In contrast to this fixed Ag–C distance of 2.47 Å in Ag–aromatic complexes, the shortest Ag–C distance in olefin complexes varies over a considerable range,[26–31] from a short 2.31 (4) Å in norbornadiene·2AgNO$_3$[26] to 2.45 Å in the 3:1 bullvalene·AgNO$_3$ complex.[30]

Acknowledgment We wish to acknowledgment financial support from NSF Grant GP-6747.

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The Crystal Structure of the Chlorine Complex of Bis(*p*-chlorophenyl) Sulfide

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Abstract: The crystal structure of a chlorine complex of bis(*p*-chlorophenyl) sulfide was determined from single-crystal Weissenberg and precession X-ray diffraction patterns from a crystal maintained at 143°K. The cell dimensions at that temperature are $a = 12.876 \pm 0.003$ Å, $b = 7.795 \pm 0.002$ Å, $c = 13.794 \pm 0.004$ Å, $\beta = 111.02 \pm 0.03°$, space group $P2_1/c$; four molecules of $(ClC_6H_4)_2SCl_2$ per cell give a calculated density of 1.796 g/cm^3. Visual estimates of the 1213 observed reflections were fitted by least-squares methods to give an R of 0.11. The structure of the complex may be described as a trigonal bipyramid about sulfur with the *p*-chlorophenyl groups and an unshared pair of electrons occupying the equatorial plane (C–S–C bond angle = 109°), and the Cl atoms occupying axial positions at 2.26 and 2.32 Å. The trigonal-bipyramid groups align themselves into long chains with the Cl–Cl distances between groups being 3.31 Å. The intermolecular interactions are nearly linear (Cl–S–Cl···Cl–S–Cl···; Cl···Cl–S angle is 162°). The configuration of the complex fits logically into the series of observed group VI–group VII complexes.

Recently, an investigation was begun to seek a new and purer synthetic route from organic sulfide compounds to the organic sulfoxide derivatives. In an intermediate step in the procedure involving halogenation of organic sulfides, solid complexes were found. The chlorine complex of bis(*p*-chlorophenyl) sulfide was one of the most stable of the products observed. Nmr work indicated that the complexing chlorine atoms were symmetrically disposed with respect to the organic portion of the molecule.[1] These studies together with the structures of reported group VI–halogen complexes indicated very strongly that there would be a trigonal-bipyramidal configuration about the sulfur atom. The single-crystal structural analysis was undertaken to verify this prediction and to determine if the bond distances would correspond to the labile chemical character of the complex.

Experimental Details

The crystals used in the investigation of the chlorine complex of bis(*p*-chlorophenyl) sulfide, $C_{12}H_8Cl_4S$, were prepared by the gaseous chlorine saturation of an ice-cold carbon tetrachloride solution of the diaryl sulfide, as described by Maner.[2] Product identification was confirmed *via* ir and nmr spectral and chemical analysis.

The crystals formed were quite unstable even under solution, being decomposed by traces of moisture and by lowering the partial pressure of chlorine. Because of these difficulties individual crystals were mounted in glass capillaries and stored under liquid nitrogen, and the X-ray diagrams were made with the crystals maintained at ~143°K. The cell dimensions were obtained from Weissenberg camera back-reflection photographs at low temperature. A least-squares treatment of the film coordinates of observable reflections gave the following cell dimensions: $a = 12.876 \pm 0.003$ Å, $b = 7.795 \pm 0.002$ Å, $c = 13.794 \pm 0.004$ Å, and $\beta = 111.02 \pm 0.03°$. The systematic absences of l odd in ($h0l$) data and of k odd in ($0k0$) data indicated the space group as $P2_1/c$.

Film intensity data were gathered for layers ($hk0$) through ($hk7$) using multiple-film equiinclination Weissenberg low-temperature techniques with Cu Kα radiation (1.5418 Å, Ni filter). The crystal used was twinned in such a fashion that reflections from the twinned portions exactly superimposed only in layers ($hk3$) and ($hk6$) (twin axis = [001]). These data were discarded. The twinned reflections were separately indexed in the remaining layers and the intensity data were utilized. Additional film intensity data taken at low temperature were obtained for layers ($0kl$) through ($5kl$) and for layers ($h0l$) through ($h3l$) utilizing Buerger precession camera techniques with Mo Kα radiation (0.7107 Å, Zr filter). The precession data sets were obtained from single crystals which were obtained by cleaving the twinned crystals which always were found.

Because of the instability of the crystalline complex and the lack of a suitable displacement medium at near-normal temperatures, the density of the compound was not determined experimentally. The sulfide complex crystals were observed, however, to have a density slightly greater than that of the chlorine-saturated CCl_4 solution from which they were grown. It seemed reasonable to assume that the density of the chlorine gas saturated solution did not deviate greatly from the density of pure carbon tetrachloride (1.594 g/ml).[3] A calculated density value of 1.796 for four molecules of $(ClC_6H_4)_2SCl_2$ per unit cell is quite compatible with the rough specific gravity observation.

The accumulated intensity data were multiply estimated by visual means. The estimates obtained for a given reflection and its sym-

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(1) R. E. Buckles and R. J. Maner, submitted for publication.

(2) R. J. Maner, Ph.D. Dissertation, University of Iowa, 1967.

(3) "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1968, p C-407.

