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The Crystal and Molecular Structure of $S_2N_2(SbCl_5)_2$

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Received February 21, 1969

The crystal structure of the antimony pentachloride diadduct of disulfur dinitride, $S_2N_2(SbCl_5)_2$, has been determined from three-dimensional X-ray diffraction counter data. The material crystallizes in space group $I\bar{4}2d$ of the tetragonal system with eight molecules in a unit cell of dimensions $a = 14.933$ (3) and $c = 15.547$ (3) Å. The calculated density of 2.64 g/cm³ agrees well with the value 2.70 g/cm³ measured by flotation. Refinement of the structure on F^2 by least-squares methods resulted in a final conventional R factor based on F of 3.8%, for 768 independent reflections above background. The structure contains a planar S_2N_2 ring with alternating sulfur and nitrogen atoms. An $SbCl_5$ group is bonded *via* the antimony atom to each nitrogen of the ring. The two antimony atoms, two nitrogen atoms, and two axial chlorine atoms all lie on a crystallographic twofold axis which passes through the molecule. The two crystallographically independent S–N distances of 1.616 (7) and 1.623 (8) Å are equal to within the estimated error, as are the two Sb–N distances of 2.281 (10) and 2.285 (11) Å. The S_2N_2 ring is nearly square with S–N–S angles of 95.4 (6) and 94.8 (6)° and N–S–N angles of 84.9 (4)°.

Introduction

The compound S_2N_2 is obtained as an unstable crystalline material from the thermal cleavage of S_4N_4.[1] On the basis of the infrared spectrum of S_2N_2, a planar ring structure of alternating nitrogen and sulfur atoms was proposed.[2] This was the first example to our knowledge of a tetraatomic molecule of this kind. An X-ray diffraction study of S_2N_2 has not been attempted, however, as the crystals polymerize to $(SN)_x$ when warmed above −80°. In a recent study of the reactions of S_2N_2 with Lewis acids,[3] a crystalline diadduct of S_2N_2 with antimony pentachloride, $S_2N_2(SbCl_5)_2$, has been prepared which is thermally stable at room temperature. From the chemical properties of $S_2N_2(SbCl_5)_2$ and the similarity of its infrared spectrum to that of S_2N_2, it was proposed that the S_2N_2 ring remains unbroken and planar after coordination by $SbCl_5$. To confirm this proposed structure and to show that a planar S_2N_2 ring does indeed exist, the crystal structure of $S_2N_2(SbCl_5)_2$ has been determined by three-dimensional X-ray analysis.

Experimental Section

Yellow crystals of $S_2N_2(SbCl_5)_2$ were prepared as described previously.[3] The crystals had moderately well-developed faces and exhibited sharp extinction under the polarizing microscope. As the crystals were extremely moisture sensitive and blackened immediately in room air, several were stuck to the inside of thin-walled quartz capillaries with Kel-F grease in a nitrogen-flushed glove box and the capillaries were sealed. These crystals were then examined under the polarizing microscope and the one whose size, clarity, extinction, and shape seemed most suitable was chosen for further study.

Precession photographs (using molybdenum radiation) of the $h0l$, $0kl$, $1kl$, hhl, and $h,2h,l$ zones and a Weissenberg photograph of the $hk0$ zone showed 4/mmm symmetry with the systematic absences: hkl, $h + k + l \neq 2n$; hhl, $2h + l \neq 4n$. The absences are consistent only with the two space groups $I\bar{4}2d$ and $I4_1md$. Preliminary cell constants were measured from the films. The density measured by flotation in a dibromomethane–carbon tetrabromide solution was 2.70 (8) g/cm³ compared with the calculated density of 2.64 g/cm³ for eight molecules in the unit cell. Slow decomposition of the compound occurred during the density measurement, hence the large assigned error estimate. Since both possible space groups have 16 general positions in the cell, the molecules must lie in special positions with twofold (in $I\bar{4}2d$) or mirror (in $I4_1md$) symmetry.

The crystal was mounted on a eucentric goniometer head with the crystal c axis parallel to the spindle direction (ϕ axis) of a General Electric XRD-5 manual goniostat equipped with a scintillation counter, pulse a height discriminator, and a scaler. Molybdenum radiation at 45 kV and 21 mA was used. The diffracted beams were filtered through 3 mils of Zr foil. The receiving aperture was 10 mm high and 3 mm wide and was positioned 15 cm from the crystal. The cell dimensions, $a = 14.933$ (3) and $c = 15.547$ (3) Å, were determined using a small takeoff angle (using Mo $K\alpha_1$, λ 0.709261 Å) and narrow detector slit by careful measurement at 22° of the Bragg angles for high-index reflections of the type $h00$, $0k0$, and $00l$. The α_1 and α_2 peaks were well resolved in these measurements and were satisfactorily narrow. The standard deviations were estimated from the error in the 2θ angles and are given in parentheses.

Intensity data were collected by the point count method. The intensities of all 1670 symmetry-allowed reflections in the $+h,+k,+l$ octant were measured out to $2\theta = 50°$ by 10-sec counts at the peak maximum with the crystal and counter stationary and at a takeoff angle of 4°. For all hhl, $h0l$, $0kl$, and $00l$ reflections, all hkl reflections with $2\theta \leq 20°$, and about one-third of the reflections with $20° < 2\theta \leq 50°$, individual backgrounds were measured by seeking a minimum on the low-2θ side of the peak. The remaining backgrounds were taken from a plot of background as a function of 2θ for various values of the orientation angles ϕ and χ. A set of arbitrarily chosen standard reflections which were monitored approximately every 100 measurements showed no change throughout the course of the measurement. The intensities I, after subtraction of background, were assigned standard deviations according to the formula $\sigma(I) = [I + 0.75B + (0.05I)^2]^{1/2}$, where the background, B, was not the actual background measured for each peak, but instead was estimated by the expression $B = 650 - 10(2\theta) + 0.02I$, which was a reasonable representation of the actual background counted. Values of I were then reduced to values of F^2 by application of Lorentz and polarization corrections.[4]

The measured reflections consisted of two sets: the first with $h \leq k$ and the second with $h \geq k$. These two sets are equivalent forms in both $I\bar{4}2d$ and $I4_1md$ since both space groups contain

(1) M. Becke-Goehring, *Inorg. Syn.*, **6**, 123 (1960).
(2) J. R. W. Warn and D. Chapman, *Spectrochim. Acta*, **22**, 1371 (1966).
(3) R. L. Patton and W. L. Jolly, *Inorg. Chem.*, **8**, 1389, 1392 (1969).

