
-0	71	68
1	84	82
2	21	19
3	25	25
4	23	28

H,K= 2, 11

L	FOBS	FCAL
-3	31	31
-2	90	92
-1	76	77
-0	62	64
1	18	23
2	49	48

H,K= 2, 12

L	FOBS	FCAL
-1	28	26
-0	55	55

H,K= 3, 0

L	FOBS	FCAL
-7	11	5
-6	108	108
-5	265	287
-4	43	44
-3	76	74
-2	311	307
-1	527	557
-0	429	416
1	110	107
2	183	178
3	318	313
4	141	140
5	76	75
6	12	10

H,K= 3, 1

L	FOBS	FCAL
-7	42	44
-6	62	62
-5	93	91
-4	58	53
-3	183	175
-2	263	253
-1	164	161
-0	184	178
1	133	128
2	204	202
3	6	8
4	193	189
5	59	60
6	65	64

H,K= 3, 2

L	FOBS	FCAL
-7	20	18
-6	122	121
-5	88	84
-4	17	17
-3	129	128
-2	90	83
-1	384	381
-0	81	71
1	117	112
2	111	109
3	123	118
4	156	153
5	49	46
6	8	8

H,K= 3, 3

L	FOBS	FCAL
-7	63	63
-6	13	11
-5	98	98
-4	264	260
-3	211	205
-2	149	144
-1	81	81
-0	83	78
1	562	580
2	166	162
3	86	86
4	99	97
5	49	49
6	63	60

H,K= 3, 4

L	FOBS	FCAL
-7	15	10
-6	50	49
-5	85	85
-4	107	107
-3	79	77
-2	146	144
-1	86	77
-0	165	173
1	61	61
2	269	264
3	71	75
4	111	111
5	44	46
6	39	39

H,K= 3, 5

L	FOBS	FCAL
-7	47	50
-6	21	22
-5	47	45
-4	154	152
-3	285	281
-2	187	184
-1	84	82
-0	146	139
1	325	322
2	164	181
3	86	84
4	70	73
5	59	54
6	65	60

H,K= 3, 6

L	FOBS	FCAL
-6	45	41
-5	85	85
-4	76	75
-3	98	98
-2	41	38
-1	119	109
-0	96	89
1	101	101
2	44	44
3	73	72
4	95	96
5	62	62

H,K= 3, 7

L	FOBS	FCAL
-6	47	48
-5	8	8
-4	42	44
-3	67	68
-2	94	94
-1	50	47
-0	83	79
1	85	85
2	56	58
3	27	26
4	106	104
5	9	16

H,K= 3, 8

L	FOBS	FCAL
-5	102	106
-4	50	50
-3	7	5
-2	144	142
-1	245	237
-0	152	149
1	61	63
2	95	97
3	136	136
4	47	47

H,K= 3, 9

L	FOBS	FCAL
-5	46	43
-4	0	4
-3	33	33
-2	37	37
-1	15	15
-0	121	119
1	35	36
2	46	46
3	50	50
4	26	29

H,K= 3, 10

L	FOBS	FCAL
-4	48	47
-3	12	3
-2	32	33
-1	91	91
-0	33	30
1	11	11
2	35	35
3	19	19

H,K= 3, 11

L	FOBS	FCAL
-3	62	63
-2	52	52
-1	15	15
-0	47	45
1	92	96
2	45	45

H,K= 4, 0

L	FOBS	FCAL
-7	125	128
-6	22	24
-5	107	107
-4	169	165
-3	273	268
-2	450	444
-1	125	123
-0	74	64
1	488	490
2	208	201
3	35	37
4	80	79
5	11	5
6	71	74

H,K= 4, 1

L	FOBS	FCAL
-7	25	24
-6	32	31
-5	68	65
-4	111	108
-3	34	34
-2	132	128
-1	95	96
-0	122	118
1	29	30
2	242	238
3	85	88
4	89	90
5	76	77
6	0	2

H,K= 4, 2

L	FOBS	FCAL
-7	41	42
-6	8	6
-5	123	122
-4	55	50
-3	275	267
-2	181	173
-1	125	118
-0	77	73
1	97	86
2	256	254
3	16	16
4	50	49
5	37	37
6	61	60

