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Crystal Structure and Related Properties of Phenothiazine Cation Radical-Hexachloroantimonate. Monoclinic(I) Form

Tokiko UCHIDA,* Masanori ITO, and Kozo KOZAWA

Department of Industrial Chemistry, Faculty of Science and Technology, Science University of Tokyo,
Noda, Chiba 278

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Three forms of crystals were obtained from mixed solutions of phenothiazine and $SbCl_5$; the crystal structure of the monoclinic(I) modification was determined using 2827 reflections at room temperature. Crystal data: $(C_{12}H_9NS)^{+\cdot}SbCl_6^-$, $F.W.=533.7$, monoclinic, $a=16.253(3)$, $b=14.334(1)$, $c=15.786(3)$ Å, $\beta=104.07(1)°$, space group C2/c, $D_m=2.00$, $D_x=1.99$ g cm^{-3}, $Z=8$, $\mu=25.73$ cm^{-1} (Mo $K\alpha$). The structure was solved by the heavy-atom method and refined by block-diagonal least-squares method to $R=0.072$. The crystal consists of phenothiazine cation radicals(PT$^{+\cdot}$) and hexachloroantimonate anions($SbCl_6^-$), and every ion exists as a monomer in the crystal. Each $SbCl_6^-$ forms a distorted octahedron. The two C–S distances of PT$^{+\cdot}$ are 1.705 and 1.711 Å, and the C–S–C angle is 103.9°. The dihedral angle between the two outer phenyl rings of PT$^{+\cdot}$ is 176.5°. From the ESR measurements of a single crystal, three principal g-values were determined: $g_1=2.003$, $g_2=2.007$ and $g_3=2.008$. The direction of g_1 is normal to the molecular plane of PT$^{+\cdot}$. These facts suggest some π-delocalization in the central ring of PT$^{+\cdot}$. Absorption spectra polarized parallel to the molecular plane of PT$^{+\cdot}$ are very similar to the polycrystalline reflection spectra of PT$^{+\cdot}$ salts obtained by other authors, and there are no intense bands in the spectra polarized perpendicular to PT$^{+\cdot}$ molecular plane over the wave number range 10 to 27×10^3 cm^{-1}.

Phenothiazine (PT) is a very characteristic electron donor possessing several stepwise oxidation states[1–3] and a variety of folding angles of the molecular plane.[4] On the other hand, antimony chlorides have been known as electron acceptors or Lewis acids strong enough to provide cation radicals of some aromatic molecules easily.[5] Many works have been published about the solid state behavior of electron donor-acceptor complexes[5–8] or graphite intercalation compounds[9] including antimony chlorides. However, few of them discussed their results on the basis of the strictly determined crystal structures, since the samples were usually obtained in very fine polycrystals. Magnetic and optical properties of polycrystalline "PT–$SbCl_5$" were described by Sato *et al.* more than ten years ago.[7,8] Recently, we have been able to distinguish at least three kinds of crystals in the precipitates of a mixture of PT and $SbCl_5$. They are different from each other in both color and crystal system.

In this paper, we wish to report the crystal structure, paramagnetic resonance and electronic absorption spectra for a brown monoclinic single crystal of phenothiazine cation radical-hexachloroantimonate.

Experimental

Preparation of Single Crystals. Both PT and $SbCl_5$ dissolved in 1,2-dichloroethane (concentration of about 3.5×10^{-3} mol dm^{-3}) were mixed in approximately 1 : 1 mol ratio in a dry box at room temperature. By slow evaporation of solvent in a dry atmosphere, three types of crystals were distinguishable in the precipitates: monoclinic(I), monoclinic(II), and triclinic modifications. The monoclinic(I) crystals are brown rectangular platelets with (010) plane developed and $[20\bar{1}]$ direction elongated. The monoclinic(II) and triclinic crystals were hexagonal prisms and black parallelepiped columns, respectively.[10] The crystals were fairly stable in the air for a month, if they were completely dried up in a nitrogen atmosphere.