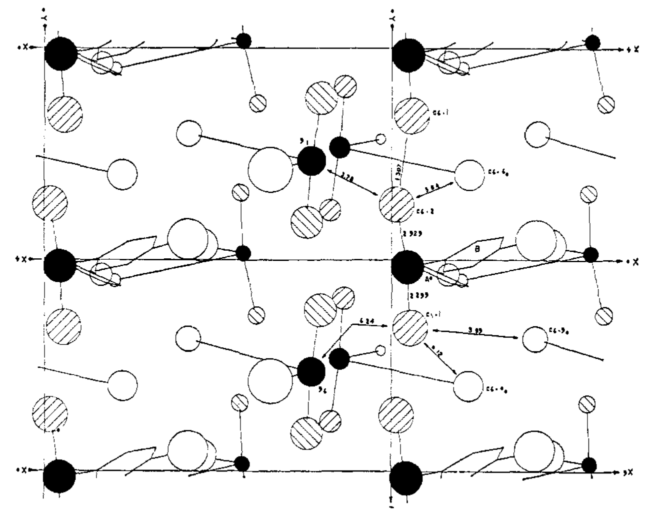

Figure 1. Projection of $[p\text{-ClC}_6\text{H}_4]_2\text{SCl}_2$ on to the (001) plane. Solid circles are S; lined circles are the complexing Cl atoms; open circles are the p-Cl atoms. Sizes of the circles are related to their z coordinate. Most of the phenyl rings have been omitted for clarity.

metry related equivalent reflections were used to obtain a resultant mean intensity and to determine a weighting factor which was based on the standard deviation of the intensity estimations. The data were corrected for Lorentz and polarization factors. A total of 2298 independent obtainable reflections were used; 1213 of these reflections had observable intensities. An absorption correction was not applied to the data sets obtained with Mo Kα radiation (μ = 11.1 cm^{-1}) because of the relatively small maximum μR value of 0.33 and the irregular shape of the crystals. Some decomposition of the crystal during the exposures inevitably occurred, making precise absorption corrections impossible. The data obtained with Cu Kα radiation (μ = 102 cm^{-1}) were treated for absorption using an approximate absorption correction involving an angular dependent averaging of sperical and cylindrical correction factors ($\mu R_{\text{max}} = 1.0$; $\mu R_{\text{min}} = 0.76$). Tests of this approximate correction indicated that the maximum errors in the approximate absorption corrections were less than 10%.

Atom-scattering factors used in the structure factors calculation were taken from the "International Tables for Crystallography." The real portion of dispersion corrections was applied throughout the refinement procedure.[4]

Refinement was carried out using an IBM 7044 computer and a locally written full-matrix least-squares refinement procedure. Three types of discrepancy factors were calculated: $R_1 = \Sigma|\Delta F|/\Sigma|F_o|$, $R_{1w} = \Sigma w|\Delta F|/\Sigma w|F_o|$, and $R_{1h}{}^5 = [\Sigma w(\Delta F)^2/\Sigma wF_o{}^2]^{1/2}$. The weighting factor used was $w = 1/S^2{}_{(F)}$ where $S_{(F)}$ was the estimated standard deviation of the mean value of the structure factor estimates. Reflections calculated equal to or less than the chosen minimum observable intensity were given zero weight unless in the refinement $|F_c|$ was greater than the minimum $|F_o|$, whereupon these reflections were treated with unit weight.

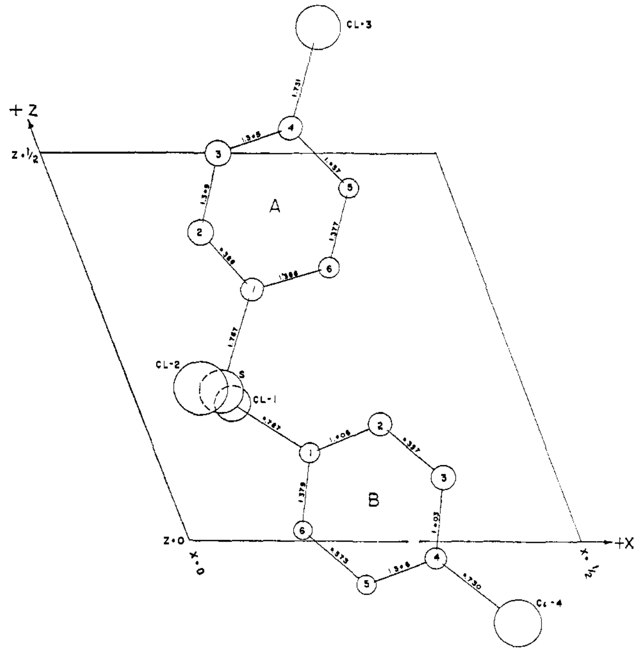

Figure 2. Projection of $[p\text{-ClC}_6\text{H}_4]_2\text{SCl}_2$ on to the (010) plane.

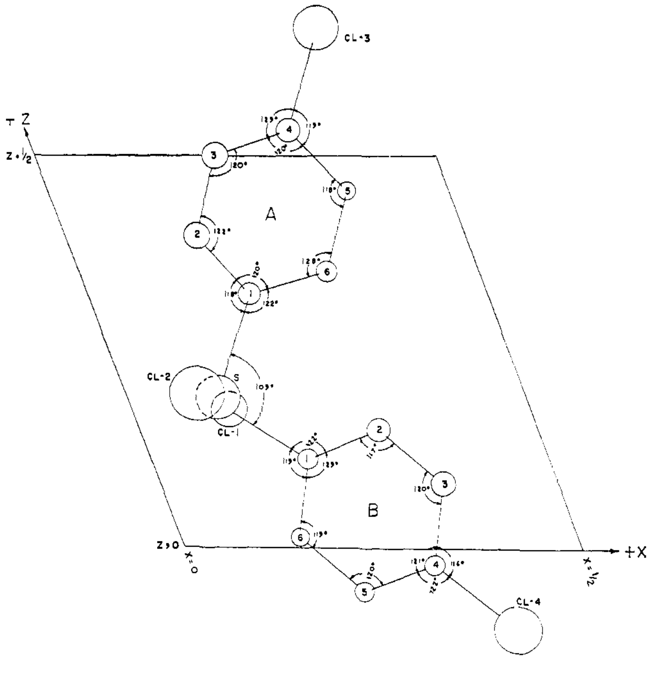

Figure 3. Projection of $[p\text{-ClC}_6\text{H}_4]_2\text{SCl}_2$ on to the (010) plane.

