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Crystal and Molecular Structure of *cis*-Dichlorobis(4,4′-dichlorodiphenyl sulfide)platinum(II)

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The crystal structure of *cis*-Pt[S(p-ClC$_6$H$_4$)$_2$]$_2$Cl$_2$ has been determined by three-dimensional X-ray diffraction techniques from 1780 reflections measured on an automated diffractometer at ambient room temperature. This compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 14.051 \pm 0.005$ Å, $b = 9.287 \pm 0.004$ Å, $c = 20.821 \pm 0.011$ Å, $\beta = 102.8 \pm 0.1°$, $d_c = 1.94$ g cm^{-3}, and $d_m = 1.93$ g cm^{-3} for $Z = 4$. The structure was solved by standard heavy-atom techniques and refined by full-matrix least squares including anisotropic temperature factors for Pt, S, and Cl to a final conventional R of 0.042. The structure consists of discrete molecules separated by ordinary van der Waals distances. The Pt, two S, and nearest two Cl atoms are distorted out of the usual square-planar arrangement toward a tetrahedral geometry with deviations from the least-squares plane of $\sim$0.06 ± 0.006 Å. The average Pt–S–C angle of 109.1 ± 0.6° indicates that sulfur uses a nonbonding sp^3 orbital and electron pair to form the σ bond with the metal. The two independent Pt–S distances of 2.292 ± 0.006 and 2.278 ± 0.007 Å, however, infer "normal" single bonds. The S–C distances (average 1.80 Å), Cl–C distances (average 1.74 Å), and C–C distances (average 1.39 Å) are all essentially normal for this type of system. The Pt–Cl distances (average = 2.298 Å) are normal single bonds and give no indication of elongation.

Introduction

It is now generally recognized that the trans effect[3] is an outdated concept when viewed in terms of details of the electronic structure[4,5] of a Pt^{2+} complex in particular. The term trans influence persists, however, and refers to the elongation of a Pt–X bond due to a substituent trans to X. If the bond weakening is sufficiently large, then it should be reflected in the lengthening of the Pt–X bond. It has been shown that the hydride ion substantially elongates the trans Pt–Br[6] and Pt–Cl[7] bond lengths from the normal single-bond distance. Earlier results had indicated that ethylene trans to chlorine substantially elongates the Pt–Cl[8] distance to 2.42 Å from the normal value of 2.30 Å.[9,10] However, a recent structure determination of Zeise's salt [K(PtCl$_3$C$_2$H$_4$)$_2$·H$_2$O][11] shows this to be incorrect, and there is no trans influence bond lengthening of Pt–Cl bonds by ethylene. The Pt–Cl bond length trans to the ethylene moiety in dipenteneplatinum(II) chloride was found to be 2.33 (1) Å.[12] There are no significant differences between Pt–Cl or Pt–N bond lengths in the cis and trans isomers of dichlorodiamineplatinum(II).[13] However, it has been shown that phosphine[14] trans to chlorine lengthens the Pt–Cl bond by almost 0.1 Å over chlorine trans to chlorine.[15]

The reaction between K$_2$PtX$_4$ (X = Cl, Br) and (C$_6$H$_5$)$_2$S in aqueous 1,4-dioxane to form complexes of the type *trans*-Pt[(C$_6$H$_5$)$_2$S]$_2$X$_2$ has recently been reported.[16] Similarly it has been found that 4,4′-dichlorodiphenyl sulfide will react with K$_2$PtX$_4$ in aqueous 1,4-dioxane to yield *trans*-Pt(DDS)$_2$X$_2$ (DDS = 4,4′-dichlorodiphenyl sulfide). The chloro derivative, *trans*-Pt(DDS)$_2$Cl$_2$, could be purified by recrystallization from hot benzene, but when dissolved in boiling acetone a cis–trans equilibrium was established, and upon slowly cooling the solution, the less soluble cis isomer deposited. The respective geometric configurations of this pair of isomers was confirmed by their infrared spectra (*vide infra*). As part of a continuing study of the trans bond length influence, we decided to examine the crystal structure of *cis*-dichlorobis(4,4′-dichlorodiphenyl sulfide)platinum(II).