H,K= 4, 3

L	FOBS	FCAL
-7	37	41
-6	68	66
-5	161	157
-4	70	69
-3	31	31
-2	53	51
-1	451	453
-0	266	257
1	99	100
2	146	143
3	51	52
4	154	152
5	47	49
6	9	13

H,K= 4, 4

L	FOBS	FCAL
-7	27	29
-6	59	59
-5	67	66
-4	104	103
-3	87	83
-2	196	189
-1	87	88
-0	226	219
1	203	200
2	136	138
3	23	26
4	89	89
5	46	45

H,K= 4, 5

L	FOBS	FCAL
-7	28	28
-6	55	55
-5	143	143
-4	112	113
-3	21	23
-2	80	77
-1	290	283
-0	240	234
1	85	83
2	84	83
3	91	89
4	104	105
5	38	38

H,K= 4, 6

L	FOBS	FCAL
-6	40	43
-5	75	79
-4	45	42
-3	52	47
-2	117	115
-1	90	90
-0	78	80
1	113	108
2	103	101
3	67	69
4	39	37
5	50	54

H,K= 4, 7

L	FOBS	FCAL
-6	12	8
-5	30	32
-4	66	64
-3	42	42
-2	57	58
-1	58	59
-0	23	19
1	16	16
2	127	125
3	17	21
4	76	76

H,K= 4, 8

L	FOBS	FCAL
-5	22	22
-4	69	72
-3	173	167
-2	161	160
-1	21	19
-0	89	86
1	176	175
2	101	98
3	47	49
4	42	42

H,K= 4, 9

L	FOBS	FCAL
-5	9	3
-4	40	38
-3	19	14
-2	80	80
-1	36	33
-0	21	16
1	59	59
2	35	34
3	55	56

H,K= 4, 10

L	FOBS	FCAL
-4	9	9
-3	73	73
-2	32	35
-1	22	20
-0	44	38
1	8	6
2	74	76

H,K= 4, 11

L	FOBS	FCAL
-2	32	34
-1	81	83
-0	64	66

H,K= 5, 0

L	FOBS	FCAL
-7	51	50
-6	36	36
-5	126	122
-4	287	287
-3	51	51
-2	28	27
-1	441	443
-0	250	240
1	54	48
2	152	156
3	18	19
4	153	154
5	42	42

H,K= 5, 1

L	FOBS	FCAL
-7	28	28
-6	21	21
-5	102	103
-4	87	87
-3	9	9
-2	26	27
-1	58	59
-0	165	163
1	141	139
2	110	110
3	82	81
4	20	21
5	73	71

H,K= 5, 2

L	FOBS	FCAL
-7	56	57
-6	11	12
-5	135	137
-4	136	133
-3	48	44
-2	63	59
-1	104	98
-0	282	278
1	37	36
2	90	86
3	49	48
4	66	66
5	81	83

H,K= 5, 3

L	FOBS	FCAL
-7	81	83
-6	11	12
-5	69	69
-4	28	31
-3	211	207
-2	308	305
-1	89	90
-0	99	96
1	76	77
2	186	184
3	66	64
4	46	45
5	24	27

H,K= 5, 4

L	FOBS	FCAL
-7	36	37
-6	29	31
-5	53	55
-4	121	114
-3	87	84
-2	128	125
-1	227	225
-0	114	110
1	13	14
2	122	121
3	89	87
4	24	27
5	50	54