(4) Programs for the CDC 6400 computer used in this study were Zalkin's EULERA and AUDIT programs for diffractometric data processing and the FORDAP Fourier program, Hamilton's GONO9 absorption program, Iber's modifications of the Busing–Levy ORFLS least-squares and ORFFE error function programs, and Johnson's ORTEP thermal ellipsoid plotting program.

diagonal mirror planes. Comparison of the measured intensities for equivalent reflections in the two sets showed systematic differences due to absorption effects.

The dimensions of the crystal were carefully measured with a micrometer eyepiece attached to a microscope. Each bounding plane of the crystal was indexed and the plane-to-plane distances were determined. The approximate dimensions of the crystal are $0.15 \times 0.26 \times 0.45$ mm. These are along *a*, *b*, and *c*, respectively. An absorption correction was then applied to each reflection.[4] For a linear absorption coefficient of 49.7 cm^{-1} the transmission factors of the measured reflections ranged from 0.474 to 0.587. The two forms were then averaged to give 859 independent reflections of which 761 were greater than three times their standard deviation. The weighted agreement between the two forms of F^2 averaged is 6%, in good agreement with the final weighted *R* factor based on F^2.

Solution and Refinement of the Structure

An unsharpened Patterson function was calculated using the data set which was uncorrected for absorption and had $h \leq k$. An initial solution was attempted in $I4_1md$. Special positions on the mirror planes at $x = 0$, $^1/_2$ and at $y = 0$, $^1/_2$ could be chosen for two independent Sb atoms separated by $\Delta z = {}^1/_2$ for which peaks corresponded to all predicted Sb–Sb vectors. However, the agreement for the weaker Sb–Cl vectors was unsatisfactory and the chlorine positions so determined required chemically unreasonable Sb–Cl bond lengths or Cl–Cl van der Waals contacts. Space group $I4_1md$ was therefore rejected. The subsequent alternate choice of $I\bar{4}2d$ was confirmed as correct by the successful refinement of the crystal structure.

Analysis of the Patterson map in $I\bar{4}2d$ led easily to two unique sets of antimony, chlorine, and sulfur positions for which all predicted positions and intensities of Sb–Sb, Sb–Cl, and Sb–S peaks were found in the 88 Patterson peaks with greater than 0.7% of the origin height. Both sets corresponded to the predicted molecular geometry of $S_2N_2(SbCl_5)_2$. This expected geometry has three different possible twofold axes, any of which may be utilized by the space group. The two solutions of the Patterson function corresponded to a choice between two of these. In both cases the long axis of the molecule (the Sb–Sb vector) lies in the *xy* plane, with the *x* and *y* coordinates of the Sb atoms very nearly equal to 0, $^1/_4$ and $^1/_2$, $^1/_4$, respectively. The first solution placed them at $z = {}^3/_8$. The antimony atoms then occupy the general position 16(e) and are related by the twofold axis passing between them at $^1/_4$, *y*, $^3/_8$. The two N–$SbCl_5$ groups are, in fact, very nearly related by a noncrystallographic axis in exactly this way. In the second, correct, solution the *z* coordinate is $^1/_8$ and the two N–$SbCl_5$ groups occupy 8(e) with the twofold axis at *x*, $^1/_4$, $^1/_8$ passing through both groups, which are then crystallographically independent. These two solutions differ significantly only in the position of the sulfur atoms of the S_2N_2 ring. In the first case these atoms must lie on the twofold axis, in the second case they are in a general position and the S_2N_2 ring need not be parallel to the *xy* plane.

After several trials the correct orientations of the $SbCl_5$ groups were determined. The extra pseudosymmetry of the structure caused some singularity problems in the initial refinements when the $SbCl_5$ groups were rotated such that the Sb–Cl_{eq} bonds were coincident with the crystal axes. In these and succeeding refinements the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, in which $|F_o|$ and $|F_c|$ are the observed and calculated structure factors and the weights, *w*, were taken as $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for neutral Sb, Cl, S, and N tabulated by Ibers[5] were used together with the values of $\Delta f'$ and $\Delta f''$ for Sb, Cl, and S given by Cromer[6] to include the effects of anomalous dispersion.[7]

After the correct orientations of the $SbCl_5$ groups were determined, the refinement was straightforward. Twelve reflections were discarded because of data collection errors or because their very high intensities gave coincidence losses. Several cycles of refinement on *F* with all atoms assigned anisotropic thermal parameters brought $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o - F_c|)^2/\Sigma w F_o^2)^{1/2}$ to 4.2 and 6.5%, respectively.

The error in an observation of unit weight was 3.06 and was found to vary linearly with F_o as approximately $E = 3.19 - 2.53(F_o/F_{max})$. The standard deviations were then revised by multiplying them by this quantity. Of 847 remaining reflections 768 had $F^2 > \sigma(F^2)$ and these were used in the final refinements, minimizing $\Sigma w(|F_o|^2 - |F_c|^2)^2$. After convergence, the final values of R_1 and R_2 based on F^2 are 5.6 and 9.7%, respectively,[8] with an error in an observation of unit weight of 0.89. The final values of R_1 and R_2 based on *F* are 3.8 and 4.9%. A final difference Fourier map showed a maximum electron density of 0.37 e$^-$/Å^3. Final values of $|F_o|$ and $|F_c|$ (in electrons $\times$ 5) are given in Table I. Those reflections for which $F_o^2 < \sigma(F^2)$ all had $F_c^2 < 3\sigma(F^2)$ and are not included in Table I. The final values of the atomic parameters along with their standard deviations estimated from the variance–covariance matrix are given in Table II.

Description and Discussion of the Structure

The unit cell contains eight discrete $S_2N_2(SbCl_5)_2$ molecules, each lying on one of the twofold rotation axes perpendicular to *c*. The bulky $SbCl_5$ groups appear to be the main factor controlling the molecular packing with the S_2N_2 rings fitting into spaces between these groups. None of the intermolecular distances observed is short enough to indicate any unusual association. Several chlorine–chlorine contacts are slightly less than the sum of their expected van der

(5) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

(6) D. T. Cromer, *Acta Cryst.*, **18**, 17 (1965).

(7) J. A. Ibers and W. C. Hamilton, *ibid.*, **17**, 781 (1964).

(8) Since $I\bar{4}2d$ lacks a center of symmetry, the intensities of centrosymmetrically related reflections are not identical. The correct assignment of the indices corresponds to a determination of the absolute configuration of the structure, even though the crystal is composed of racemic pairs of $S_2N_2(SbCl_5)_2$ molecules. The two configurations differ only in a rotation of 90° about *c*. That is, although the structure is its own enantiomorph, the *x* direction is the mirror image of the *y* direction. To test the assigned configuration, additional refinements were carried out with the signs of *h*, *k*, and *l* reversed. Both R_1 and R_2 were somewhat larger (5.9 and 10.0), indicating that the assigned configuration is correct.