Experimental Section

Methods and Materials.—The infrared spectra were recorded on a Beckman IR-12 spectrophotometer as Nujol mulls between CsI plates. Melting points are uncorrected and were measured with a Fisher-Johns melting point apparatus. Microanalyses were determined by A. Bernhardt, Mülheim, West Germany. 4,4′-dichlorodiphenyl sulfide was prepared by reduction of the corresponding sulfoxide with zinc in acetic acid.[17]

***trans*-Pt(DDS)$_2$Cl$_2$.**—A hot, filtered solution of 0.41 g (0.0010 mol) of potassium chloroplatinate(II) in 10 ml of water was mixed with 0.52 g (0.0020 mol) of 4,4′-dichlorodiphenyl sulfide in 20 ml of warm 1,4-dioxane. The resulting clear red solution was then shaken for *ca.* 24 hr. The precipitate which formed was filtered under reduced pressure and washed successively with hot water, ethanol, and ether. The complex separated from the minimum amount of boiling benzene as orange-colored hexagonal plates with some solvent of crystallization which was lost when the complex was dried *in vacuo*. *Anal.* Calcd for Pt(DDS)$_2$Cl$_2$: C, 37.11; H, 2.06. Found: C, 36.35; H, 2.64; mp 177–179°. Far-infrared data: ν(Pt–Cl) 341 cm^{-1} (other bands: 364, 370 cm^{-1}).

***cis*-Pt(DDS)$_2$Cl$_2$.**—The trans isomer was dissolved in the minimum amount of boiling acetone; the resulting solution was filtered hot and allowed to cool *slowly*. Rapid cooling often resulted in the deposition of a mixture of cis and trans isomers. The lemon yellow crystals of the cis isomer were dried *in vacuo* without further noticeable change. Suitable crystals for X-ray analysis were obtained in this manner. *Anal.* Calcd for Pt-

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[1] In partial fulfillment of Ph.D. requirements.

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TABLE I

Atom Positional and Thermal Parameters

Atom	x	y	z
Pt	0.24350 (7)	0.48229 (9)	0.50680 (5)
S(1)	0.2232 (4)	0.6991 (7)	0.5546 (3)
S(2)	0.2272 (4)	0.5870 (6)	0.4060 (3)
Cl(1)	0.2672 (4)	0.3885 (7)	0.6112 (3)
Cl(2)	0.2552 (4)	0.2550 (6)	0.4652 (3)
Cl(3)	−0.1084 (4)	1.0004 (9)	0.3470 (3)
Cl(4)	0.6107 (4)	1.0517 (7)	0.6040 (3)
Cl(5)	0.5253 (5)	0.3164 (10)	0.2581 (4)
Cl(6)	−0.1965 (4)	0.5006 (10)	0.2367 (3)
C(1)	0.1325 (14)	0.7988 (22)	0.4941 (10)
C(2)	0.0365 (15)	0.7423 (25)	0.4888 (12)
C(3)	−0.0387 (15)	0.8155 (24)	0.4442 (10)
C(4)	−0.0143 (17)	0.9241 (29)	0.4064 (12)
C(5)	0.0784 (15)	0.9753 (29)	0.4125 (10)
C(6)	0.1542 (17)	0.9120 (27)	0.4585 (12)
C(7)	0.3313 (13)	0.8076 (23)	0.5634 (10)
C(8)	0.3324 (14)	0.9452 (24)	0.5858 (10)
C(9)	0.4198 (14)	1.0280 (29)	0.5981 (10)
C(10)	0.5020 (15)	0.9574 (28)	0.5874 (10)
C(11)	0.5023 (16)	0.8225 (27)	0.5631 (11)
C(12)	0.4141 (16)	0.7365 (26)	0.5513 (11)
C(13)	0.3059 (12)	0.5049 (26)	0.3613 (9)
C(14)	0.2806 (17)	0.3971 (26)	0.3152 (12)
C(15)	0.3455 (19)	0.3365 (30)	0.2798 (14)
C(16)	0.4405 (17)	0.3949 (28)	0.2973 (12)
C(17)	0.4696 (14)	0.5032 (29)	0.3422 (10)
C(18)	0.4012 (17)	0.5607 (26)	0.3763 (12)
C(19)	0.1067 (15)	0.5522 (24)	0.3586 (11)
C(20)	0.0704 (18)	0.6581 (28)	0.3098 (13)
C(21)	−0.0259 (19)	0.6395 (28)	0.2728 (13)
C(22)	−0.0797 (14)	0.5245 (27)	0.2849 (10)
C(23)	−0.0424 (18)	0.4229 (27)	0.3341 (13)
C(24)	0.0525 (17)	0.4385 (26)	0.3708 (12)