H,K= 5, 5

L	FOBS	FCAL
-6	47	51
-5	66	66
-4	40	41
-3	183	178
-2	215	213
-1	26	26
-0	53	45
1	105	105
2	153	151
3	63	63
4	50	49

H,K= 5, 6

L	FOBS	FCAL
-6	28	29
-5	23	24
-4	88	88
-3	49	49
-2	77	76
-1	107	100
-0	77	73
1	64	65
2	60	59
3	78	80
4	55	54

H,K= 5, 7

L	FOBS	FCAL
-5	48	52
-4	30	29
-3	11	10
-2	27	23
-1	25	23
-0	92	86
1	69	71
2	85	85
3	30	31
4	12	12

H,K= 5, 8

L	FOBS	FCAL
-5	77	79
-4	112	112
-3	14	16
-2	53	49
-1	149	151
-0	144	141
1	70	69
2	51	52
3	33	37

H,K= 5, 9

L	FOBS	FCAL
-4	31	31
-3	25	27
-2	12	16
-1	49	52
-0	32	32
1	66	65
2	12	10

H,K= 5, 10

L	FOBS	FCAL
-3	36	34
-2	28	28
-1	9	11
-0	70	71
1	20	18

H,K= 6, 0

L	FOBS	FCAL
-7	50	51
-6	114	117
-5	26	22
-4	26	25
-3	227	229
-2	243	243
-1	94	90
-0	145	144
1	7	12
2	210	209
3	86	89
4	26	28