This report concerns the monoclinic(I) modification that consists of the ionic salt of phenothiazine cation radical(PT$^{+\cdot}$) and hexachloroantimonate anion($SbCl_6^-$).[11] Triclinic crystals, which will be reported elsewhere, are (3,7-dichlorophenothiazine)$^{+\cdot}$ $SbCl_6^-$, but the components of monoclinic(II) crystals still remain unknown.

X-Ray Data Collection. After determining preliminary cell constants and space group from Weissenberg photographs, a crystal of $0.3\times0.2\times0.08$ mm^3 was mounted on a Hilger & Watts diffractometer with Mo $K\alpha$ radiation at room temperature. From the 12 setting angles, θ's of which were greater than 10.7°, the lattice constants were calculated by a least-squares method. Intensity data were collected by the θ-2θ scan technique at every 0.01° of θ step up to $2\theta\leq55°$. The scan width of θ was 0.8° for all the reflections. Counting time was 1 s per step for peak measurements, and each background was measured for 10 s at the beginning and the end of the scan range. Three standard reflections were monitored every 50 measurements to check both crystal and apparatus. No systematic changes in intensities of the standard reflections were observed throughout the data collection. Lorentz and polarization effects were corrected, but no absorption correction was made. Of the 4345 independent reflections measured, 2827 with $F_o\geq3\sigma(F)$ were used in the subsequent analysis. Density was observed by the flotation method. Crystal data are shown in Table 1. The systematic absences indicated the space group to be either Cc or C2/c, but the further study showed it to be C2/c.

Electronic Absorption Spectra. The solution spectra and

TABLE 1. CRYSTAL DATA

$(C_{12}H_9NS)^{+\cdot}$ $SbCl_6^-$
$F.W.=533.7$
Monoclinic
C2/c
$a=16.253(3)$ Å
$b=14.334(1)$ Å
$c=15.786(3)$ Å
$\beta=104.07(1)°$
$V=3567$ Å^3
$Z=8$
$D_m=2.00$ g cm^{-3}
$D_x=1.99$ g cm^{-3}
μ(Mo $K\alpha$)$=25.73$ cm^{-1}

polycrystalline reflection spectra were recorded on a Hitachi spectrophotometer, Model 323, at room temperature. Solution spectra were measured with 1,2-dichloroethane as solvent. Polarized absorption spectra with single crystals were observed with Olympus MSP-A-IV microspectrophotometer over the wave number range 10 to 27×10^3 cm^{-1} at room temperature.

Electron Spin Resonance. Measurements of electron spin resonance(ESR) were carried out with a JES-FE3X spectrometer operating at 9.4 GHz microwave and 100 KHz magnetic field modulation. The polycrystalline sample was measured both at room temperature and at 77 K. Angular dependence of resonance field about a single crystal was observed at room temperature. New orthogonal coordinates. a′, b′, and c′, were defined to rotate a specimen: a′ was parallel to the developing $[20\bar{1}]$ axis, b′ agreed with the crystal b axis, and the c′ was perpendicular to the a′b′ plane. The resonance field was recorded at every 15° rotation around the a′, b′, and c′ axes. The *g*-values were calculated from spectra in which the resonance fields of both specimen and Mn^{2+}/MgO (a_{Mn}= 8.69 mT) were recorded simultaneously. The spin concentrations were not measured.