Table I

Observed and Calculated Structure Amplitudes (in Electrons $\times 5$) for $S_2N_2(SbCl_5)_2$

K	L	FO	FC
H=0			
0	0	0	1273
0	12	1714	1606
0	16	746	676
H=1			
0	1	62	55
0	3	245	251
0	5	803	848
0	7	68	90
0	9	79	22
0	13	162	182
1	2	1362	1338
1	6	907	972
1	10	183	171
1	14	292	229
H=2			
0	0	706	657
0	4	959	990
0	6	623	623
0	10	1010	1107
0	12	296	297
0	14	1281	1264
0	18	335	348
1	1	265	230
1	3	283	244
1	5	325	338
1	7	442	442
1	11	119	109
2	4	836	755
2	8	2144	2075
2	12	1099	1068
2	16	537	476
H=3			
1	0	1140	1081
1	2	408	391
1	4	451	453
1	6	329	325
1	8	498	253
1	10	92	73
1	12	253	245
1	14	190	164
1	16	108	97
2	1	331	337
2	3	246	260
2	5	391	429
2	9	364	392
2	11	55	54
2	15	78	81
2	17	73	81
3	2	909	849
3	6	844	852
3	10	245	237
3	14	519	468
H=4			
0	2	130	126
0	4	1825	1875
0	6	649	597
0	8	2130	2176
0	10	373	361
0	12	1111	1118
0	14	204	203
0	16	477	477
1	1	385	363
1	3	384	396
1	5	497	509
1	7	323	325
1	9	168	171
1	11	101	98
1	13	228	249
2	2	1648	1644
2	4	315	297
2	6	2224	2273
2	8	301	236
2	10	901	891
2	12	233	210
2	14	878	840
2	16	70	33
3	1	531	527
3	3	414	426
3	5	513	571
3	7	90	107
3	9	287	299
3	13	187	185
4	0	1126	1059
4	4	762	731
4	8	1066	1045
4	12	704	717
4	16	312	316
H=5			
0	1	1339	1371
0	5	289	293
0	7	315	348
0	9	416	449
0	11	157	174
1	2	1556	1543
1	4	1209	1213
1	6	1427	1478
1	8	1040	1027
1	10	295	330
1	12	374	385
1	14	509	501
1	16	136	131
2	1	345	339
2	3	789	823
2	5	407	471
2	7	720	698
2	9	92	108
2	11	194	179
2	13	177	175
2	15	159	156
3	0	1790	1830
3	2	121	157
3	4	872	835
3	6	346	388
3	8	1241	1203
3	10	121	126
3	12	656	652
3	14	206	186
3	16	204	211
4	1	311	327
4	3	123	123
4	5	280	263
4	7	329	293
4	9	189	211
4	11	200	207
4	13	220	221
4	15	84	94
5	2	1322	1280
5	6	1611	1593
5	10	540	604
5	14	587	575
H=6			
0	0	1482	1548
0	2	2288	2374
0	4	1219	1153
0	6	1959	1978
0	8	413	420
0	10	1014	1043
0	12	315	354
0	14	718	723
1	1	408	423
1	3	255	247
1	7	362	393
1	9	244	230
1	11	210	203
1	13	174	179
1	15	143	97
2	2	942	930
2	4	2176	2209
2	6	625	634
2	8	1446	1460
2	10	159	170
2	12	825	852
2	14	117	114
2	16	366	375
3	1	295	293
3	3	457	467
3	5	263	246
3	7	383	383
3	9	240	173
3	11	90	102
3	13	217	211
3	15	138	145
4	0	658	643
4	2	1603	1549
4	4	532	536
4	6	1316	1275
4	8	286	258
4	10	751	759
4	14	489	485
5	1	760	758
5	3	351	359
5	5	358	328
5	7	316	320
5	9	279	276
5	11	239	237
5	13	117	107
5	15	78	98
6	0	1816	1736
6	4	1775	1738
6	8	1069	1071
6	12	634	658
6	16	265	286
H=7			
0	1	630	614
0	3	489	498
0	5	641	627
0	7	530	535
0	9	190	158
0	11	70	71
0	13	251	239
0	15	197	195
1	0	1928	1919
1	2	1229	1165
1	4	656	585
1	6	1178	1156
1	8	888	869
1	10	353	351
1	12	505	496
1	14	428	409
1	16	234	239
2	1	763	755
2	3	244	221
2	5	476	498
2	7	541	530
2	9	271	289
2	11	265	241
2	13	133	152
2	15	111	113
3	2	1756	1717
3	4	101	84
3	6	1687	1643
3	8	597	528
3	10	648	641
3	12	282	269
3	14	571	562
3	16	146	131
4	1	593	577
4	3	429	433
4	5	508	481
4	7	456	428
4	9	375	388
4	11	160	150
4	13	220	220
4	15	156	140
5	0	2396	2432
5	2	273	267
5	4	1802	1701
5	6	547	506
5	8	1202	1188
5	10	223	223
5	12	782	768
5	14	120	134
5	16	296	299
6	1	752	738
6	3	732	724
6	5	654	606
6	7	593	568
6	9	297	289
6	11	223	229
6	13	239	230
6	15	141	148
7	2	2548	2534
7	6	1811	1750
7	10	873	889
7	14	541	540
H=8			
0	0	1795	1823
0	2	778	753
0	4	1753	1747
0	6	516	546
0	8	1073	1113
0	10	216	222
0	12	737	717
0	14	275	272
0	16	354	352
1	1	276	279
1	3	344	339
1	5	397	392
1	7	318	331
1	9	104	129
1	11	182	177
1	13	73	112
1	15	82	86
2	0	649	671
2	2	2004	1215
2	4	338	299
2	6	1216	1250
2	8	222	242
2	10	815	831
2	12	270	259
2	14	359	367
2	16	66	69
3	1	492	477
3	3	480	471
3	5	80	80
3	7	354	371
3	9	110	104
3	11	202	174
3	13	80	66
4	0	1056	1015
4	2	196	216
4	4	1047	1004
4	6	123	125
4	8	538	538
4	10	97	117
4	12	441	427
4	14	144	125
5	1	185	189
5	3	353	334
5	5	286	261
5	7	221	221
5	11	145	140
5	13	87	101
5	15	114	117
6	0	906	860
6	2	852	790
6	4	624	591
6	6	651	629
6	8	318	316
6	10	543	531
6	12	158	149
6	14	248	238
7	1	504	478
7	3	425	418
7	5	331	362
7	7	422	427
7	9	185	231
7	11	257	230
7	13	107	111
8	0	125	160
8	4	445	433
8	8	366	320
8	12	227	205
H=9			
0	1	729	690
0	3	485	465
0	5	292	278
0	7	542	549
0	9	353	355
0	11	124	125
0	13	256	239
1	0	1331	1287
1	2	790	751
1	4	541	517
1	6	797	811
1	8	583	572
1	10	367	343
1	12	242	231
1	14	395	368
2	1	579	564
2	3	120	130
2	5	617	647
2	7	339	360
2	9	259	274
2	11	80	92
2	13	243	251
2	15	143	136
3	0	863	877
3	2	350	369
3	4	572	534
3	6	492	447
3	8	665	666
3	10	105	118
3	12	454	442
3	14	195	177
4	1	351	351
4	3	162	168
4	5	307	321
4	7	223	233
4	9	220	214
4	11	106	107
4	13	263	248
4	15	80	83
5	2	711	688
5	6	807	817
5	10	560	541
5	14	413	394
6	1	431	414
6	3	175	192
6	5	304	304
6	7	303	298
6	9	245	251
6	11	152	155
6	13	186	167
7	0	1099	1080
7	2	221	232
7	4	979	927
7	6	158	179
7	8	662	669
7	10	124	125
7	12	565	539
8	1	287	276
8	3	172	182
8	5	427	429
8	7	198	201
8	9	200	218
8	11	78	103
8	13	173	165
9	2	758	749
9	6	603	621
