The Crystal and Molecular Structure of Dichloro[1,3-bis(di-*t*-butylphosphino)propane]platinum(II) Chlorobenzene Solvate

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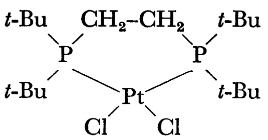
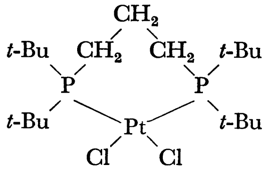
(Received September 9, 1978)

X-Ray crystal structure analysis of $[PtCl_2\{(t\text{-}Bu)_2P(CH_2)_3P(t\text{-}Bu)_2\}]\cdot 0.5C_6H_5Cl$ has been carried out. Crystals belong to monoclinic system: $a=11.532(2)$, $b=14.984(5)$, $c=16.455(4)$ Å, $\beta=106.96(2)°$, space group $P2_1/c$ with $Z=4$. The structure, solved by the heavy-atom method, has been refined anisotropically by least-squares procedure to $R=0.056$ for 5019 non-zero reflections. The coordination around the platinum atom is approximately square-planar, however, it showed a slight deviation toward the tetrahedral geometry; Pt–P=2.281(3) and 2.282(3), Pt–Cl=2.359(3) and 2.362(3) Å, P–Pt–P=99.05(9) and Cl–Pt–Cl=83.18(11)°.

In co-operation with the studies on a series of bis(disubstituted phosphino)alkaneplatinum complexes by Sei Otsuka and his coworkers,[1] we have carried out the determination of X-ray molecular structures of these complexes. Recently, we have reported the crystal and molecular structures of dichloro[1,2-bis(di-*t*-butylphosphino)ethane]platinum(II) (**1**) and its chlorobenzene solvate.[2] We report here the crystal structure analysis of dichloro[1,3-bis(di-*t*-butylphosphino)propane]platinum(II) (**2**) chlorobenzene solvate.



(**1**)



(**2**)

Experimental

Crystals of $[PtCl_2\{(t\text{-}Bu)_2P(CH_2)_3P(t\text{-}Bu)_2\}]\cdot 0.5C_6H_5Cl$ were kindly provided by Professor Sei Otsuka and co-workers. The space group was uniquely determined as $P2_1/c$ from the preliminary Weissenberg photographs. Accurate unit-cell dimensions were determined at 20 °C by a least-squares fit of 2θ values of high order reflections measured on a Rigaku automated, four-circle diffractometer. The crystal data are given in Table 1.

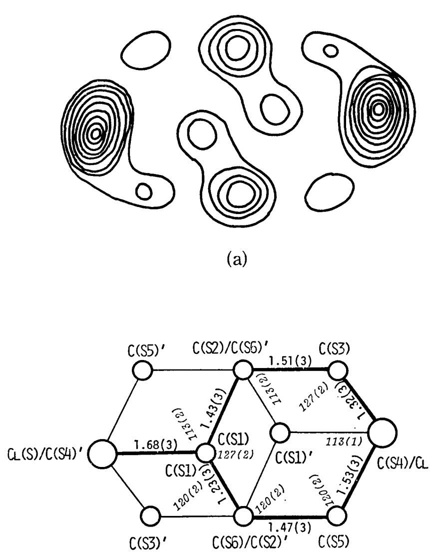
Table 1. Crystal data of $[PtCl_2(\{t\text{-}Bu)_2\cdot PC(H_2)P(t\text{-}Bu)_2\}]\cdot 0.5C_6H_5Cl$

$C_{14}H_{26.5}P_2Cl_{2.5}Pd$	*F.W.* 654.77
Monoclinic	Space group $P2_1/c$
$a=11.532(2)$ Å	$D=1.61$ g cm^{-3}
$b=14.984(5)$	$Z=4$
$c=16.455(4)$	$D=1.599$ g cm^{-3}
$\beta=106.96(2)°$	μ(Mo $K\alpha$)$=57.94$ cm^{-1}
$U=2719.8(12)$ Å^3	