Anisotropic Temperature Factors of the Form
$\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})] \times 10^4$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	29.5 (4)	82 (1)	19.1 (3)	−6 (1)	5.4 (2)	1.1 (8)
S(1)	37 (3)	123 (10)	18 (2)	−8 (4)	5 (2)	−3 (3)
S(2)	42 (4)	94 (9)	23 (2)	−7 (4)	9 (2)	−5 (3)
Cl(1)	56 (4)	150 (11)	20 (2)	−13 (5)	0 (2)	13 (4)
Cl(2)	63 (4)	98 (9)	30 (2)	6 (5)	12 (3)	2 (4)
Cl(3)	48 (3)	228 (13)	32 (2)	27 (7)	1 (2)	13 (6)
Cl(4)	43 (3)	129 (11)	35 (2)	−27 (4)	2 (2)	−4 (4)
Cl(5)	72 (6)	344 (19)	35 (3)	43 (7)	18 (3)	−13 (6)
Cl(6)	48 (3)	275 (14)	34 (2)	28 (7)	−4 (2)	−23 (7)

Isotropic Temperature Factors for Carbon

Atom	B, Å^2	Atom	B, Å^2	Atom	B, Å^2	Atom	B, Å^2
C(1)	2.6 (8)	C(7)	2.0 (8)	C(13)	3.1 (7)	C(19)	3.4 (10)
C(2)	4.0 (11)	C(8)	3.1 (9)	C(14)	4.1 (12)	C(20)	4.8 (13)
C(3)	2.7 (9)	C(9)	3.3 (9)	C(15)	5.9 (14)	C(21)	4.5 (13)
C(4)	3.9 (11)	C(10)	3.4 (9)	C(16)	3.8 (12)	C(22)	3.5 (9)
C(5)	3.6 (9)	C(11)	3.4 (10)	C(17)	3.8 (9)	C(23)	4.3 (12)
C(6)	4.0 (11)	C(12)	3.8 (11)	C(18)	4.6 (12)	C(24)	4.4 (12)

$(DDS)_2Cl_2$: C, 37.11; H, 2.06. Found: C, 37.44; H, 2.06; mp 192–194°. Far-infrared data: ν(Pt–Cl) 343, 329 cm^{-1} (other bands: 324, 364 cm^{-1}).