Structure Determination

The heavy atoms of the structure were originally located using a three-dimensional Patterson map. Refinement of the intensity data with a least-squares procedure varying positional parameters and the over-all scale factor resulted in a unit weight residual factor (R_1) of 0.37. A three-dimensional electron density map at this point revealed the approximate positions of the carbon atoms. The carbon atoms from one phenyl group were initially added to the refinement procedure and individual scale factors were now allowed to vary. The result was a weighted residual factor (R_{1w}) of 0.27. The carbon atoms of the second phenyl group were then added and the refinement continued in the same manner to a R_{1w} value of 0.18. At this point, the isotropic temperature parameters of the atoms were allowed to vary and the refinement continued to a R_{1w} value of 0.137. The positions of the phenyl hydrogen atoms were hereafter calculated prior to each cycle of refinement. All hydrogen parameters were then held fixed throughout the refinement. Isotropic refinement led to a R_{1w} value of 0.105. Anisotropic thermal refinement followed with a decrease in the R_{1w} value of 0.088. Equivalent

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(4) "International Tables of Crystallography," Vol. II, Kynoch Press, Birmingham, England, 1959, pp 295, 302.

(5) W. C. Hamilton, *Trans. Am. Cryst. Assoc.*, **1**, 17 (1965).

Table I. Fractional Atomic Position Parameters[a]

	x	y	z
S	0.1140 (1)	0.0319 (2)	0.1936 (2)
Cl(1)	0.1222 (2)	0.3195 (2)	0.1796 (2)
Cl(2)	0.0895 (2)	0.7371 (2)	0.1972 (2)
Cl(3)	0.4173 (2)	0.0713 (3)	0.6625 (2)
Cl(4)	0.3756 (2)	0.9059 (3)	0.8967 (2)
C(1A)	0.2045 (6)	0.0418 (8)	0.3246 (6)
C(2A)	0.1663 (6)	0.9768 (9)	0.3993 (6)
C(3A)	0.2278 (6)	0.9853 (9)	0.5015 (7)
C(4A)	0.3318 (6)	0.0557 (10)	0.5332 (6)
C(5A)	0.3762 (6)	0.1221 (11)	0.4572 (6)
C(6A)	0.3104 (6)	0.1112 (8)	0.3537 (6)
C(1B)	0.1957 (6)	0.9981 (8)	0.1135 (6)
C(2B)	0.2987 (6)	0.9128 (11)	0.1515 (6)
C(3B)	0.3537 (6)	0.8899 (11)	0.0816 (7)
C(4B)	0.3037 (6)	0.9467 (11)	0.9788 (7)
C(5B)	0.2024 (7)	0.0261 (11)	0.9452 (7)
C(6B)	0.1484 (6)	0.0564 (9)	0.0131 (7)
H(2A)	0.0851	0.9167	0.3767
H(3A)	0.1941	0.9362	0.5576
H(5A)	0.4580	0.1794	0.4776
H(6A)	0.3419	0.1572	0.2953
H(2B)	0.3340	0.8668	0.2308
H(3B)	0.4346	0.8286	0.1070
H(5B)	0.1649	0.0650	0.8646
H(6B)	0.0699	0.1249	0.9879

[a] Estimates of the standard deviations in the last significant digit are given in parentheses.

Table II. Atomic Anisotropic Temperature Factors[a]

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
S	23 (1)	57 (3)	22 (1)	−15 (3)	19 (2)	−2 (3)
Cl(1)	40 (1)	64 (3)	28 (1)	−2 (3)	33 (2)	4 (3)
Cl(2)	43 (1)	60 (3)	32 (1)	−20 (3)	28 (3)	−11 (3)
Cl(3)	46 (2)	149 (4)	20 (1)	14 (4)	7 (3)	−11 (4)
Cl(4)	39 (1)	141 (4)	29 (1)	15 (4)	43 (2)	−37 (4)
C(1A)	32 (5)	31 (9)	12 (4)	−44 (12)	22 (8)	−23 (11)
C(2A)	24 (4)	58 (11)	31 (6)	−1 (13)	25 (9)	36 (14)
C(3A)	28 (5)	34 (10)	41 (6)	20 (12)	37 (9)	11 (14)
C(4A)	30 (5)	93 (13)	12 (5)	53 (14)	3 (9)	−22 (13)
C(5A)	31 (5)	83 (12)	21 (5)	−12 (14)	25 (9)	5 (15)
C(6A)	22 (5)	104 (14)	26 (5)	22 (14)	39 (9)	1 (16)
C(1B)	32 (5)	20 (10)	18 (5)	−36 (11)	7 (8)	−23 (12)
C(2B)	31 (5)	99 (14)	11 (4)	−30 (14)	−12 (9)	−16 (13)
C(3B)	30 (5)	115 (14)	21 (5)	3 (16)	34 (10)	−27 (17)
C(4B)	23 (5)	109 (13)	25 (5)	−53 (14)	31 (9)	−26 (15)
C(5B)	37 (5)	104 (13)	15 (5)	−30 (15)	33 (9)	50 (15)
C(6B)	40 (6)	35 (10)	31 (6)	−78 (13)	10 (10)	−6 (13)

[a] Anisotropic temperature factor: $\exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{12} + hlb_{13} + klb_{23})]$. All b values × 10^4. Estimates of the standard deviations in the last signifiant digit are given in parentheses. Hydrogen atoms were assigned the same b values as those of the carbon atoms to which they were bonded.