A crystal with dimensions of *ca.* 0.2×0.2×0.3 mm, sealed in a thin-walled glass capillary tube, was mounted on the diffractometer for the intensity data collection. Graphite-monochromatized Mo $K\alpha$ radiation was used. The θ—2θ scan technique was employed. The integrated intensity was determined by scanning over the peak at a rate of 4° min^{-1}, and substracting the background obtained by averaging the two values measured for 6 s at both ends of a scan. The scan width was calculated by the equation: $\Delta(2\theta)=(2.4+0.69\tan\theta_c)°$, where θ_c is the calculated value of the Bragg angle using λ (Mo $K\alpha_1$)$=0.70926$ Å. The starting angle of the scan was $(2\theta_c-1.2)°$. Usual Lorentz and polarization corrections were applied, but absorption correction was ignored. Throughout the data collection four standard reflections were measured after every 60 reflections, which remained constant within the error limits. A total of 5936 independent reflections was measured out to a 2θ value of 54°, and of these 917 reflections were less than $3\sigma(F)$ and they were recorded as $F_o=0$.

Solution and Refinement of the Structure

The structure was solved by the heavy atom method and was refined by the block-diagonal least-squares procedure. HBLS V program was used,[3] the function minimized being $\sum w(|F_o|-k|F_c|)^2$. Starting from isotropic temperature factors, anisotropic thermal parameters were introduced in the refinement. When the R value decreased to 0.086 the Fourier map calculated revealed an existence of the chlorobenzene molecule disordered near a crystallographic center of symmetry, and they were then included in the refinement. How-



(a)

(b)

Fig. 1. Disordered structure of chlorobenzene (a) Electron density map. (b) A pair of disoldered half molecules.

TABLE 2. ATOMIC FRACTIONAL COORDINATES AND THERMAL PARAMETERS ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Anisotropic temperature factors are expressed in the form: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	0.45637(3)	0.18692(2)	0.24936(2)	0.00567(2)	0.00346(1)	0.002841(13)	0.00059(3)	0.00189(3)	0.00180(2)
Cl(1)	0.3692(2)	0.1125(2)	0.3435(2)	0.0095(2)	0.00612(15)	0.00496(12)	0.0010(3)	0.0059(3)	0.0049(2)
Cl(2)	0.6166(2)	0.0851(2)	0.3039(2)	0.0079(2)	0.00516(13)	0.0067(1)	0.0038(3)	0.0040(3)	0.0049(2)
P(1)	0.2785(2)	0.2609(2)	0.19134(15)	0.0058(2)	0.00452(12)	0.00314(9)	0.0009(2)	0.0021(2)	0.0025(2)
P(2)	0.5758(2)	0.2610(2)	0.18284(15)	0.0059(2)	0.00387(11)	0.00336(9)	0.0006(2)	0.0032(2)	0.0016(2)
C(1)	0.2843(9)	0.3507 8)	0.1152(7)	0.0078(9)	0.0062(6)	0.0043(5)	0.0040(12)	0.0042(10)	0.0056(9)
C(2)	0.3725(10)	0.3387(9)	0.0646(7)	0.0097(10)	0.0073(7)	0.0040(5)	0.0019(14)	0.0040(11)	0.0040(9)
C(3)	0.5034(9)	0.3562(7)	0.1153(7)	0.0075(8)	0.0054(5)	0.0052(5)	0.0011(11)	0.0058(11)	0.0062(9)
C(10)	0.1574(9)	0.1817(8)	0.1241(7)	0.0065(8)	0.0070(7)	0.0044(5)	0.0015(12)	−0.0001(10)	0.0021(9)
C(11)	0.0359(11)	0.2296(11)	0.0794(11)	0.0077(11)	0.0081(9)	0.0099(10)	−0.003(2)	−0.004(2)	0.005(2)
C(12)	0.213(2)	0.1365(14)	0.0567(10)	0.020(2)	0.0145(15)	0.0062(8)	−0.017(3)	0.010(2)	−0.011(2)
C(13)	0.1278(13)	0.1019(9)	0.1745(9)	0.016(2)	0.0063(7)	0.0059(7)	−0.005(2)	0.001(2)	0.0033(11)
C(20)	0.2175(9)	0.3260(7)	0.2689(7)	0.0080(9)	0.0058(6)	0.0043(5)	0.0034(11)	0.0066(11)	0.0021(8)
C(21)	0.1365(10)	0.4050(8)	0.2284(8)	0.0091(10)	0.0053(6)	0.0068(7)	0.0046(12)	0.0048(13)	0.0022(10)
C(22)	0.3302(10)	0.3671(9)	0.3366(8)	0.0098(11)	0.0065(7)	0.0054(6)	0.0010(14)	0.0025(13)	−0.0004(10)
C(23)	0.1444(12)	0.2682(9)	0.3149(9)	0.0130(13)	0.0068(7)	0.0079(8)	0.001(2)	0.014(2)	0.0045(12)
C(30)	0.7022(9)	0.3233(7)	0.2627(7)	0.0067(8)	0.0047(5)	0.0052(5)	−0.0008(10)	0.0038(10)	0.0015(8)
C(31)	0.7799(11)	0.3773(8)	0.2171(8)	0.0108(11)	0.0063(7)	0.0065(7)	−0.0063(14)	0.0072(14)	0.0007(11)
C(32)	0.6435(10)	0.3876(8)	0.3120(8)	0.0087(10)	0.0054(6)	0.0068(6)	0.0001(12)	0.0056(13)	−0.0019(10)
C(33)	0.7877(10)	0.2644(8)	0.3308(7)	0.0092(10)	0.0054(6)	0.0049(5)	0.0004(12)	0.0000(12)	0.0002(9)
C(40)	0.6356(10)	0.1878(7)	0.1086(8)	0.0095(10)	0.0053(6)	0.0053(5)	0.0020(12)	0.0061(12)	0.0008(9)
C(41)	0.6556(14)	0.2409(10)	0.0334(8)	0.018(2)	0.0088(9)	0.0047(6)	0.003(2)	0.012(2)	0.0012(12)
C(42)	0.5402(11)	0.1136(8)	0.0726(8)	0.0115(12)	0.0061(7)	0.0060(6)	−0.0034(15)	0.0068(14)	−0.0038(11)
C(43)	0.7574(11)	0.1423(8)	0.1549(9)	0.0107(11)	0.0058(7)	0.0075(7)	0.0042(14)	0.009(2)	−0.0011(11)
C(S1)	0.976(2)	−0.0136(15)	0.5247(11)	0.009(2)	0.0059(11)	0.0026(7)	−0.005(2)	0.001(2)	−0.0009(14)
C(S3)	1.007(2)	0.073(2)	0.4075(14)	0.012(2)	0.0051(11)	0.0037(9)	0.002(3)	0.000(2)	−0.001(2)
C(S5)	1.157(2)	−0.0281(14)	0.4872(15)	0.007(2)	0.0050(11)	0.0061(12)	0.002(2)	0.002(2)	−0.005(2)
C(S2)	0.9251(11)	0.0517(8)	0.4618(7)	0.0129(13)	0.0048(6)	0.0048(5)	0.0006(14)	0.0018(13)	−0.0013(9)
Cl(S)/ C(S4′)	1.1146(6)	0.0376(5)	0.4136(4)	0.0176(7)	0.110(4)	0.0062(3)	−0.0127(9)	0.0114(8)	−0.0058(6)