9	10	537	502
H=10			
0	0	1392	1410
0	2	341	330
0	4	925	892
0	6	481	464
0	8	798	802
0	10	727	661
0	12	506	483
0	14	225	240
1	1	281	278
1	3	272	285
1	7	256	246
1	9	98	76
1	11	102	95
2	0	93	90
2	2	392	373
2	4	583	568
2	6	621	639
2	8	344	353
2	10	308	289
2	12	295	294
2	14	250	260
3	1	147	153
3	3	62	42
3	5	258	274
3	7	74	101
3	9	108	94
3	11	75	47
3	13	80	67
4	0	283	306
4	2	720	716
4	4	208	222
4	6	401	410
4	8	403	383
4	10	454	429
4	12	281	256
4	14	137	156
5	1	204	192
5	3	90	97
5	5	207	191
5	7	116	135
6	0	461	436
6	2	543	518
6	4	568	561
6	6	378	379
6	8	338	338
6	10	141	165
6	12	195	205
7	1	137	141
7	3	258	264
7	5	292	290
7	7	161	166
7	9	148	143
7	11	130	118
7	13	114	116
8	0	470	454
8	2	459	459
8	4	272	267
8	6	288	293
8	8	138	132
8	10	182	194
8	12	97	86
9	1	258	238
9	3	233	243
9	5	122	132
9	7	172	172
9	9	186	191
9	11	114	108
10	0	242	217
10	4	135	135
10	8	78	72
H=11			
0	1	302	298
0	3	300	303
0	5	180	185
0	7	634	618
0	9	104	105
0	11	245	240
0	13	172	179
1	0	715	715
1	2	265	258
1	4	491	478
1	6	245	238
1	8	538	541
1	10	120	130
1	12	296	302
1	14	163	158
2	1	467	469
2	3	303	295
2	5	339	318
2	7	370	391
2	9	239	240
2	11	227	220
2	13	196	195
3	0	712	720
3	2	548	533
3	4	428	445
3	6	629	621
3	8	300	302
3	10	399	401
3	12	124	146
3	14	249	271
4	1	559	555
4	3	404	395
4	5	292	289
4	7	459	451
4	9	196	190
4	11	224	220
4	13	188	176
5	0	970	977
5	2	195	193
5	4	1019	1002
5	6	99	114
5	8	791	768
5	12	475	470
6	1	447	424
6	3	440	437
6	5	333	312
6	7	451	422
6	9	185	206
6	11	234	227
6	13	187	180
7	0	282	267
7	2	836	824
7	4	177	169
7	6	764	769
7	10	577	550
8	1	425	398
8	3	343	349
8	5	318	318
8	7	314	325
8	9	212	213
8	11	200	199
9	0	763	768
9	2	119	94
9	4	766	763
9	6	68	32
9	8	549	548
10	1	219	214
10	3	256	263
10	5	155	147
10	7	246	240
10	9	69	73
11	2	473	480
11	6	399	431
H=12			
0	0	520	528
0	2	1191	1159
0	4	940	912
0	6	1031	1032
0	8	511	473
0	10	455	454
1	1	302	285
1	5	210	228
1	7	122	135
1	9	114	119
1	13	66	82
2	0	708	698
2	2	346	331
2	4	468	439
2	6	153	177
2	8	530	511
2	10	257	269
2	12	290	307
3	1	102	106
3	3	165	80
3	5	214	192
3	7	157	130
3	13	81	87
4	0	304	271
4	2	656	651
4	4	411	412
4	6	721	711
4	8	130	183
4	10	358	354
4	12	98	107
5	1	317	336
5	3	294	314
5	5	368	366
5	7	209	197
5	9	161	157
5	11	81	86
6	0	589	591
6	2	102	150
6	4	418	442
6	6	112	95
6	10	105	107
6	8	338	353
6	12	206	223
7	1	382	403
7	3	360	361
7	5	230	226
7	7	248	244
7	9	151	153
7	11	158	142
8	2	460	457
8	4	315	310
8	6	109	58
8	8	164	166
8	10	281	309
9	1	203	184
9	3	347	336
9	5	116	100
9	7	173	177
9	9	114	92
10	0	85	81
10	4	121	103
10	6	127	120
10	8	64	43
11	1	127	134
11	3	132	132
11	5	89	86
11	7	112	113
12	0	109	67
H=13			
0	1	679	682
0	3	468	446
0	5	648	662
0	7	489	478
0	9	380	403
0	11	310	277
1	0	351	342
1	2	957	948
1	4	325	330
1	6	692	695
1	8	306	305
1	10	429	424
1	12	190	167
2	1	694	678
2	3	641	647
2	5	506	493
2	7	510	521
2	9	351	353
2	11	240	240
3	0	835	831
3	2	445	443
3	4	754	746
3	6	336	328
3	8	456	462
3	10	217	234
3	12	243	278
4	1	631	633
4	3	443	431
4	5	488	495
4	7	359	350
4	9	285	299
4	11	226	225
5	0	260	246
5	2	1057	1026
5	4	181	158
5	6	733	736
5	10	449	456
6	1	332	325
6	3	282	289
6	5	284	293
6	7	316	317
6	9	229	246
7	0	602	598
7	2	74	66
7	4	659	643
7	6	74	27
8	1	450	459
8	3	303	302
8	5	314	324
8	7	304	295
9	0	307	300
9	2	213	231
9	4	728	713
9	6	559	556
10	1	399	390
10	3	291	293
10	5	273	311
10	7	221	219
11	0	480	466
11	2	192	198
11	4	429	445
12	1	237	248
H=14			
0	0	1320	1287
0	2	552	514
0	4	849	833
0	6	241	242
0	8	569	589
0	10	206	214
1	1	389	369
1	3	183	172
1	5	243	245
1	7	253	257
1	9	148	153
2	0	102	108
2	2	611	600
2	4	228	228
2	6	519	520
2	10	258	266
3	1	220	224
3	3	112	85
3	5	151	159
3	7	210	215
4	0	610	599
4	2	387	377
4	4	458	454
4	6	138	144
4	8	349	372
4	10	113	112
5	1	222	228
5	3	108	126
5	5	152	152
5	7	113	122
5	9	151	135
6	0	76	58
6	2	235	230
6	4	112	105
6	6	265	264
6	8	108	76
7	1	170	194
7	3	204	204
7	5	198	219
7	7	152	169
8	0	238	233
8	4	206	201
8	6	78	49
9	1	228	236
9	3	225	243
9	5	78	190
10	0	196	208
10	4	150	168
H=15			
0	1	144	157
0	3	101	103
0	5	303	290
0	7	94	90
0	9	257	234
1	0	178	197
1	4	281	272
1	8	168	183
2	1	283	274
2	3	314	301
2	5	200	208
2	7	241	245
2	9	178	167
3	0	143	145
3	2	363	359
3	4	226	217
3	6	203	217
3	8	79	105
4	1	404	394
4	3	322	304
4	5	334	336
4	7	183	186
5	0	498	512
5	4	490	476
5	8	264	269
6	1	295	290
6	3	212	226
6	5	281	295
6	7	170	188
7	0	125	124
7	2	436	440
7	6	321	329
8	1	240	247
8	3	260	255
8	5	220	220
9	0	401	410
9	2	84	78
H=16			
0	0	156	145
0	2	312	301
0	4	217	208
0	6	285	295
1	1	159	161
1	3	68	85
1	5	69	64
1	7	245	221
2	0	332	340
2	2	123	125
2	4	241	257
2	6	75	74
3	1	224	225
3	3	73	94
3	5	165	147
3	7	176	172
4	0	77	48
4	2	324	331
4	4	281	283
4	6	197	190
5	1	233	243
5	3	103	92
6	0	396	406
6	2	91	87
6	4	349	355
7	1	213	215
7	3	169	170
H=17			
0	1	81	72
0	3	163	192
0	5	91	82
1	0	85	54
1	4	125	136
2	1	117	119
2	3	167	157
3	0	65	90
3	4	166	160
4	1	65	65
4	3	133	146