H,K= 6, 1

L	FOBS	FCAL
-7	68	71
-6	41	39
-5	41	43
-4	76	76
-3	63	63
-2	71	69
-1	178	177
-0	111	112
1	30	33
2	59	59
3	93	93
4	44	44

H,K= 6, 2

L	FOBS	FCAL
-6	57	57
-5	33	37
-4	33	31
-3	52	51
-2	193	189
-1	50	49
-0	62	58
1	35	34
2	57	54
3	125	126
4	12	17

H,K= 6, 3

L	FOBS	FCAL
-6	14	21
-5	57	54
-4	235	237
-3	57	55
-2	20	21
-1	107	108
-0	151	145
1	120	121
2	81	83
3	27	27
4	51	56

H,K= 6, 4

L	FOBS	FCAL
-6	35	32
-5	65	66
-4	49	46
-3	119	135
-2	42	40
-1	22	18
-0	90	89
1	121	120
2	63	61
3	63	64
4	17	18

H,K= 6, 5

L	FOBS	FCAL
-6	26	26
-5	83	82
-4	145	144
-3	21	23
-2	42	42
-1	95	94
-0	175	172
1	90	93
2	60	59
3	12	16
4	37	39

H,K= 6, 6

L	FOBS	FCAL
-5	8	10
-4	38	37
-3	47	47
-2	61	58
-1	47	50
-0	53	51
1	82	82
2	60	60
3	62	62

H,K= 6, 7

L	FOBS	FCAL
-5	9	12
-4	37	29
-3	41	43
-2	35	28
-1	89	91
-0	64	66
1	21	18
2	19	22
3	42	44

H,K= 6, 8

L	FOBS	FCAL
-4	15	17
-3	86	85
-2	129	131
-1	62	63
-0	36	37
1	54	54
2	72	78

H,K= 6, 9

L	FOBS	FCAL
-3	43	40
-2	19	23
-1	47	48
-0	19	16
1	20	18

H,K= 7, 0

L	FOBS	FCAL
-6	0	3
-5	54	54
-4	186	190
-3	65	64
-2	49	52
-1	20	22
-0	175	177
1	150	152
2	29	29
3	68	71
4	0	2

H,K= 7, 1

L	FOBS	FCAL
-6	37	43
-5	33	32
-4	54	54
-3	130	134
-2	75	80
-1	45	45
-0	76	73
1	86	85
2	84	87
3	84	89

H,K= 7, 2

L	FOBS	FCAL
-6	9	14
-5	8	5
-4	87	90
-3	43	39
-2	23	20
-1	38	34
-0	43	42
1	116	115
2	25	28
3	28	24

H,K= 7, 3

L	FOBS	FCAL
-6	112	116
-5	14	15
-4	29	25
-3	77	78
-2	85	85
-1	154	158
-0	89	87
1	13	13
2	85	86
3	66	69

H,K= 7, 4

L	FOBS	FCAL
-5	44	43
-4	14	13
-3	11	10
-2	20	19
-1	113	118
-0	66	62
1	35	37
2	31	30
3	71	69

H,K= 7, 5

L	FOBS	FCAL
-5	26	28
-4	41	42
-3	55	59
-2	141	141
-1	104	107
-0	42	42
1	29	32
2	44	47

H,K= 7, 6

L	FOBS	FCAL
-4	55	56
-3	16	21
-2	20	17
-1	54	51
-0	32	35
1	63	61
2	55	59

H,K= 7, 7

L	FOBS	FCAL
-4	9	7
-3	64	64
-2	31	34
-1	12	12
-0	22	26
1	42	40

H,K= 7, 8

L	FOBS	FCAL
-2	21	23
-1	48	52
-0	71	73

H,K= 8, 0

L	FOBS	FCAL
-5	28	27
-4	20	19
-3	34	39
-2	89	89
-1	179	185
-0	33	28
1	68	67
2	24	29

H,K= 8, 1

L	FOBS	FCAL
-5	52	53
-4	31	29
-3	41	45
-2	37	40
-1	58	57
-0	104	102
1	76	81
2	32	34

H,K= 8, 2

L	FOBS	FCAL
-5	27	34
-4	56	59
-3	42	46
-2	33	31
-1	79	80
-0	38	41
1	14	10
2	31	29

H,K= 8, 3

L	FOBS	FCAL
-5	23	24
-4	47	49
-3	114	121
-2	42	43
-1	14	7
-0	86	86
1	71	73
2	29	32

H,K= 8, 4

L	FOBS	FCAL
-4	33	35
-3	75	80
-2	38	38
-1	16	17
-0	33	39
1	55	56

H,K= 8, 5

L	FOBS	FCAL
-4	75	77
-3	79	84
-2	12	7
-1	37	38
-0	45	48
1	83	87

H,K= 8, 6

L	FOBS	FCAL
-3	12	16
-2	9	1
-1	64	67
-0	53	58

H,K= 9, 0

L	FOBS	FCAL
-4	25	24
-3	142	150
-2	19	15
-1	35	37
-0	52	51

H,K= 9, 1

L	FOBS	FCAL
-4	20	21
-3	27	31
-2	71	74
-1	34	37
-0	31	37

H,K= 9, 2

L	FOBS	FCAL
-3	53	57
-2	33	38
-1	17	11
-0	36	36

H,K= 9, 3

L	FOBS	FCAL
-3	12	10
-2	46	48
-1	68	71
-0	34	37

The most interesting result of this work is the apparent ionic nature of the material. The material consists of a $S_3N_2C\ell^+$ ion and a $C\ell^-$ ion. The chloride ion is $C\ell(2)$ and its closest approachs 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 $S_3N_2C\ell^+$ ion labelled with distances and angles.

The three sulfurs and two nitrogens form a slightly puckered five membered ring with a $C\ell$ atom, $C\ell(1)$ attached to the thio sulfur, i.e. $C\ell$-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 $C\ell(1)$ 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 $S_3N_2C\ell_2$ is the smallest such ring system in a series of cyclic azyl systems. Six membered rings are present in $(NSCC\ell)_3$,[9] $(NSC\ell)_3$,[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

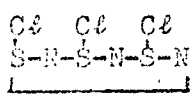
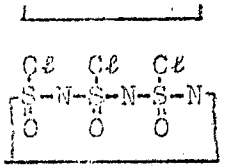
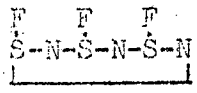
Formula	S-S	S-N	S-Cℓ	Reference
$C\ell-S-N-S-N-S^{+}C\ell^{-}$	2.136 Å	1.543-1.617 Å	2.168 Å	This work
		1.600-1.614 Å	2.084-2.150 Å	(10)
		1.546-1.578 Å	1.991-1.999 Å	(9)
		1.540-1.660 Å		(11)
$S-N-S-N-S-N-S^{+}NO_3^{-}$	2.064 Å	1.493-1.582 Å		(12)
$N_4S_4H_4$		1.65		(13)

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

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(1) Work done under the auspices of the U. S. Atomic Energy Commission.

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Captions

Figure 1.- Distances and angles in $S_3N_2C\ell^+$. The estimated standard deviations are about 0.005 Å on the distances, and about 0.3° on the angles.

Figure 2.- Projection of $S_3N_2C\ell_2$ down the c axis.