ever, peaks assigned for Cl(S), C(S2), C(S4), and C(S6) (or C(S4)′, C(S6)′, Cl(S)′, and C(S2)′) could not be resolved (Fig. 1), and the unresolved Cl(S)/C(S4)′ (or C(S4)/Cl(S)′) and C(S2)/C(S6)′ (or C(S6)/C(S2)′) atoms were treated as peaks of a hypothetic (Cl+C)/2 and a single carbon atoms, respectively.

The final R value is 0.080 (0.056 for non-zero reflections). The weighting scheme employed was: $w=(\sigma(F)^2+0.03289|F_o|+0.00159|F_o|^2)^{-1}$ for $|F_o|>0$ and $w=0.06036$ for $|F_o|=0$. The atomic scattering factors used were those of neutral atoms given in International Tables for X-Ray Crystallography, Vol. IV,[4] and those for the hypothetic (Cl+C)/2 atom were assumed as the mean value of those for Cl and C. The effect of the anomalous dispersion of Pt, Cl, and P atoms was included in the calculation: the values of $\Delta f'$ and $\Delta f''$ being also taken from the International Tables for X-Ray Crystallography.[5]

The final positional and thermal parameters are listed in Table 2.†

Results and Discussion

Molecular Structure. A stereoscopic drawing of the molecule is given in Fig. 2. Bond lengths and bond angles are listed in Table 3. Selected bond lengths and