Table III. Interatomic Distances[a]

	Intramolecular Distances		
S–Cl(1)	2.259 (3)	S–C(1A)	1.767 (7)
S–Cl(2)	2.323 (3)	S–C(1B)	1.797 (9)
S–Cl(3)	6.249 (3)		
S–Cl(4)	6.243 (3)		
Cl(1)–Cl(2)	6.692 (3)		
Cl(1)–Cl(4)	6.710 (3)		
Cl(2)–Cl(3)	6.809 (3)		
Cl(2)–Cl(4)	6.591 (3)		
C(1A)–C(2A)	1.386 (11)	C(1B)–C(2B)	1.406 (10)
C(2A)–C(3A)	1.349 (12)	C(2B)–C(3B)	1.397 (13)
C(3A)–C(4A)	1.365 (10)	C(3B)–C(4B)	1.403 (12)
C(4A)–C(5A)	1.457 (12)	C(4B)–C(5B)	1.366 (11)
C(5A)–C(6A)	1.377 (11)	C(5B)–C(6B)	1.373 (13)
C(6A)–C(1A)	1.386 (10)	C(6B)–C(1B)	1.376 (11)
C(4A)–Cl(3)	1.731 (8)	C(4B)–Cl(4)	1.730 (9)
	Intermolecular Distances[b]		
Cl(1)...Cl(2_1)	3.307 (3)		
Cl(3)...Cl(4_1)	3.692 (3)		
Cl(4)...Cl(4_3)	4.70		
Cl(1)...Cl(2_3)	3.75	1.	(x, y, z)
S...Cl(2_3)	3.78	2.	$(\bar{x}, \bar{y}, \bar{z})$
Cl(2)...Cl(4_4)	3.84	3.	$(\bar{x}, {}^1/_2 + y, {}^1/_2 - z)$
Cl(1)...Cl(3_4)	3.91	4	$(x, {}^1/_2 - y, {}^1/_2 + z)$
Cl(3)...Cl(4_3)	3.99		
Cl(1)...Cl(4_4)	4.12		
S...Cl(1_3)	4.34		
	Interatomic Distances of Ring Carbon Atoms to the Complexed Chlorine Atoms		
C(1A)	2.89	C(1A)	3.00
C(2A)	3.95	C(6A)	4.08
C(3A)	4.93	C(5A)	5.06
C(4A)	5.09	C(4A)	5.17
C(5A)	4.32	C(3A)	4.37
C(6A)	3.17	C(2A)	3.20
C(1B)	2.92	C(1B)	2.90
C(2B)	3.97	C(6B)	3.82
C(3B)	4.94	C(5B)	4.78
C(4B)	5.08	C(4B)	5.01
C(5B)	4.34	C(3B)	4.37
C(6B)	3.16	C(2B)	3.24

[a] Values given in ångstroms. Estimates of the standard deviation in the last significant digit are given in parentheses. [b] Subscripts refer to equivalent position.

reflections of the precession data were then averaged. The individual layer scale factors were fixed and an overall scale factor was allowed to vary. The final residual factors were: $R_1 = 0.115$, $R_{1w} = 0.087$, and $R_{1h} = 0.11$. The standard deviation in an observation of unit weight is 2.9.

The structure of the sulfide complex is illustrated by the projections on to the (001) plane in Figure 1 and on to the (010) plane in Figures 2 and 3. Table I gives a listing of the final atomic positions. Table II lists the atoms and their final anisotropic temperature factors. Tables III and IV respectively contain pertinent interatomic distances and interatomic angles, together with the estimates of the standard deviations based on the least-squares error matrix. Equations of planes of atoms plus selected angles between planes are given in Table V. Figure 4 is an illustration of the (100) plane with interatomic distances of interest. Figure 5 is a projection of a unit cell upon the (010) plane illustrating the packing arrangement of the molecules. Calculated and observed structure factors are available.[6]

An analysis of the thermal motion was attempted in order to obtain some guide to the size of thermal corrections to bond lengths. It was assumed that no coupling between the translational and libration motion existed so that the treatment of thermal motion due to Cruickshank[7] could be applied. The quality of the data prob-

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(6) A list of calculated and observed structure factors has been deposited as Document No. NAPS-00487 with the ASIS National Auxiliary Publication Service, c/o CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001. A copy may be secured by citing the document number and by remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

(7) D. W. J. Cruickshank, *Acta Cryst.*, **9**, 754 (1956).

Table IV. Interatomic Angles[a]

Cl(1)–S–Cl(2)	174.5 (1.1)	C(1A)–S–C(1B)	108.6 (0.4)
S-Cl(1)–Cl(2)	162.9 (0.3)	C(4A)–S–C(4B)	113.9 (0.2)
S-Cl(2)–Cl(1)	161.8 (0.3)		
Cl(1)–S–C(1A)	91.3 (0.3)	Cl(3)–S–Cl(4)	113.8 (0.1)
Cl(1)–S–C(1B)	91.4 (0.3)		
Cl(2)–S–C(1A)	93.8 (0.3)	Cl(1)–S–Cl(3)	91.3 (0.0)
Cl(2)–S–C(1B)	89.0 (0.3)	Cl(1)–S–Cl(4)	91.9.(0.1)
		Cl(2)–S–Cl(3)	93.8 (0.0)
		Cl(2)–S–Cl(4)	88.2 (0.1)
S-C(1A)-C(2A)	117.7 (0.3)	S-C(1B)–C(2B)	121.5 (0.4)
S-C(1A)-C(6A)	122.2 (0.4)	S-C(1B)-C(6B)	115.1 (0.7)
C(6A)–C(1A)-C(2A)	120.1 (0.4)	C(6B–C(1B)–C(2B)	123.2 (1.1)
C(1A)–C(2A)-C(3A)	121.8 (1.0)	C(1B)–C(2B)–C(3B)	116.6 (0.4)
C(2A)–C(3A)–C(4A)	119.7 (0.7)	C(2B)–C(3B)–C(4B)	119.7 (1.0)
C(3A)–C(4A)–C(5A)	120.3 (0.4)	C(3B)–C(4B)–C(5B)	121.5 (1.1)
C(4A)–C(5A)–C(6A)	118.0 (1.0)	C(4B)–C(5B)–C(6B)	120.2 (0.4)
C(5A)–C(6A)–C(1A)	120.0 (0.7)	C(5B)–C(6B)–C(1B)	118.7 (1.1)
C(3A)–C(4A)–Cl(3)	123.1 (0.4)	C(3B)–C(4B)–Cl(4)	116.4 (1.0)
C(5A)–C(4A)–Cl(3)	116.6 (0.8)	C(5B)–C(4B)–Cl(4)	122.1 (0.2)
C(1A)–C(4A)–Cl(3)	176.8 (8.7)		
C(1B)–C(4B)–Cl(4)	177.3 (10.9)		