Table II

Positional and Thermal Parameters ($\times 10^5$) for $S_2N_2(SbCl_5)_2$

Atom	Position	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sb_1	8d	03348 (6)	$^1/_4$	$^1/_8$	305 (4)	487 (7)	420 (6)	0	0	17 (8)
Sb_2	8d	48558 (6)	$^1/_4$	$^1/_8$	319 (5)	402 (6)	457 (6)	0	0	21 (7)
Cl_{11}	16e	05877 (33)	40153 (33)	14122 (66)	842 (26)	411 (21)	2294 (76)	154 (20)	113 (45)	7 (36)
Cl_{12}	16e	04539 (27)	23087 (71)	27216 (28)	547 (17)	2097 (69)	476 (17)	70 (40)	17 (14)	181 (34)
Cl_{13}	8d	−12118 (27)	$^1/_4$	$^1/_8$	306 (17)	1476 (57)	708 (27)	0	0	51 (63)
Cl_{21}	16e	46035 (33)	39338 (40)	16963 (55)	648 (23)	647 (31)	2559 (97)	−1 (20)	−36 (32)	−798 (42)
Cl_{22}	16e	47346 (35)	20357 (71)	26555 (40)	742 (28)	2729 (126)	710 (31)	−273 (37)	−106 (20)	657 (49)
Cl_{23}	8d	64049 (26)	$^1/_4$	$^1/_8$	299 (16)	776 (35)	1053 (37)	0	0	−74 (51)
S	16e	25907 (21)	32866 (18)	13913 (28)	387 (12)	369 (13)	973 (25)	−8 (12)	7 (21)	−139 (13)
N_1	8d	18623 (70)	$^1/_4$	$^1/_8$	307 (48)	353 (70)	424 (61)	0	0	−33 (82)
N_2	8d	33258 (72)	$^1/_4$	$^1/_8$	303 (48)	375 (73)	500 (69)	0	0	−170 (89)

[a] The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Waals radii (3.6 Å); Cl_{12}–Cl_{22}, 3.337 Å; Cl_{21}–Cl_{21}, 3.397 Å; Cl_{11}–Cl_{11}, 3.425 Å; Cl_{13}–Cl_{23}, 3.559 Å. These may be compared with some close intermolecular Cl–Cl contacts found in previous structures involving $SbCl_5$ groups such as: $SbCl_5$, 3.33 Å;[9] $SbCl_5 \cdot SeOCl_2$, 3.33 Å;[10] $SbCl_5 \cdot POCl_3$, 3.41 Å.[11] All intermolecular distances less than 3.8 Å are listed in Table III.

The molecular structure contains an S_2N_2 ring formed of alternating sulfur and nitrogen atoms (Figures 1 and 2). Each of the nitrogen atoms is coordinated to an $SbCl_5$ group, and the N–$SbCl_5$ groups are then roughly octahedral. The crystallographic twofold axis passes through the axial chlorine, antimony, and nitrogen atoms. This twofold symmetry constrains the S_2N_2 ring to planarity. The S–N bond distances, given in Table IV, are equal to within the experimental error. Their weighted mean is 1.619 (5) Å. The internal angles of the ring are 84.9 (4) and 95.1 (4)° for the N–S–N and averaged S–N–S angles, respectively. These values are in remarkable agreement with those predicted from the infrared spectrum for the planar

(9) S. M. Ohlberg, *J. Am. Chem. Soc.*, **81**, 811 (1959).
(10) Y. Hermodsson, *Acta Chem. Scand.*, **21**, 1313 (1967).
(11) C. I. Brändén and I. Lindquist, *ibid.*, **17**, 353 (1963).