The needle (symmetry axis) crystals of *cis*-dichlorobis(4,4′-dichlorodiphenyl sulfide)platinum(II) were found to be monoclinic and preliminary Weissenberg and precession data showed systematic extinctions: for $h0l$, $l = 2n + 1$, and for $0k0$, $k = 2n + 1$, indicating space group $P2_1/c$.[18] The cell constants, obtained from a least-squares refinement of the χ, ϕ, and 2θ angles of 13 accurately centered general reflections at a takeoff angle of 1.7°, with Mo Kα radiation (λ 0.71068 Å) at room temperature, were found to be a = 14.051 (4) Å, b = 9.287 (4) Å, c = 20.82 (1) Å, and β = 102.8 (1)°. (All numbers in parentheses here and elsewhere in this report are estimated standard deviations of least significant digits.) The calculated density with four molecules per unit cell is 1.94 g cm^{-3} in good agreement with the observed value of 1.93 (2) g cm^{-3} measured by flotation in a carbon tetrachloride–bromoform mixture. A needle crystal specified by prominent faces of the forms {100}, {10$\bar{1}$}, {100}, and {010} with distances from the center of the crystal to these faces of 0.054, 0.050, 0.024, and 0.15 mm, respectively, was mounted with the long direction approximately parallel to the ϕ axis on a Picker automated diffractometer. The crystal was aligned by variations of well-known methods.[19] With Mo Kα radiation 4732 intensities were measured by conventional θ–2θ scan techniques for 90 sec (1.5° 2θ) and backgrounds were estimated at ±0.75° from 2θ of the peak maxima by stationary counting for 40 sec each. The source to crystal distance was 18 cm while the crystal to counter distance was 26 cm. The takeoff angle was 3.7° and the counter aperture was 6 mm × 8 mm high. A random sampling of 48 symmetry-related reflections gave agreement to within two standard deviations of the counting statistics (see below) and only independent (hkl, $\bar{h}kl$) reflections were measured. The width of an average peak at half peak height was found to be ~0.2° 2θ. The counting rate never exceeded 5000 counts/sec. Reflections were examined out to a 2θ maximum value of 50°. The integrated intensity was calculated as $I(\text{net}) = I(\text{scan}) - 1.125(B_1 + B_2)$ where I(scan) is the number of counts over the scan range, B_1 and B_2 are the background counts, and 1.125 is a constant used to scale the total background time to the total scan time. A standard reflection was measured after every tenth reflection to monitor the stability of operation and any crystal decomposition that might occur. Taking $\sigma[I(\text{net})] = [I(\text{scan}) + (1.125)^2(B_1 + B_2)]^{1/2}$, then the variation in I(net) was less than 3σ [σ = 2.5% of average I(net)] during the period of data collection. A reflection was considered above background when I(net) was greater than $2.0[1.125^2(B_1 + B_2)]^{1/2}$. By this criterion 1780 nonzero hkl reflections were retained. The linear absorption coefficient was calculated to be 63.1 cm^{-1}. Absorption corrections were computed[20] for the crystal with faces and

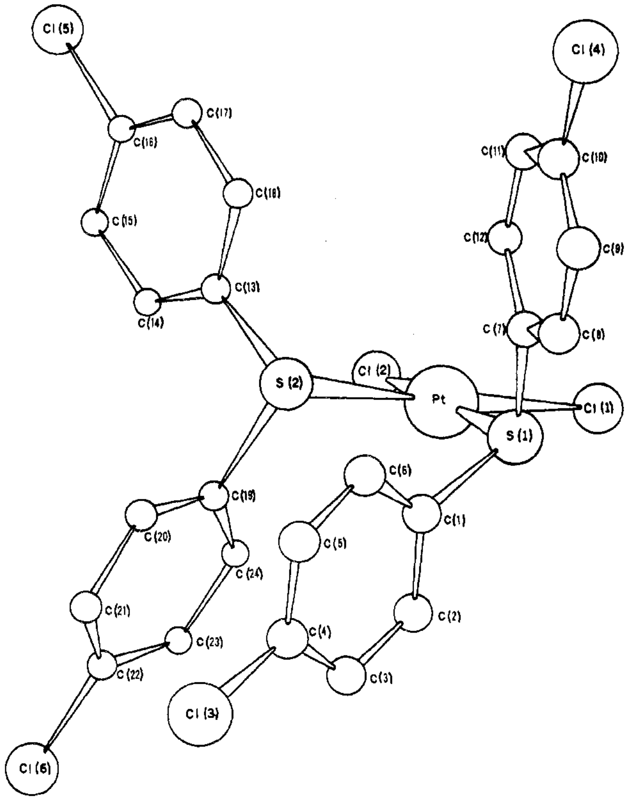

Figure 1.—A view of the *cis*-Pt[S(p-ClC$_6$H$_4$)$_2$]$_2$Cl$_2$ molecule showing the most important distances and angles.