[a] Values given in degrees. Estimates of the standard deviation in the last significant digit are given in parentheses.

ably does not justify a more elaborate treatment. The values of the T (Å^2) and W^2 (deg^2) tensors obtained from this treatment are

$$\begin{array}{llll}
T_{11} = & 0.0152 \pm 0.0022 & W_{11} = & 2.9 \pm 0.7 \\
T_{22} = & 0.0149 \pm 0.0023 & W_{22} = & 1.6 \pm 0.6 \\
T_{33} = & 0.0152 \pm 0.0017 & W_{33} = & 5.0 \pm 0.1 \\
T_{12} = & -0.0042 \pm 0.0021 & W_{12} = & -1.0 \pm 0.6 \\
T_{13} = & 0.0009 \pm 0.0017 & W_{13} = & 0.4 \pm 0.9 \\
T_{23} = & -0.0007 \pm 0.0017 & W_{23} = & 1.1 \pm 1.0
\end{array}$$

The unit vectors on which these tensors are based are $\mathbf{i} = \mathbf{a}/|a|$, $\mathbf{j} = \mathbf{b}/|b|$, and $\mathbf{k} = \mathbf{c}^*/|c^*|$, where c^* is the reciprocal cell vector.

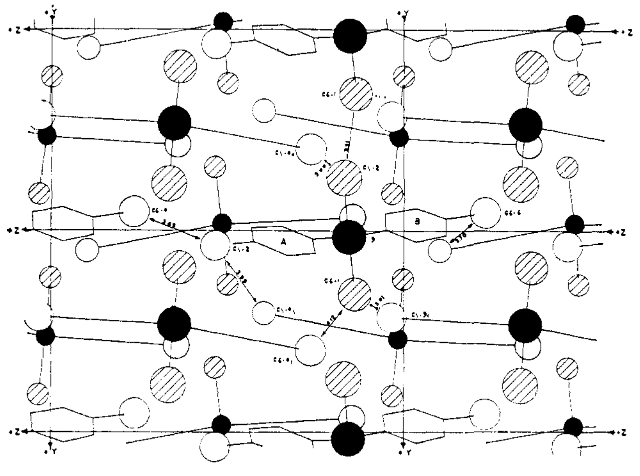

Figure 4. Projection of [p-ClC$_6$H$_4$]$_2$SCl$_2$ on to the (100) plane. Solid circles are S; lined circles are the complexing Cl atoms; open circles are the p-Cl atoms. Sizes of the circles are related to their z coordinates. Most of the phenyl rings have been omitted for clarity.

The interatomic distances which are given in the following part of the paper have not been corrected for the effects of thermal vibration because of the uncertainty in the interpretation of the data. An order of magnitude calculation based on analysis above, however, indicates that the bond lengths would be lengthened by less than 0.001 Å, which is considerably less than the standard deviations in the bond lengths.

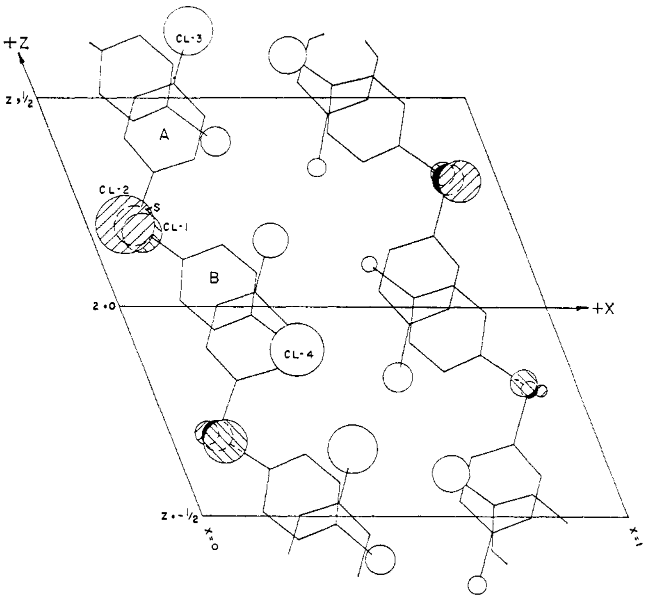

Figure 5. Projection of [p-ClC$_6$H$_4$]$_2$SCl$_2$ on to the (010) plane to show the packing arrangement of the molecules.

Discussion of the Structure

The crystallographic configuration of bis(p-chlorophenyl) sulfide dichloride is trigonal bipyramidal about the sulfur atom. The aryl groups occupy two equatorial positions with a lone pair of electrons occupying a position along the third. The angle between the aryl equatorial vectors of 109° is quite consistent with previously observed results (see Table VI). In the third equatorial direction in which the orbital which contains the unshared pair of electrons should be located, there are no near-neighbor atoms. The nearly linear chlorine–sulfur–chlorine grouping (angle = 174.5°) is approximately normal to the plane of the sulfur and the

Table V. Planes Formed by Atomic Positions

Equations of planes in the form: $pi + qj + rk = d$ (in Å)[a]

					Deviation from plane, Å								
Ring	*p*	*q*	*r*	*d*	*S*	Cl(3)	Cl(4)	C1	C2	C3	C4	C5	C6
A	0.435	−0.898	−0.058	−4.381				−0.014	0.011	−0.002	−0.004	0.000	0.009
B	−0.388	−0.885	−0.259	−14.418				−0.009	0.012	−0.006	−0.003	0.003	0.003
A (S, *p*-Cl)	0.433	−0.899	−0.066	−4.551	−0.037	−0.024		0.006	0.027	0.004	−0.004	0.005	0.023
B (S, *p*-Cl)	−0.390	−0.882	−0.265	−14.493	0.042		0.033	−0.018	−0.004	−0.020	−0.007	0.005	−0.032