Solution and Refinement of the Structure

The structure was solved by the heavy-atom method. From the Patterson synthesis, two Sb atoms were found to occupy two different special equivalent positions (b and e of Wyckoff positions), one on the center of symmetry and the other on the two-fold rotation axis. A Fourier map, computed using the phases from two Sb atoms, revealed the positions of all the non-hydrogen atoms. After five cycles of the isotropic block-diagonal least-squares refinements, the discrepancy index R converged at 0.112. Then, five additional cycles of the anisotropic refinement gave the R to be 0.075. At this stage of the refinements, the difference Fourier map clearly revealed all the hydrogen atoms. The final cycle was calculated including hydrogen atom parameters with a fixed isotropic thermal parameters, B= 4.0 Å^2, and converged to R=0.072. The quantity minimized was $\sum w(|F_o|-k|F_c|)^2$, where the weighting scheme $w=(F_{max}/F_o)^2$ for $F_o>F_{max}$, and $w=1$ for $F_o\leq F_{max}$. F_{max}=32.5 after scaling F_o to F_c.[12] In the final cycle, the parameter shifts almost converged to zero except for those of hydrogen atoms which were less than the corresponding standard deviations. A final difference Fourier map showed no extra peaks. The neutral atomic scattering factors and anomalous dispersion factors of Sb were taken from the "International Tables for X-Ray Crystallography."[13] All the computations were carried out at the Computer Centre of the University of Tokyo with the UNICS program system.[14]

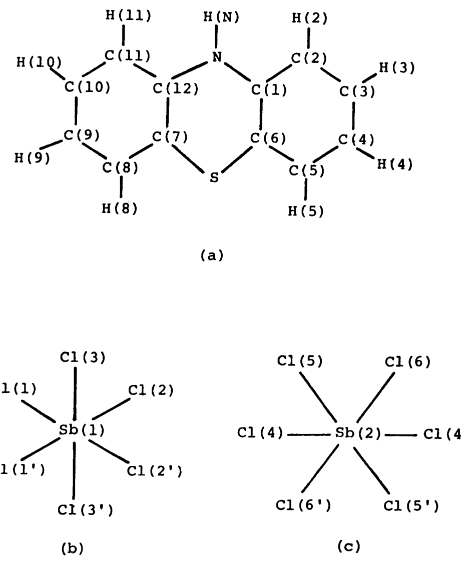

Fig. 1. The numbering of atoms.
(a): $PT^{+\cdot}$. (b): $SbCl_6^-$ with 2 symmetry. (c): $SbCl_6^-$ with $\bar{1}$ symmetry.

Results and Discussion

Crystal Structure. The atomic positional parameters with their estimated standard deviations are

TABLE 2. THE FINAL POSITIONAL PARAMETERS ($\times10^4$; for H, $\times10^3$) AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS

Estimated standard deviations are given in parentheses. The equivalent isotropic thermal paramers for non-hydrogen atoms are calculated using the expression: $B_{eq}=\frac{4}{3}\Sigma_i\Sigma_j a_i a_j \beta_{ij}$, where the a_i's are the unit cell edges in direct space. The isotropic thermal parameter of hydrogen atoms is fixed, B=4 0 Å^2.

	x	y	z	B_{eq}/Å^2
Sb(1)	0000	727(1)	2500	3.0(0)
Sb(2)	0000	5000	0000	3.0(0)
Cl(1)	1(2)	−438(2)	1435(2)	3.9(1)
Cl(2)	40(3)	1898(3)	1463(3)	5.1(1)
Cl(3)	1509(2)	673(3)	2911(3)	4.4(1)
Cl(4)	−327(3)	6507(3)	429(3)	5.2(1)
Cl(5)	−44(3)	5569(3)	−1425(2)	4.6(1)
Cl(6)	1462(2)	5343(4)	462(3)	5.1(1)
S	1717(2)	851(3)	521(3)	4.3(1)
N	3241(7)	209(10)	1964(8)	4.2(4)
C(1)	3136(8)	1143(11)	1839(9)	4.0(4)
C(2)	3774(10)	1757(14)	2379(10)	5.2(6)
C(3)	3684(15)	2677(15)	2229(15)	7.3(11)
C(4)	3012(13)	3077(12)	1606(13)	5.8(7)
C(5)	2405(10)	2497(12)	1100(11)	4.9(5)
C(6)	2478(8)	1505(10)	1197(9)	3.9(6)
C(7)	2020(8)	−274(10)	793(9)	3.5(4)
C(8)	1556(9)	−997(12)	358(11)	4.6(6)
C(9)	1785(10)	−1893(11)	552(11)	4.5(5)
C(10)	2472(11)	−2126(11)	1188(12)	5.2(6)
C(11)	2974(11)	−1433(13)	1683(11)	5.2(6)
C(12)	2746(8)	−500(11)	1485(8)	3.6(4)
H(N)	361(11)	8(13)	229(12)	
H(2)	438(11)	142(13)	282(13)	
H(3)	389(11)	308(13)	250(12)	
H(4)	290(12)	387(13)	157(12)	
H(5)	198(11)	272(13)	69(12)	
H(8)	114(11)	−80(13)	−1(13)	
H(9)	139(11)	−235(13)	14(12)	
H(10)	282(12)	−278(13)	132(12)	
H(11)	358(11)	−153(13)	218(12)	