TABLE III

NONBONDED DISTANCES UNDER 3.8 Å

Intramolecular distances[a]				Intermolecular distances		
Cl_{13}–Cl_{11}	3.522 (6)	Cl_{23}–Cl_{21}	3.507 (6)	Cl_{13}–Cl_{23}	(1)[b]	3.559 (6)
Cl_{13}–Cl_{12}	3.392 (5)	Cl_{23}–Cl_{22}	3.388 (6)	Cl_{13}–S	(2)	3.745 (4)
Cl_{11}–Cl_{12}'	3.268 (11)	Cl_{21}–Cl_{22}	3.209 (12)	Cl_{12}–Cl_{23}	(3)	3.703 (5)
Cl_{11}–Cl_{12}	3.225 (12)	Cl_{21}–Cl_{22}'	3.228 (10)	Cl_{12}–Cl_{21}	(4)	3.758 (11)
Cl_{11}–N_1	2.968 (8)	Cl_{21}–N_2	2.951 (9)	Cl_{12}–Cl_{22}	(5)	3.337 (11)
Cl_{12}–N_1	3.121 (8)	Cl_{22}–N_2	3.111 (9)	Cl_{12}–S	(4)	3.521 (6)
Cl_{11}–S	3.183 (6)	Cl_{21}–S	3.193 (6)	Cl_{11}–Cl_{11}	(6)	3.425 (11)
Sb_1–S	3.574 (3)	Sb_2–S	3.587 (3)	Cl_{21}–Cl_{21}	(7)	3.397 (11)
N_1–N_2	2.186 (15)			S–Cl_{22}	(8)	3.568 (6)
S–S	2.390 (5)					

[a] Primed atoms are related to those in Table II by the crystallographic (and molecular) twofold axis. [b] These numbers correspond to the following transformations of the positions given in Table II: (1) $x - 1, y, z$; (2) $y - {}^1/_2, x, z - {}^1/_4$; (3) ${}^1/_2 - y, x - {}^1/_2, {}^1/_2 - z$; (4) $y - {}^1/_2, {}^1/_2 - x, {}^1/_2 - z$; (5) ${}^1/_2 - x, y, {}^3/_4 - z$; (6) $-x, -y + 1, z$; (7) $-x + 1, -y + 1, z$; (8) ${}^1/_2 - y, 1 - x, z - {}^1/_4$.

TABLE IV

BOND DISTANCES AND ANGLES IN $S_2N_2(SbCl_5)_2$

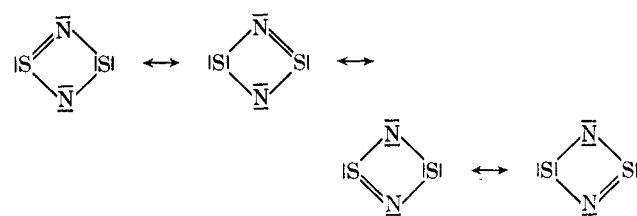
	Distance, Å			Angle, deg	
Atoms	Sb_1	Sb_2	Atoms[a]	Sb_1	Sb_2
S–N	1.616 (7)	1.623 (8)	S–N–S′	95.39 (59)	94.85 (61)
Sb–N	2.281 (10)	2.285 (11)	N_1–S–N_2	84.88 (42)	
Sb–Cl_1	2.308 (5)	2.282 (5)	Sb–N–S	132.31 (30)	132.57 (31)
Sb–Cl_2	2.313 (4)	2.300 (6)	N–Sb–Cl_1	80.58 (12)	80.50 (12)
Sb–Cl_3	2.310 (4)	2.313 (4)	N–Sb–Cl_2	85.59 (10)	85.49 (13)
			N–Sb–Cl_3	180	180
			Cl_1–Sb–Cl_2	90.03 (37)	88.91 (34)
			Cl_1–Sb–Cl_2'	88.53 (36)	89.60 (34)

Wtd av bond distances			Wtd av bond angles		
Bond type	No.	Av distance, Å	Angle	No.	Av angle
Sb–Cl	6[b]	2.305 (2)	S–N–S	2	95.11 (42)
S–N	2	1.619 (5)	Cl_1–Sb–N	2	80.54 (9)
Sb–N	2	2.283 (8)	Cl_2–Sb–N	2	85.55 (8)
			Cl_1–Sb–Cl_2	4	89.26 (18)

[a] The primed atoms are related to those in Table II by the twofold rotation. [b] This is the number of crystallographically independent bonds; the averaging is over all 10 Sb–Cl bonds.

S_2N_2 ring itself.[2] The predicted bond length and angles were 1.61 Å, 85°, and 95°. In fact, it is reasonable to assume that the coordination with $SbCl_5$ has not significantly changed the dimensions of the S_2N_2 ring. This is supported by the apparent weakness of the N→ $SbCl_5$ coordinate bond as evidenced by the ease with which one $SbCl_5$ can be removed,[3] by the similar infrared absorption frequencies of S_2N_2 and $S_2N_2(SbCl_5)_2$,[2,3] and by the relatively long Sb–N distance. The much stronger $S_4N_4 \cdot SbCl_5$ adduct is very difficult to dissociate[12] and has a significantly shorter Sb–N bond.[13] However, even in this case the average S–N distance in the eight-membered puckered ring remains the same as in S_4N_4 itself.[14]

The S–N distance in $S_2N_2(SbCl_5)_2$ is the same as that determined for S_4N_4, 1.616 (10) Å. Using a recent correlation of bond order *vs.* bond length in S–N compounds,[15] this corresponds to a bond order near 1.3. The most reasonable resonance structures which explain a fractional double-bond character and are consistent with equivalent S–N bonds are the set



These resonance forms correspond directly to a molecular orbital description which uses only the valence s and p orbitals of nitrogen and sulfur. The basic features of such a description are the filled σ-bonding network (a_g, b_{2u}, b_{1g}, and b_{3u}, based on point group D_{2h}) and the nonbonding unshared electron pairs ($2a_g$, b_{2u}, and b_{3u}). In addition, there is one filled π-bonding orbital (b_{1u}) and two filled, nonbonding π orbitals (b_{2g} and b_{3g}). Although there is possibly some involvement of the sulfur 3d orbitals in the bonding, similar to that proposed by Craig[16] and by Dewar, Lucken, and Whitehead[17] for other S–N and P–N ring systems, this does not fundamentally alter the bonding scheme just described.