Plane	*p*	*q*	*r*	*d*
A [S, Cl(1), C(1A)]	0.952	−0.108	−0.286	2.767
B [S, Cl(2), C(1B)]	−0.570	0.066	−0.819	−16.862
C [S, C(1A), C(1B)]	0.122	0.989	−0.082	7.715
D [S, Cl(1), Cl(2)]	0.773	−0.125	−0.622	−4.046
E [S, Cl(1), C(1B)]	−0.583	−0.029	−0.812	−17.629
F [S, Cl(2), C(1A)]	0.948	−0.143	−0.284	2.490

Angle between normals to ring 1 and ring 2 = 50.1°
Angle between normals to ring 1A and ring 2A = 50.1°
Angle between normals to plane A and plane B = 71.6°
Angle between normals to plane C and plane D = 88.7°
Angle between normals to plane E and plane F = 71.4°
Angle between normals to plane C and ring 1 = 33.8°
Angle between normals to plane C and ring 2 = 26.1°

[a] The coordinate system used is that of a rectangular system upon conversion from the monoclinic system of the crystal cell: $i = \mathbf{a}/|a|$, $j = \mathbf{b}^*/|b^*|$, $k = \mathbf{c}^+/|c^+|$.

two equatorial vectors of the aryl systems (angle = 88.7°). The sulfur–chlorine bond lengths of 2.259 and 2.323 Å are much longer than their normal covalent radii sum of 2.03 Å. These results are consistent with axial bonding positions in a trigonal-bipyramid configuration.[8]

The three projections illustrate the general position of the axial vectors parallel to the *y* axis and the interleaving of the equatorial groups in the *x*–*z* plane. The aryl groups exhibit compact packing as shown by the 3.69-Å distance between neighboring *para*-chlorine atoms. The (010) projection illustrates that the aryl groups are approximately stacked along the *b* axis. The complexing positions appear in this projection as perpendicular rods.

The sulfur–carbon bonding distances of 1.767 and 1.797 Å are less than two standard deviations apart, and the difference is not considered significant. The *para*-chlorine atoms are bonded to the phenyl groupings at a distance of 1.73 Å, and the two sulfur atom to *para*-chlorine atom distances are 6.24 and 6.25 Å. The average carbon–carbon bond lengths of the two rings, A and B, are both 1.387 Å.

A particular distinguishing feature of the sulfide complex is the significant discrepancy between the two sulfur atom to complexing chlorine atom bond lengths, 2.259 and 2.323 Å. This type of distortion has been observed previously in trigonal-bipyramidal complexes (see Table VI). The difference in bond length is generally explained in terms of the crystal cell packing situation, and the same argument can be applied here. The sulfur–chlorine bond distances observed indicate a weakening of the bond from that of a single bond. This assumption is further substantiated by the instability of the complex. Thus, it seems reasonable to assume that the molecular packing of the crystal might cause a distortion of 0.06 Å to achieve a maximum lattice binding energy.

Outside of an axial nearly linear interaction of 3.31 Å between chlorine atoms of adjacent molecules there are no interatomic distances present in the system less than typical van der Waals distances. However, the complexing chlorine atom, Cl(2), lies at a position 3.78 Å from a sulfur atom of another molecule (van der Waals radii sum = 3.70 Å). The nearest intermolecular sulfur interaction with Cl(1) is 4.34 Å. The spatial arrangement is such that the chlorine atom lies between the volume taken up by the lone pair of electrons of the sulfur atom and the aryl ring, B, and the chlorine atom is displaced toward the aryl ring (see Figure 1).

The two phenyl rings should be expected to twist about their sulfur linkage because of the *ortho*-hydrogen atom interaction. This rotation about the aryl axis is observed, but not to an equivalent degree for each ring. Ring A twists 33.8° while ring B twists only 26.1° relative to the equatorial plane. The smaller rotation of ring B is consistent with the movement of the Cl(2) atom toward the ring. Neither Cl(1) nor Cl(2) is equidistant from all the atoms in the phenyl groups. The Cl(1) atom, however, has equivalent distances to both phenyl groups as shown by comparison of interatomic Cl(1) to aryl positions (see Table III). The Cl(2) is less symmetrically located. The degree of the asymmetry to the aryl groups by Cl(2) is most emphatically exhibited by the Cl(2) to *para*-chlorine distances of 6.81 (ring A) and 6.59 (ring B) Å and the Cl(2) to carbon-1 distances of 3.00 (A) and 2.90 (B) Å. In contrast, the Cl(1) to *para*-chlorine distances are 6.71 (A) and 6.69 (B) Å and to the carbon-1 atoms, 2.89 (A) and 2.92 (B) Å. The over-all repulsive effect on the Cl(2) atom causes a greater movement of this atom from its most symmetrical bonding position with sulfur. The result is a weaker bond and correspondingly longer bond length.

The remaining distinctive feature of the observed structure is the nearly linear interaction between the complexing chlorine atoms of one molecule to that of an adjacent molecule. This Cl(1) · · · Cl(2) interaction distance of 3.307 Å is well below that of the van der

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[8] M. C. Day, Jr., and J. Selbin, "Theoretical Inorganic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1962, p 207.