Table 3. Bond distances and angles of SbCl$_6^-$ anions

Bond distance l/Å	Bond angle	ϕ/°
Sb(1)–Cl(1) 2.369(4)	Cl(1)–Sb(1)–Cl(2)	90.3(2)
Sb(1)–Cl(2) 2.357(5)	Cl(1)–Sb(1)–Cl(3)	89.6(1)
Sb(1)–Cl(3) 2.381(4)	Cl(1)–Sb(1)–Cl(1′)	90.4(1)
	Cl(1)–Sb(1)–Cl(2′)	178.4(2)
	Cl(1)–Sb(1)–Cl(3′)	87.8(1)
	Cl(2)–Sb(1)–Cl(3)	90.7(2)
	Cl(2)–Sb(1)–Cl(2′)	89.2(2)
	Cl(2)–Sb(1)–Cl(3′)	92.0(2)
	Cl(3)–Sb(1)–Cl(3′)	176.3(2)
Sb(2)–Cl(4) 2.362(5)	Cl(4)–Sb(2)–Cl(5)	90.0(2)
Sb(2)–Cl(5) 2.377(4)	Cl(4)–Sb(2)–Cl(6)	90.1(2)
Sb(2)–Cl(6) 2.361(5)	Cl(5)–Sb(2)–Cl(6)	91.0(2)

Table 4. Bond distances and angles of PT$^{+\bullet}$ cation radical

Bond distance	l/Å	Bond angle	ϕ/°
N–C(1)	1.36(2)	C(1)–N–C(12)	127(1)
C(1)–C(2)	1.47(3)	N–C(1)–C(2)	117(1)
C(2)–C(3)	1.34(3)	N–C(1)–C(6)	122(1)
C(3)–C(4)	1.40(3)	C(2)–C(1)–C(6)	121(1)
C(4)–C(5)	1.39(3)	C(1)–C(2)–C(3)	117(2)
C(5)–C(6)	1.43(2)	C(2)–C(3)–C(4)	124(2)
C(6)–C(1)	1.38(2)	C(3)–C(4)–C(5)	119(2)
S–C(6)	1.71(2)	C(4)–C(5)–C(6)	120(2)
S–C(7)	1.71(2)	C(1)–C(6)–C(5)	119(1)
C(7)–C(8)	1.37(2)	S–C(6)–C(1)	125(1)
C(8)–C(9)	1.35(2)	C(6)–S–C(7)	103.9(7)
C(9)–C(10)	1.35(3)	S–C(6)–C(5)	117(1)
C(10)–C(11)	1.40(3)	S–C(7)–C(8)	120(1)
C(11)–C(12)	1.40(2)	S–C(7)–C(12)	122(1)
C(7)–C(12)	1.44(2)	C(8)–C(7)–C(12)	118(1)
N–C(12)	1.40(2)	C(7)–C(8)–C(9)	121(2)
		C(8)–C(9)–C(10)	122(2)
		C(9)–C(10)–C(11)	120(2)
		C(10)–C(11)–C(12)	118(2)
		N–C(12)–C(7)	120(1)
		N–C(12)–C(11)	119(1)
		C(7)–C(12)–C(11)	119(1)

presented in Table 2. The atomic numbering is given in Fig. 1.