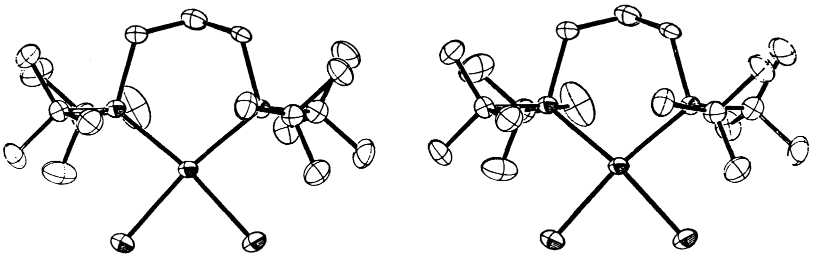


Fig. 2. Stereoscopic drawing of $[PtCl_2\{(t\text{-}Bu)_2P(CH_2)_3P(t\text{-}Bu)_2\}]$.

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† The table of observed and calculated structure factors is kept as Document No. 7910 at the Chemical Society of Japan.

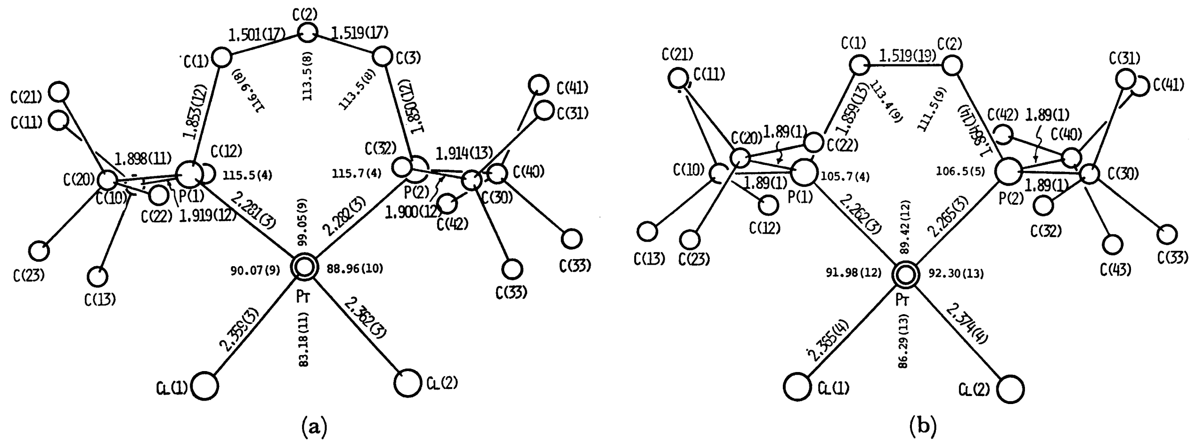

Fig. 3. Selected bond lengths and bond angles in (a) $[PtCl_2\{(t\text{-}Bu)_2P(CH_2)_3P(t\text{-}Bu)_2\}]$ compared with those in (b) $[PtCl_2\{(t\text{-}Bu)_2P(CH_2)_2P(t\text{-}Bu)_2\}]$.

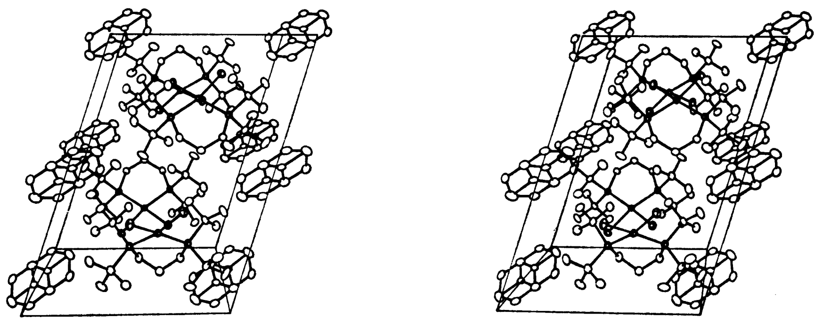

Fig. 4. Stereoscopic drawing of molecular packing in the unit cell. Disordered chlorobenzene molecules are shown.

bond angles are compared with those of **1**[2] in Fig. 3.

The co-ordination around the platinum atom can be described as approximately square-planar, however, the remarkable feature is that, different from **1**, there observed a slight distortion towards the tetrahedral geometry (Table 4). The dihedral angle between two planes defined by P(1), Pt, and P(2) and Cl(1), Pt, and Cl(2) is 12.0°.