Attempts to determine the importance of different

(12) K. J. Wynne and W. L. Jolly, *Inorg. Chem.*, **6**, 107 (1967).
(13) D. Neubauer and J. Weiss, *Z. Anorg. Allgem. Chem.*, **303**, 28 (1960).
(14) B. D. Sharma and J. Donohue, *Acta Cryst.*, **16**, 891 (1963).
(15) O. Glemser, A. Müller, D. Böhler, and B. Krebs, *Z. Anorg. Allgem. Chem.*, **367**, 184 (1968).
(16) D. P. Craig and N. L. Paddock, *Nature*, **181**, 1052 (1958); D. P. Craig, *J. Chem. Soc.*, 997 (1959).
(17) M. J. S. Dewar, E. A. C. Lucken, and M. A. Whitehead, *ibid.*, 2423 (1960).

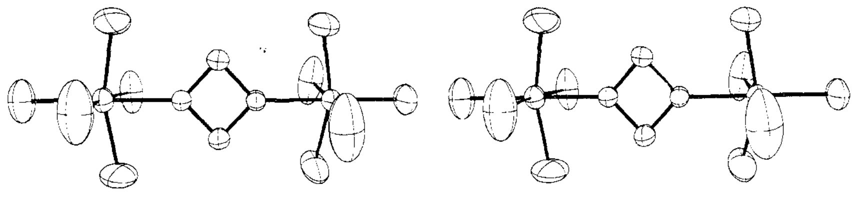


Figure 1.—A stereoscopic pair of drawings of the $S_2N_2(SbCl_5)_2$ molecule. The horizontal axis is *a;* the vertical axis is *b*. The $SbCl_5$ groups on the left and right contain Sb_1 and Sb_2, respectively. The thermal ellipsoids in this and the following drawings represent 50% probability contours.

Table V

	Root-mean-square amplitudes of vibration along principal axes, Å			Bond lengths corrected for thermal motion	Distances, Å		
Atoms	Axis 1	Axis 2	Axis 3	Atoms	*a*	*b*	*c*
Sb_1	0.1858 (13)	0.2248 (19)	0.2365 (21)	$S-N_1$	1.616 (7)		1.695
Sb_2	0.1899 (14)	0.2117 (17)	0.2378 (16)	$S-N_2$	1.623 (8)		1.705
Cl_{13}	0.1858 (52)	0.2937 (57)	0.4089 (80)	Sb_1-N_1	2.281 (10)		2.325
Cl_{23}	0.1837 (50)	0.2932 (73)	0.3616 (69)	Sb_2-N_2	2.285 (11)	2.285	2.329
Cl_{11}	0.2021 (57)	0.3158 (50)	0.5309 (88)	Sb_1-Cl_{11}	2.308 (5)	2.368	2.406
Cl_{12}	0.2358 (44)	0.2483 (41)	0.4897 (81)	Sb_1-Cl_{12}	2.313 (4)	2.358	2.397
Cl_{21}	0.2018 (62)	0.2707 (47)	0.5880 (109)	Sb_1-Cl_{13}	2.310 (4)	2.341	2.388
Cl_{22}	0.2496 (61)	0.2826 (56)	0.5804 (129)	Sb_2-Cl_{21}	2.282 (5)	2.353	2.394
S	0.1957 (36)	0.2093 (34)	0.3500 (44)	Sb_2-Cl_{22}	2.300 (6)	2.372	2.407
N_1	0.1863 (144)	0.1969 (229)	0.2303 (183)	Sb_2-Cl_{23}	2.313 (4)	2.338	2.382
N_2	0.1722 (276)	0.1851 (148)	0.2718 (236)				

[a] Uncorrected for thermal motion. [b] Corrected for thermal motion—riding model.[d] [c] Corrected for thermal motion—independent model.[d] [d] H. Binas, *Z. Anorg. Allgem. Chem.*, **352**, 271 (1967).

resonance forms by correlating them to the indicated bond order must be tempered by the recognition that the bonds are obviously strained in the four-membered ring. This four-membered ring is the smallest in a series of compounds containing rings composed only of sulfur and nitrogen atoms. Examples of other ring sizes are a five-membered ring in $S_3N_2Cl_2$,[18] a six-membered ring in $(NSCl)_3$,[19] a seven-membered ring in $S_4N_3NO_3$,[20] and an eight-membered ring in S_4N_4.[14]

Coordination with nitrogen has changed the configuration around the antimony from the trigonal bypyramid in crystalline $SbCl_5$[9] to a distorted octahedron with four equatorial chlorine atoms surrounding a linear Cl–Sb–N axis. Although crystallographically independent, the two $NSbCl_5$ groups are structurally equivalent to within experimental error. The Sb_2-Cl_{21} bond is the only one which appears to deviate significantly from the average of 2.305 (3) Å. However, this deviation is very dependent on corrections for thermal motion.[21] These bond length corrections and the rms amplitudes of vibration are listed in Table V.

The S_2N_2 ring is rotated 10.59 (21)° out of the *xy* plane. This and other dihedral angles are given in Table VI. By averaging two dihedral angles one can obtain a measure of the rotation of the $SbCl_5$ groups out of the *xy* plane. This rotation (where 0° would correspond to the equatorial Sb–Cl bonds being in the *xz* or *xy* planes) is 6.7 (2°) around Sb_1 and 17.8 (2)° around Sb_2. These dihedral angles are shown in Figure 3. The ease of vibrational or librational motion around the long molecular axis can be seen in the shapes of the

Table VI

Dihedral Angles between Planes Defined by Three Atoms

Plane 1	Plane 2	Angle, deg
$Cl_{11}-Sb_1-Cl_{13}$	$Cl_{12}-Sb_1-Cl_{13}$	90.8 (4)
$Cl_{11}-Sb_1-Cl_{13}$	$Cl_{12}'-Sb_1-Cl_{13}$	89.2 (4)
$Cl_{11}-Sb_1-Cl_{13}$	N_1-S-N_2	4.2 (3)
$Cl_{11}-Sb_1-Cl_{13}$	*xy* plane	6.3 (3)
$Cl_{12}-Sb_1-Cl_{13}$	$Cl_{22}-Sb_2-Cl_{23}$	10.5 (4)
$Cl_{21}-Sb_2-Cl_{23}$	$Cl_{22}-Sb_2-Cl_{23}$	89.6 (3)
$Cl_{21}-Sb_2-Cl_{23}$	$Cl_{22}'-Sb_2-Cl_{23}$	90.4 (3)
N_2-S-N_1	*xy* plane	10.6 (2)
$Cl_{21}-Sb_2-Cl_{23}$	N_1-S-N_2	7.4 (3)
$Cl_{21}-Sb_2-Cl_{23}$	*xy* plane	18.0 (2)
$Cl_{22}-Sb_2-Cl_{23}$	*xy* plane	107.6 (3)
$Cl_{12}-Sb_1-Cl_{13}$	*xy* plane	97.1 (3)

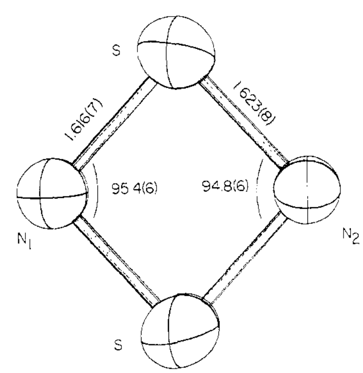


Figure 2.—A perspective drawing of the S_2N_2 ring in $S_2N_2(SbCl_5)_2$ as viewed normal to the plane of the ring.