Table VI. Listing of Previous Crystallographic Group VI–halogen Complexes

No.	Chemical formula	Ref	Complex type[a]	E − X₁,[b] Å	E − X₂, Å	X₁ − X₂,[b] Å
1	$C_4H_4O_2\cdot 2ICl$	*c*	MC (O···I–Cl)	2.6 (0.9)		2.3 (0.0)
2	$C_4H_4O_2\cdot Br_2$	*d*	MC (O···Br–Br···O)	2.71 (0.87)		2.31 (0.03)
3	$C_4H_8S_2\cdot 2I_2$	*e*	MC	2.867 (0.50)		2.787 (0.13)
4	$(p\text{-}CH_2C_6H_4)_2S\cdot I_2$	*f*	MC	2.78 (0.41)		2.819 (0.16)
	$(p\text{-}ClC_6H_4)_2S\cdot Cl_2$		TB	2.259 (0.23)	2.323 (0.29)	
5	$C_4H_8Se\cdot I_2$	*g*	MC	2.762 (0.26)		2.914 (0.31)
6	$C_4H_8Se_2\cdot 2I_2$	*h*	MC	2.81 (0.31)		2.83 (0.17)
7	$C_4H_8OSe\cdot ICl$	*i*	MC(Se–I···Cl)	2.630 (0.13)		2.73 (0.50)
8	$C_4H_8OSe\cdot I_2$	*j*	MC(Se···I–I)	2.755 (0.255)		2.956 (0.30)
9	$C_4H_8SSe\cdot Br_2$	*k*	TB(Br–Se–Br)	2.545 (0.235)	2.548 (0.24)	
10	$(C_6H_5)_2Se\cdot Cl_2$	*l*	TB	2.30 (0.14)	2.30	
11	$(C_6H_5)_2Se\cdot Br_2$	*m*	TB	2.52 (0.19)	2.52	
12	$(CH_3C_6H_4)_2Se\cdot Cl_2$	*n*	TB	2.38 (0.22)	2.38	
13	$(CH_3C_6H_4)_2Se\cdot Br_2$	*n*	TB	2.55 (0.24)	2.55	
14	$\alpha\text{-}(CH_3)_2Te\cdot Cl_2$	*o*	TB	2.480 (0.12)	2.51 (0.18)	
15	$(C_6H_5)_2Te\cdot Br_2$	*p*	TB	2.682 (0.17)	2.682	
16	$(p\text{-}ClC_6H_4)_2Te\cdot I_2$	9	TB	2.922 (0.22)	2.947 (0.25)	

No.	Equatorial group angle, deg	Complexing group angle, deg	Shortest "linear" or "perpendicular" intermolecular interaction [van der Waals sum in brackets]	
1		180	Cl···Cl(3.38 Å [3.60])	I–Cl···Cl (176°)
2		178	Not applicable in this situation	
3	101.5	177.9	I···S (3.789 Å [4.00])	I–I···S (74°) I···S–I (85°)
			I···I (4.067 Å [4.30])	I–I···I (157°)
4	93	179	I···I (4.33 Å [4.30])	I–I···I (173°)
	108.6°	174.5	Cl···Cl (3.307 Å [3.60])	S–Cl···Cl (163°)
5	93.2	179.4	Se···I (3.638 Å [4.15])	I–Se···I (167°) Se···I–I (167°)
6	100.5	176	Se···I (3.889 Å [4.15])	I–Se···I (83°) Se···I–I (78°)
7	96	175.8	Se···Cl (3.61 Å [3.80])	I–Se···Cl (177°) Se···Cl–I (178°)
8	94	174.8	Se···I (4.01 Å [4.15])	I–Se···I (145°) Se···I–I (108°)
9	105	175	S···Br (3.50 Å [3.80])	S···Br–S (134°)
10	118	180	Cl···Cl (4.16 Å [3.60])	Cl···Cl–Se (156°)
11	110	180	Br···Br (4.04 Å [3.80])	Br···Br–Se (125°)
12	106.5	177.5	Cl···Cl (3.72 Å [3.60])	Cl···Cl–Se (171°)
13	108	177	Br···Br (3.58 Å [3.80])	Br···Br–Se (173°)
14	98.2	172.3	Cl···Cl (4.13 Å [3.60])	Cl···Cl–Te (86°)
15	93.9	178	Te···Br (3.93 A [4.35])	Te···Br–Te (139°)
16	101.1	173.5	I···I (3.85 Å [4.30])	I···I–Te (159°)

[a] TB = trigonal bipyramid, MC = molecular complex. [b] E = group VI element, X = halogen, difference from that of sum of covalent radii in parentheses. [c] O. Hassel and J. Hvoslef, *Acta Chem. Scand.*, **10**, 138 (1956). [d] O. Hassel, and J. Hvoslef, *ibid.*, **8**, 873 (1954). [e] G. Y. Chao and J. D. McCullough, *Acta Cryst.*, **13**, 727 (1960). [f] C. Roemming, *Acta Chem. Scand.*, **14**, 21425 (1960). [g] H. Hope and J. D. McCullough, *Acta Cryst.*, **17**, 712 (1964). [h] G. Y. Chao and J. D. McCullough, *ibid.*, **14**, 940 (1961). [i] C. Knobler and J. D. McCullough, *Inorg. Chem.*, **7**, 365 (1968). [j] H. Maddox and J. D. McCullough, *ibid.*, **5**, 522 (1966); [k] L. Battelle, C. Knobler, and J. D. McCullough, *ibid.*, **5**, 958 (1966). [l] J. D. McCullough and G. Hamburger, *J. Am. Chem. Soc.*, **64**, 508 (1942). [m] J. D. McCullough, and G. Hamburger, *ibid.*, **63**, 803 (1941). [n] J. D. McCullough and R. E. Marsh, *Acta Cryst.*, **3**, 41 (1950). [o] G. D. Christofferson, R. A. Sparks, and J. D. McCullough, *ibid.*, **11**, 782 (1958). [p] G. D. Christofferson and J. D. McCullough, *ibid.*, **11**, 249 (1958).

Waals radii sum of 3.60 Å. The two angles of interaction about the chlorine atoms are 163 and 162°. This structural feature, however, is not unique and has been observed previously in several examples given in Table VI.

The structural configuration of the dichloride complex of bis(*p*-chlorophenyl) sulfide is very similar to the bis(*p*-chlorophenyl)tellurium diiodide structure examined by Chao and McCullough.[9] These workers discovered a trigonal-bipyramidal arrangement with near-linear connecting axial iodine atom positions at a distance of 3.85 Å. Chao and McCullough cited this interaction as an indication of the complex's tendency to pass into a molecular complex configuration involving a linear bonding chain of Te–I–I atoms. This contrast was apparent in the light of two previously studied structures of chlorine and bromine complexing with an organic tellurium molecule (see Table VI).