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[20] Absorption corrections made with a local variation of GONO9 originally written by W. C. Hamilton, Brookhaven National Laboratory, Upton N. Y.

TABLE II

Interatomic Distances and Angles

Bonded Distances,[a] Å

Pt–S(1)	2.292 (6)
Pt–S(2)	2.278 (7)
Pt–Cl(1)	2.298 (7)
Pt–Cl(2)	2.301 (6)
S(1)–C(1)	1.83 (2)
S(1)–C(7)	1.80 (2)
S(2)–C(13)	1.77 (2)
S(2)–C(19)	1.79 (2)
Cl(3)–C(4)	1.75 (3)
Cl(4)–C(10)	1.73 (2)
Cl(5)–C(16)	1.75 (3)
Cl(6)–C(22)	1.74 (2)

Nonbonded Distances, Å
Intramolecular

S(1)–S(2)	3.27 (1)
S(1)–Cl(1)	3.13 (1)
S(2)–Cl(2)	3.31 (1)
Cl(1)–Cl(2)	3.25 (1)
S(2)–C(1)	3.18 (2)
S(2)–C(6)	3.44 (3)
S(2)–C(12)	3.80 (2)
Cl(2)–C(13)	3.35 (2)
Cl(2)–C(14)	3.48 (3)
Cl(2)–C(24)	3.52 (2)

Intermolecular

Cl(3)–C(20)	3.73 (3)
Cl(3)–C(21)	3.68 (3)
Cl(6)–C(15)	3.73 (3)
Cl(2)–C(5)	3.59 (3)
Cl(2)–C(6)	3.48 (3)
C(21)–C(23)	3.71 (4)

Angles,[b] Deg

S(1)–Pt–S(2)	91.6 (2)
S(1)–Pt–Cl(1)	85.8 (2)
S(1)–Pt–Cl(2)	174.6 (2)
S(2)–Pt–Cl(1)	176.2 (2)
S(2)–Pt–Cl(2)	92.6 (2)
Cl(1)–Pt–Cl(2)	90.1 (2)
Pt–S(1)–C(1)	106.2 (7)
Pt–S(1)–C(7)	110.7 (7)
Pt–S(2)–C(13)	110.7 (7)
Pt–S(2)–C(19)	108.6 (8)
C(1)–S(1)–C(7)	103 (1)
C(13)–S(2)–C(19)	105 (1)
S(1)–C(1)–C(2)	112 (2)
S(1)–C(1)–C(6)	124 (2)
S(1)–C(7)–C(8)	120 (2)
S(1)–C(7)–C(12)	116 (2)
S(2)–C(13)–C(14)	126 (2)
S(2)–C(13)–C(18)	114 (2)
S(2)–C(19)–C(20)	114 (2)
S(2)–C(19)–C(24)	123 (2)
Cl(3)–C(4)–C(3)	117 (2)
Cl(3)–C(4)–C(5)	119 (2)
Cl(4)–C(10)–C(9)	117 (2)
Cl(4)–C(10)–C(11)	118 (2)
Cl(5)–C(16)–C(15)	115 (2)
Cl(5)–C(16)–C(17)	120 (2)
Cl(6)–C(22)–C(21)	119 (2)
Cl(6)–C(22)–C(23)	119 (2)
S(1)–C(1)–C(4)	174 (1)
S(1)–C(7)–C(10)	175 (1)
S(2)–C(13)–C(16)	175 (1)
S(2)–C(19)–C(22)	175 (1)