The Pt-P bond lengths [2.281(3) and 2.282(2) Å] are significantly longer, whereas the Pt-Cl bond lengths [2.359(3) and 2.362(3) Å] are slightly shorter than those observed in **1** (Fig. 3). The shortening of the Pt-Cl lengths in the present complex indicates that the *trans*-influence of the phosphorus atoms is somewhat less than that in **1** because of the distortion of the $5d6s6p^2$ hybrid orbitals of the platinum atom.[6]

The P(1)-Pt-P(2) angle [99.05(9)°] is considerably greater than the corresponding angle in **1** [89.42(2)°], and other three angles around the platinum atom are smaller than the corresponding angles in **1**. This widening of the P-Pt-P angle in the present complex is probably due to an increased number of methylene groups in bis(di-*t*-butylphosphino)alkane ligand, which results in a distortion of dsp^2 hybrid orbitals of the platinum atom. Similar coordination geometry is observed in $[cis\text{-}PtCl_2(PMe_3)_2]$,[7] in which there seems to exist a steric repulsion between *cis*-PMe_3 groups.

As is found in **1** two P-C(CH_2) bond lengths [1.853(12) and 1.850(11) Å] are shorter than four P-C(*t*-Bu) bonds [1.919(12), 1.898(11), 1.900(12) and 1.914(13) Å].

The Pt-P-C(CH_2) angles [115.5(4) and 115.7(4)°] are about 10° larger than the corresponding angles in **1**. This is also probably affected by the increased number of methylene groups.

In the central propane moiety, the C(1)-C(2) and C(2)-C(3) bonds [1.50(2) and 1.52(2) Å] have normal single bond length, and bond angles around the C(1), C(2), and C(3) show slight deviations from the tetrahedral angle, however these are not significant except the P(1)-C(1)-C(2) [116.9(8)°]. The conformations about the C(1)-C(2) and C(2)-C(3) bonds are both nearly gauche. The torsion angles P(1)-C(1)-C(2)-C(3) and P(2)-C(3)-C(2)-C(1) are −75.7 and 80.3° respectively. The displacements of three methylene carbon atoms, C(1), C(2), and C(3) from the plane defined by Pt, P(1), and P(2) are 0.01, −0.67, and 0.13 Å, respectively.

Bond lengths and bond angles in *t*-butyl groups are normal values [1.55 Å and 109.4°]. Two *t*-butyl groups attached to the same phosphorus atom are mutually in a staggered position.

Solvated Chlorobenzene Molecule. In the crystal 0.5 chlorobenzene molecule per one platinum complex is contained. There observed a disorder of chlorobenzene molecules: a pair of molecules with 0.5 occupancy being related by a crystallographic center of