(18) A. Zalkin, T. E. Hopkins, and D. H. Templeton, *Inorg. Chem.*, **5**, 1767 (1966).
(19) G. A. Wiegers and A. Vos, *Acta Cryst.*, **20**, 192 (1966).
(20) A. W. Cordes, R. F. Kruh, and E. K. Gordon, *Inorg. Chem.*, **4**, 681 (1965).
(21) C. K. Prout and J. D. Wright, *Angew. Chem. Intern. Ed. Engl.*, **7**, 659 (1968).

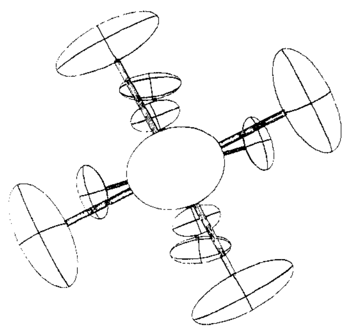


Figure 3.—A perspective drawing of $S_2N_2(SbCl_5)_2$ which shows the relative orientations of the S_2N_2 ring and the $SbCl_5$ groups. The view is down the *a* axis, from Sb_2 to Sb_1. The horizontal axis is $-c$; the vertical axis is $+b$.

thermal ellipsoids for the equatorial chlorine atoms, shown in Figures 1 and 3.

The octahedral geometry of the $N-SbCl_5$ groups is distorted by a shift of the equatorial chlorines toward the nitrogen donor atom such that the Cl_{eq}–Sb–N angles are all less than 90° whereas the Cl_{eq}–Sb–Cl_{ax} angles are correspondingly larger than 90°. This tendency of the equatorial chlorines to move in toward the donor atom is characteristic of $SbCl_5$ adducts. For example, $SbCl_5 \cdot SeOCl_2$,[10] $SbCl_5 \cdot S_4N_4$,[13] and $SbCl_5 \cdot CH_3CN$[22] exhibit average Cl_{eq}–Sb–donor atom angles of 86.2, 89.0, and 84.9°, respectively. The average Sb–Cl bond length in $S_2N_2(SbCl_5)_2$, 2.305 (3) Å, falls at the short end of the range of distances previously reported for similar adducts. Some of these are: $SbCl_5 \cdot SO_2(CH_3)_2$, 2.32 Å;[10] $SbCl_5 \cdot POCl_3$, 2.33 Å;[11] $SbCl_5 \cdot SeOCl_2$, 2.34 Å;[10] $SbCl_5 \cdot PO(CH_3)_3$, 2.34 Å;[11] $SbCl_5 \cdot SO(C_6H_5)_2$, 2.35 Å;[10] $SbCl_5 \cdot CH_3CN$, 2.36 Å;[22] $SbCl_5 \cdot S_4N_4$, 2.39 Å.[13] The $SbCl_5$ bond lengths reported for solid antimony pentachloride at −30° are 2.29 Å for the three basal chlorines and 2.34 Å for the two apical chlorines (average 2.31 Å).[9]

(22) H. Binas, *Z. Anorg. Allgem. Chem.*, **352**, 271 (1967).

Table VII

	$S_4N_4 \cdot SbCl_5$[a]	$CH_3CN \cdot SbCl_5$[b]	$S_2N_2(SbCl_5)_2$[c]	$SbCl_5$[d]
N–Sb, dist, Å	2.17	2.23	2.283	
Sb–Cl dist, Å	2.39	2.36	2.305	2.31
Cl_{eq}–Sb–N, deg	89.0	84.9	83.04	

[a] Reference 13. [b] Reference 22. [c] This work. [d] Reference 9.

We find, then, that in comparison with known structures of similar adducts of $SbCl_5$ with Lewis bases, $S_2N_2(SbCl_5)_2$ contains the longest Sb–N bond, the shortest Sb–Cl bonds, and the greatest displacement of the equatorial chlorines toward the donor atom (smallest average Cl_{eq}–Sb–donor atom angle). It appears that all three properties are functions of the strength of the adduct, and the data summarized in Table VII show that $S_2N_2(SbCl_5)_2$ is then the weakest such adduct reported to date. This correlation is apparently a general property of electron donor–acceptor complexes. In a recent review of this type of complex, Prout and Wright[21] presented an analogous table of these properties for a series of $N-BF_3$ adducts which showed the same trends with increasing donor strength that we describe here for $N-SbCl_5$ adducts.

Acknowledgment.—We thank Professor William L. Jolly for his interest in this work and Professor David Templeton and Dr. Allen Zalkin for the use of their laboratory facilities. R. L. P. expresses his thanks to the United States Atomic Energy Commission for support through the Lawrence Radiation Laboratory Inorganic Materials Research Division.

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Preparation and Nuclear Quadrupole Resonance Interpretation of the Structure of *cyclo*-Tri-μ-nitrido-dichlorophosphorusbis(oxochlorosulfur)

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Received March 4, 1969

A new preparation of *cyclo*-tri-μ-nitrido-dichlorophosphorusbis(oxochlorosulfur), $NPCl_2(NSOCl)_2$, based on a pyrolytic decomposition of the product of a Kirsanov reaction between a linear phosphonitrilic chloride and sulfamic acid is presented. The infrared spectrum of $NPCl_2(NSOCl)_2$ in polar solution is similar to that of the solid state but relative intensities and positions of some of the bands in the solution spectra are solvent polarity dependent. The ^{35}Cl nuclear quadrupole resonance spectrum complements the known crystal structure and its temperature dependence provides additional evidence of the departure of molecular symmetry from C_s in the solid state. The interactions are assigned and interpreted by comparison with those of other cyclic inorganic systems.

Introduction

There has been considerable interest in the structure and properties of cyclic phosphonitrilic halides, though no consensus has been reached concerning the bonding involved in such compounds. Cyclic trimeric sulfanuric halides have also been reported and characterized. A preparation of the title compound, $NPCl_2(NSOCl)_2$, was reported by van de Grampel and Vos in 1963.[1] It can be thought of as a ring composed of

(1) J. C. van de Grampel and A. Vos, *Rec. Trav. Chim.*, **82**, 246 (1963).