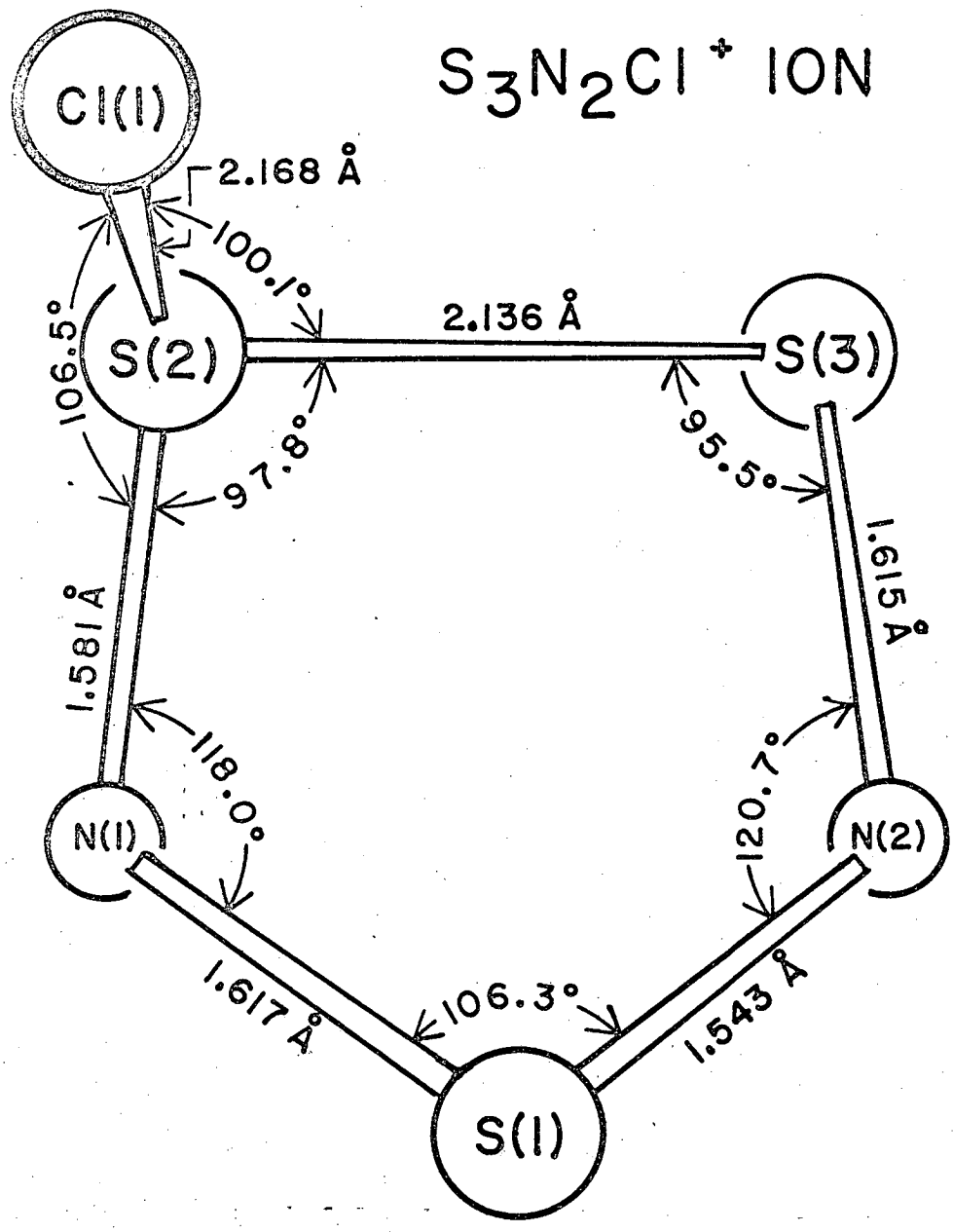
$S_3N_2Cl^+$ ION
Cl(1)
2.168 Å
100.1°
106.5°
S(2)
2.136 Å
S(3)
97.8°
95.5°
1.581 Å
1.615 Å
118.0°
120.7°
N(1)
N(2)
1.617 Å
106.3°
1.543 Å
S(1)
MUB-9583

Figure 1.