Table 3. Bond lengths and bond angles

Bond lengths [l/Å]			
Pt–P(1)	2.281(3)	C(10)–C(11)	1.56(2)
Pt–P(2)	2.282(2)	C(10)–C(12)	1.59(2)
Pt–Cl(1)	2.359(3)	C(10)–C(13)	1.549(19)
Pt–Cl(2)	2.362(3)	C(20)–C(21)	1.534(17)
P(1)–C(1)	1.853(12)	C(20)–C(22)	1.570(17)
P(2)–C(3)	1.850(11)	C(20)–C(23)	1.551(19)
P(1)–C(10)	1.919(12)	C(30)–C(31)	1.554(18)
P(1)–C(20)	1.898(11)	C(30)–C(32)	1.538(18)
P(2)–C(30)	1.900(12)	C(30)–C(33)	1.537(17)
P(2)–C(40)	1.914(13)	C(40)–C(41)	1.54(2)
C(1)–C(2)	1.501(17)	C(40)–C(42)	1.556(18)
C(2)–C(3)	1.519(17)	C(40)–C(43)	1.547(19)
Bond angles [ϕ/°]			
P(1)–P–Pt(2)	99.05(9)	Cl(1)–Pt–Cl(2)	83.18(11)
P(1)–Pt–Cl(1)	90.07(9)	P(2)–Pt–Cl(1)	167.87(9)
P(1)–Pt–Cl(2)	168.79(10)	P(2)–Pt–Cl(2)	88.96(10)
Pt–P(1)–C(1)	115.5(4)	Pt–P(2)–C(3)	115.7(4)
Pt–P(1)–C(10)	110.8(4)	Pt–P(2)–C(3)	110.9(4)
Pt–P(1)–C(20)	115.7(4)	Pt–P(2)–C(40)	114.1(4)
C(1)–P(1)–C(10)	102.9(5)	C(3)–P(2)–C(30)	99.1(5)
C(1)–P(1)–C(20)	100.1(5)	C(3)–P(2)–C(40)	104.0(5)
C(10)–P(1)–C(20)	110.8(5)	C(30)–P(2)–C(40)	112.1(5)
P(1)–C(1)–C(2)	116.9(8)	P(2)–C(3)–C(2)	113.5(8)
C(1)–C(2)–C(3)	113.5(8)		
P(1)–C(10)–C(11)	113.0(9)	P(2)–C(30)–C(31)	110.9(8)
P(1)–C(10)–C(12)	107.0(10)	P(2)–C(30)–C(32)	107.8(8)
P(1)–C(10)–C(13)	114.0(9)	P(2)–C(30)–C(33)	115.0(8)
P(1)–C(20)–C(21)	113.8(8)	P(2)–C(40)–C(41)	112.5(9)
P(1)–C(20)–C(22)	106.6(8)	P(2)–C(40)–C(42)	107.8(9)
P(1)–C(20)–C(23)	113.7(8)	P(2)–C(40)–C(43)	112.5(9)
C(11)–C(10)–C(12)	111.1(12)	C(31)–C(30)–C(32)	109.5(10)
C(11)–C(10)–C(13)	107.5(11)	C(31)–C(30)–C(33)	108.3(10)
C(12)–C(10)–C(13)	104.0(12)	C(32)–C(30)–C(33)	105.2(10)
C(21)–C(20)–C(22)	106.2(10)	C(41)–C(40)–C(42)	108.6(11)
C(21)–C(20)–C(23)	107.1(10)	C(41)–C(40)–C(43)	107.2(11)
C(22)–C(20)–C(23)	109.2(10)	C(42)–C(40)–C(43)	108.2(11)

Table 4. Least-squares planes through various groups of atoms, the deviations (l/Å) of the atoms from the plane and the dihedral angles between the selected planes

Equation of the plane is of the form $AX+BY+CZ+D=0$, where X, Y, Z, and D are measured in Å unit: $X=ax+cz\cos\beta$, $Y=by$, $Z=cz\sin\beta$.

a. Coordination plane Pt, Cl(1), Cl(2), P(1) and P(2)

$-0.1284X-0.6595Y-0.7407Z+5.2821=0$

Pt	Cl(1)	Cl(2)	P(1)	P(2)
0.006	−0.169	0.173	0.179	−0.169

b. Plane defined by C(1), C(2), and C(3)

$0.0312X-0.9634Y+0.2663Z+4.4943=0$

c. Plane defined by Pt, P(1), and P(2)

$-0.0284X-0.6624Y-0.7486Z+4.9089=0$

d. Plane defined by Pt, Cl(1), and Cl(2)

$-0.2356X-0.6508Y-0.7218Z+5.6135=0$

Dihedral angles [ϕ/°]	
between planes *a* and *b*	64.3
c and *d*	12.0

symmetry. Figure 1(b) shows a drawing of a disordered molecular pair. Owing to the difficulty resolving each of the overlapped peaks in two (Fig. 1(a)), the Cl(S)/C(S4)′ (or C(S4)/Cl(S)′) and C(S2)/C(S6)′ (or C(S(6)/C(S2)′) atoms are drawn as a single hybrid (Cl+C)/2 and single carbon atoms. Consequently, bond lengths and bond angles shown in Fig. 1(b) are less satisfactory.

Crystal Structure. The crystal structure is shown in Fig. 4 as a stereoscopic drawing. Pairs of disordered chlorobenzene half molecules are also shown on the center of symmetry. All the intermolecular atomic contacts are the usual van der Waals distances.

Computations throughout the present study were carried out on a NEAC 2200-700 computer at Osaka University. Figures 2, 4, and 5 were drawn on a NUMERICON 7000 systems at Osaka University with a local version of ORTEP.[8]

The authors wish to express their deep thanks to Professor Sei Otsuka and his coworkers for providing crystals and helpful discussions.

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