A trend is present in Table VI which enables one to predict the nature of halogen interaction configuration with group VI elements having two additional groups attached. The rule can be simply stated that if the group VI element has a electronegativity less than that of the complexing halogen, then the resulting configuration is a trigonal bipyramid. Otherwise, the result is a molecular complex structure. The rule as demonstrated in the listing of previous structures in Table VI is without exception. The crystal structure of β-dimethyltellurium iodide, β-$(CH_3)_2TeI_2$, has been determined,[10] but appears to be formed from two ions, $[(CH_3)_3Te]^+$ and $[CH_3TeI_4]^-$.

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(9) G. Y. Chao and J. D. McCullough, *Acta Cryst.*, **15**, 887 (1962).

(10) F. Einstein, J. Trotter, and C. Williston, *J. Chem. Soc.*, 2018 (1967).

In most of the examples cited in Table VI, an intermolecular interaction of a linear nature was present involving one or more of the complexed halogen atoms. Iodine atoms occasionally exhibited this interaction also at right angles to the intramolecular iodine–halogen bond. This type of interaction is analogous to the central atom bonding situation in polyhalide molecules and ions. Three simple qualitative bonding discussions have appeared in the literature regarding polyhalide configurations.[11–13] Rundle has pointed out that the terminal atoms of trihalide groupings have greater electron density from the bonding and nonbonding molecular orbitals. (See the discussion of the molecular orbital scheme later in this paper.) The center atom of the grouping is always the largest, in keeping with decreasing electronegativity with increase in atom size. The nature of the I–Cl molecular complexes with group VI elements is in accord with the above statements. In both cases these are near-linear intermolecular interactions. In keeping with the center halogen atom theory above, the iodine atom has the much stronger intermolecular bonding interaction.

Where the two complexing halogen atoms in molecular complexes are all of the same type, the situation does not differ except that preferential positioning is unnecessary. Furthermore, terminal halogen atoms exhibit a tendency to coordinate linearly with the axial positions of nearby intermolecular group VI atoms. The same situation is present in the trigonal-bipyramidal configurations. The intermolecular interactions are most noticeable in compounds comprising a group VI element and a halogen element that borders the heavy transition line in Table VII. This is confirmatory evidence of the tendency of the structural configuration of this series of compounds to pass from that of trigonal-bipyramidal to molecular complex or *vice versa*.

Table VII. Halogens

Group VI	Cl (2.83)	Br (2.74)	I (2.21)		
O (3.50)		MC	MC	1.	
				2.	$C_4H_4O_2 \cdot Br_2$
				3.	$C_4H_4O_2 \cdot 2ICl$
S (2.44)	TB		MC	1.	$(p\text{-}ClC_6H_4)_2S \cdot Cl_2$
				2.	
				3.	$(p\text{-}CH_2C_6H_4)_2S \cdot I_2$
Se (2.48)	TB	TB	MC	1.	$(CH_3C_6H_4)_2Se \cdot Cl_2$
				2.	$(CH_3C_6H_4)_2Se \cdot Br_2$
				3.	$C_4H_8Se \cdot I_2$
Te (2.01)	TB	TB	TB	1.	$\alpha\text{-}(CH_3)_2Te \cdot Cl_2$
				2.	$(C_6H_5)_2Te \cdot Br_2$
				3.	$(p\text{-}ClC_6H_4)_2Te \cdot I_2$

Rundle's discussion of the trihalide bonding situation[12] can be applied to the series of compounds of Table VI. If one describes the axially bonded atoms in the trigonal-bipyramid complex in the same manner as the linear trihalide groupings, one would expect that the axially bonded distances would be much longer than the covalent radii sum. Three localized molecular orbitals can be constructed from two p orbitals of the halogen atoms and a p orbital of the central group VI atom. The four electrons occupy the bonding and the nonbonding localized molecular orbitals, placing a greater electron density on the more electronegative halogen atoms, and giving a bond order of $^1/_2$ to the halogen–group VI element bond. From Pauling's rule relating bond distance to bond order,[14] a $^1/_2$ bond would be expected to be 0.18 Å longer than a single covalent bond. Bond lengthening in excess of that amount might be expected where there would be appreciable intermolecular [*e.g.*, X–VI–X· · ·X–VI–X] interactions and thus shorter intermolecular interaction distances. This effect is generally observed in the structures of Table VI. Larger group VI atoms and bulkier equatorial bonding groups will make halogen–halogen intermolecular interactions more difficult. The result would be a shorter intermolecular complex bond distance and longer intermolecular distances. This trend can be seen in the three tellurium examples. The smaller the halogen, the more tightly it is held and a weaker intermolecular interaction results. In contrast, the sulfur–dichloride complex has indicated that in this situation a substantial intermolecular interaction is present.

The crystallographic structure determination of the bis(*p*-chlorophenyl) sulfide dichloride complex fills a void in the examined series of group VI–halogen complexes. This latest addition to the series is entirely consistent with the trends of previous results. At least two more structures remain to be examined. A fluorine complex with oxygen should be trigonal bipyramidal about the oxygen atom. Perhaps more realistically obtainable is a bromine complex with a sulfur compound. If the compound were to behave according to the rule of electronegativity, a trigonal-bipyramidal configuration should result.

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(11) (a) R. C. L. M. Slater, *Acta Cryst.*, 12, 187 (1959); (b) J. C. Slater, *ibid.*, 12, 197 (1959).

(12) R. E. Rundle in "Survey of Progress in Chemistry," Academic Press, New York, N. Y., p 81.

(13) E. H. Wiebenga, E. E. Havinga, and K. H. Boswijk, *Advan. Inorg. Chem. Radiochem.*, Academic Press, New York, N. Y., 1961, p 133.

(14) L. Pauling, *J. Am. Chem. Soc.*, 69, 542 (1947).