Equations of Least-Squares Planes of the Type[c]
$Ax + By + Cz - D = 0$

	Plane no.				
	1	2	3	4	5
A	0.2996	−0.0126	−0.1089	0.0505	−0.9789
B	−0.6413	0.3368	0.6883	−0.5400	−0.1373
C	−0.7064	−0.9415	−0.7172	−0.6736	−0.1514
D	11.9737	8.2709	2.3211	7.7561	3.2351

	Plane no.			
	1	2	3	4
C(6*I* − 5)	0.00 (2)	0.00 (2)	0.00 (2)	0.00 (2)
C(6*I* − 4)	0.02 (2)	0.00 (2)	0.00 (3)	0.00 (3)
C(6*I* − 3)	−0.03 (2)	0.01 (2)	0.01 (3)	0.00 (3)
C(6*I* − 2)	0.02 (3)	−0.02 (2)	−0.01 (3)	0.00 (2)
C(6*I* − 1)	0.01 (2)	0.02 (2)	0.01 (2)	0.00 (2)
C(6*I*)	−0.02 (3)	0.01 (2)	0.00 (2)	0.00 (2)
Cl(*I* + 2)[d]	0.101 (7)	−0.061 (7)	−0.090 (8)	0.063 (6)
S(1)[d]	0.029 (6)	−0.154 (6)		
S(2)[d]			−0.016 (6)	0.073 (6)

	Plane no. 5		Plane no. 5
Pt	−0.005 (1)	Cl(1)	−0.064 (6)
S(1)	0.066 (6)	Cl(2)	0.063 (6)
S(2)	−0.059 (6)		

Rms Displacements along Principal Axes, Å

Atom	Axis 1	Axis 2	Axis 3
Pt	0.162 (2)	0.192 (2)	0.202 (2)
S(1)	0.184 (8)	0.194 (10)	0.235 (9)
S(2)	0.189 (9)	0.202 (10)	0.226 (10)
Cl(1)	0.188 (10)	0.224 (9)	0.280 (9)
Cl(1)	0.205 (10)	0.239 (10)	0.253 (9)
Cl(3)	0.193 (8)	0.273 (8)	0.325 (10)
Cl(4)	0.172 (9)	0.257 (9)	0.283 (9)
Cl(5)	0.216 (11)	0.280 (11)	0.398 (11)
Cl(6)	0.197 (7)	0.260 (12)	0.374 (12)

[a] All C–C intra-ring distances are within two standard deviations (0.03 Å) of the average of 1.396 Å. [b] All C–C intra-ring angles are within three standard deviations (2.2°) of the average of 120°. [c] *x*, *y*, and *z* refer to an internal orthogonal coordinate system: J. S. Kasper and K. Lonsdale, Ed., "International Tables for X-Ray Crystallography," Vol. II, Kynoch Press, Birmingham, England, 1967, p 61. [d] Atoms excluded from the calculation of least-squares planes.

orientation as defined above. The transmission coefficient was found to vary from 0.717 to 0.552. Lorentz polarization corrections were made and the intensities were reduced to structure factors.

Structure Determination

The structure was solved by standard heavy-atom methods[21] and refined by full-matrix least squares[22] with scattering factors from a standard source.[23] Real and imaginary dispersion corrections for the Pt, S, and Cl atoms were applied.[24] Isotropic temperature factor refinement yield an *R* of 0.098. Refinement with the Pt, S, and Cl atoms anisotropic converged after several cycles of refinement to a final *R* of 0.0416, weighted *R* of 0.0405, and standard error of 1.55.[25a] Weights were assigned by an accepted scheme.[25b] Carbon atoms were all varied isotropically. A final difference Fourier was computed and showed no unusual features. The listing of observed and calculated structure factors is found elsewhere.[26] Final atomic coordinates and thermal parameters are enumerated in Table I. Interatomic distances, angles, and errors[27] are listed in Table II. Table II also contains various dihedral angles, rms displacements,[27] and appropriate least-squares planes.[28]

Description and Discussion of Structure

The structure of *cis*-Pt(DDS)$_2$Cl$_2$ is made up of discrete molecules separated by ordinary van der Waals distances (Figures 1 and 2). The platinum and its four bonded neighbors are in an almost square–planar arrangement slightly distorted toward tetrahedral geometry. The two S and two Cl atoms in this arrangement deviate by 0.06 ± 0.006 Å from the least-squares plane, Table II. The Pt–Cl distances are 2.298 (7)

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(21) Patterson and electron density calculations done on an IBM 7040 with the ERFR-3 program, a modification of the Sly–Shoemaker–van den Hende ERFR-2 by D. R. Harris, 1964.