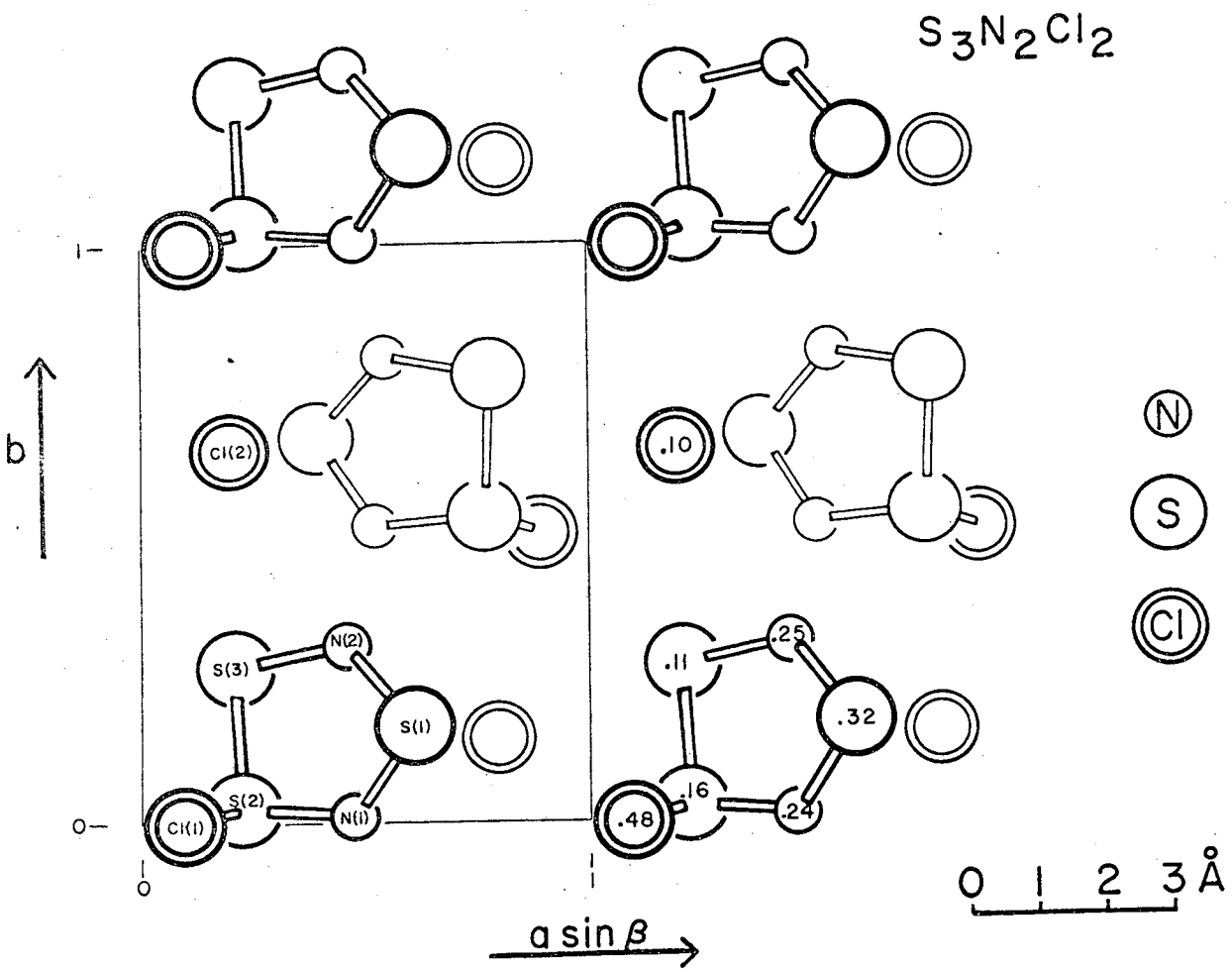
$S_3N_2Cl_2$
b
a sin β
Cl(2)
.10
N(2)
S(3)
S(1)
S(2)
N(1)
Cl(1)
.11
.25
.32
.16
.24
.48
N
S
Cl
0 1 2 3 Å
MUB-9584

Figure 2.

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