(22) Least-squares refinement performed (with anomalous dispersion) with a local modification of ORFLS: W. Busing, K. O. Martin, and H. Levy, "A Fortran Crystallographic Least-Squares Program," Report ORNL-TM-395, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(23) (a) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965); (b) D. T. Cromer, *ibid.*, **18**, 17 (1965).

(24) Anomalous dispersion corrections made to F_c, as suggested by J. A. Ibers and W. C. Hamilton, *ibid.*, **17**, 781 (1964).

(25) (a) $R = \Sigma||F_o - F_c||/\Sigma|F_o|$; weighted $R = [\Sigma w(F_o - F_c)^2]^{1/2}/[\Sigma wF_o^2]^{1/2}$; standard error $= [\Sigma w(F_o - F_c)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$, where NO = 1790 and NV = 173. (b) G. H. Stout and L. H. Jensen, "X-ray structure Determination," Macmillan, New York, N. Y., 1968, p 457.

(26) A listing of structure factor amplitudes will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

(27) Distances, angles, dihedral angles, rms displacements, and errors were computed (with local modifications on the IBM 7040) with ORFFE: W. Busing, K. O. Martin, and H. Levy, "A Fortran Crystallographic Function and Error Program," Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(28) Least-squares planes were calculated on the IBM 1620 with a program by W. A. Spofford, III.

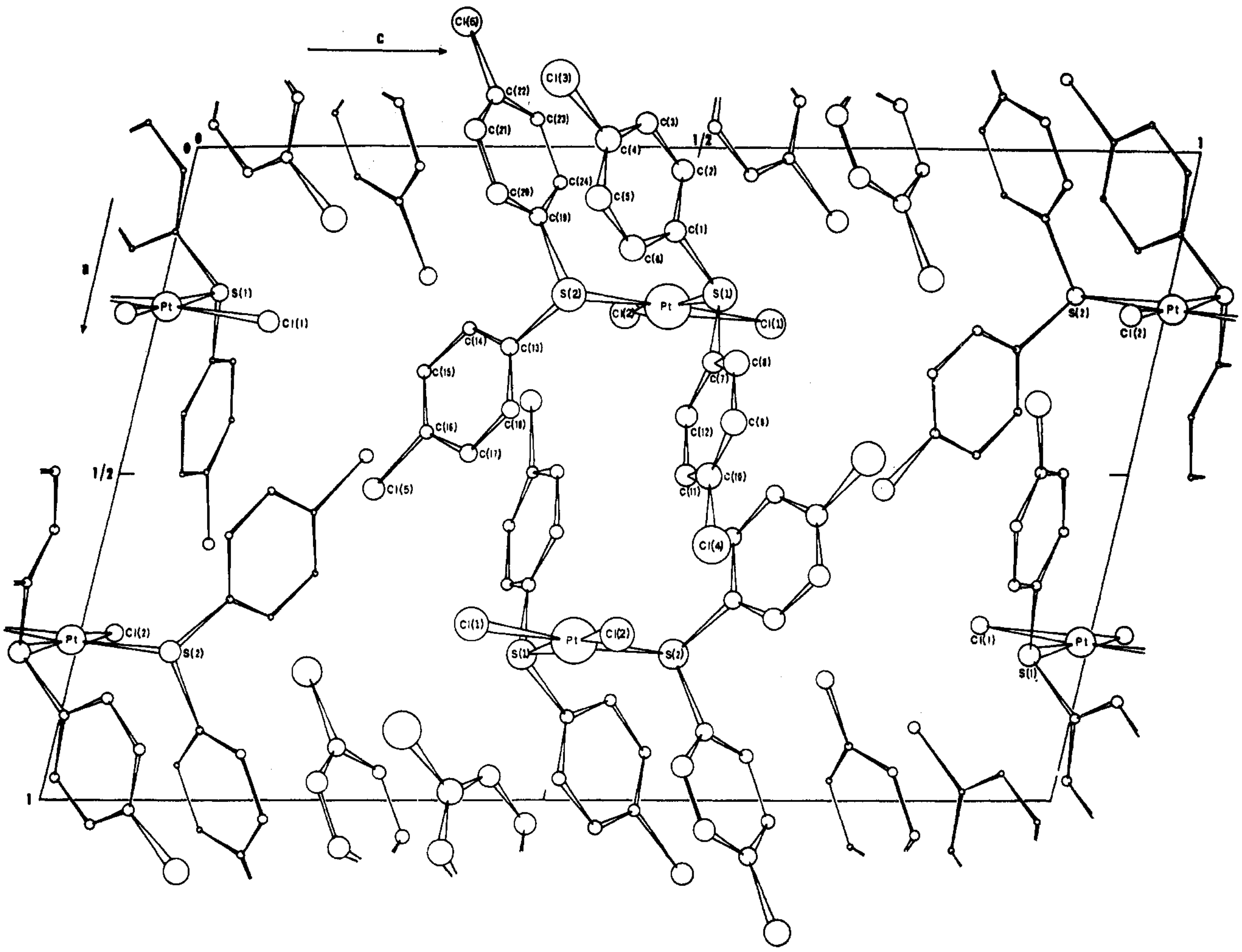

Figure 2.—A view of the unit cell of *cis*-Pt[S(p-ClC$_6$H$_4$)$_2$]$_2$Cl$_2$ down the "*b*" axis.

and 2.301 (6) Å, not significantly different from the 2.30 Å expected from the sum of single-bond radii nor from that found in *trans*-Pt[P(C$_2$H$_5$)$_3$]$_2$Cl$_2$.[15] Hence, the (p-ClC$_6$H$_4$)$_2$S ligand in the trans position to Cl does not significantly alter the Pt–Cl bond length from the normal single-bond distance. This result is in contrast to that found for *cis*-Pt[P(CH$_3$)$_3$]$_2$Cl$_2$[14] in which the Pt–Cl bond length is ~0.1 Å longer than 2.30 Å. The Pt–S distances of 2.292 (6) and 2.278 (7) Å are somewhat shorter than the sum of single-bond radii (2.34 Å) but are comparable to the 2.30–2.32-Å Pt–S distances with individual esd's of ±0.006 observed in tetrakis(thiourea)platinum(II) chloride.[29] The Pt–S bridging distance in (R$_2$S)$_2$Pt$_2$X$_4$ was found to be 2.22 (1) Å[30] but is sufficiently unusual that it should not be used for comparison purposes.

The Pt–S–C and C–S–C angles (110–104°) leave no doubt that the best description of the sulfur bonding is in terms of tetrahedral sulfur orbitals. It is interesting to note that although the Pt–S bonding in tetrakis(thiourea)platinum(II) chloride involves sulfur sp^2 orbitals, the Pt–S distance is essentially invariant.

The C–C ring, C–Cl, and S–C distances are the expected values within experimental error. There is no evidence for any delocalized electronic interaction between the p-chlorophenyl groups and the metal atom. The orientation of these ligand groups is probably determined by packing requirements.

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(29) R. L. Girling and E. L. Amma, to be submitted for publication.

(30) (a) D. L. Sales, J. Stokes, and P. Woodward, *J. Chem. Soc. A*, 1852 (1968); (b) P. L. Goggin, R. J. Goodfellow, D. L. Sales, J. Stokes, and P. Woodward, *Chem. Commun.*, 31 (1968).