There are two crystallographically different halves of (SbCl$_6^-$)'s and a PT$^{+\bullet}$ in an asymmetrical unit. Each SbCl$_6^-$ anion forms a slightly distorted octahedron. The bond lengths and angles, given in Table 3, are consistent with those found in other SbCl$_6^-$.[15] Of the six independent Sb–Cl distances, Sb(1)–Cl(3) and Sb(2)–Cl(5) are slightly longer than the other four.

In Table 4, the bond distances and angles of PT$^{+\bullet}$ are presented. The C–S bond distances are significantly shorter than those of neutral PT (1.762 Å for orthorhombic form[16] and 1.770 Å for monoclinic form[17]). The sum of the covalent radii is 1.81 Å for C–S single bond, and is 1.61 Å for C–S double bond.[18] The observed C–S bond length of 1.71(2) Å is just an average of these values. It suggests the π-delocalization is spread over the whole molecule of PT$^{+\bullet}$ including the central ring. Similar C–S distances, around 1.71 Å, were found in many compounds,[19] in which the shortening of the C–S bonds and the planarity of the systems characterized a π-delocalization including S atoms.

Much attention has been paid to the planarity of PT$^{+\bullet}$, namely, the dihedral angle between the external two benzene rings of PT molecule (these two planes are denoted as Bz1 and Bz2 in this paper. See Table 5). For substituted phenothiazines, this angle ranges from 134.4° to 173.6°, depending on the kinds and the positions of the substituents at the external benzene rings.[4] Andreetti *et al.* discussed the dihedral angle (so-called butterfly angle) of PT derivatives related to the degree of delocalization in the central ring, which was estimated from the shortening of the C–S bond lengths.[4] Table 5 lists the dihedral angles and related value of PT moieties in complex compounds[20–24] as well as the two modifications of PT itself.[16,17] The top two compounds in Table 5 are PT$^{+\bullet}$ ion radical salts and the next four compounds are charge-transfer (CT) complexes of weak π-π type. Every dihedral angle between Bz1 and Bz2 of PT moiety is close to 180° except for PT–DNB,[24] and the flattened PT moiety

Table 5. Comparison of some parameters of PT species

Compound	Dihedral angle θ/° a)				Bond distance l/Å		Bond angle ϕ/°		Ref.
	Bz1-Bz2	P1-P2	Bz1-P1	Bz2-P2	C–S (average)	CN (average)	C–S–C	C–N–C	
PT$^{+\bullet}$–SbCl$_6^-$	175.8	177.1	178.5	179.5	1.71	1.38	104	127	This work
PT$^{+\bullet}$–Ni(tfd)$_2^-$	172.2 b)	177.44	179.09	179.56	1.73	1.41	102.8	121	20
PT–PMDA	176.4	173.8	178.6	178.6	1.758	1.403	103.2	125.3	21
PT–TCNQ	Planar c)				1.73	1.36	104	134	22
PT–TNB	Planar within the accuracy				1.76	1.40	102	126	23
PT–DNBA	156 d)	—	—	—	1.76	1.39	101	123	24
PT(orthorh)	158.5	—	—	—	1.762	1.399	100.9	124.4	16
PT(monocl)	153.3	—	—	—	1.770	1.406	99.6	121.5	17

a) Least squares planes are defined as follows. A maximum deviation of constituent atom of each plane is presented in parenthesis. Bz1: C(1), C(2), C(3), C(4), C(5), and C(6)(0.009 Å); Bz2: C(7), C(8), C(9) C(10), C(11), and C(12) (0.01 Å); P1: S, N, C(1) and C(6) (0.009 Å); P2: S, N, C(7) and C(12) (0.001 Å). b) Folding angle of two halves being approximated planar. c) Fundamental structure in disordered crystal. d) Dihedral angle between two planar halves folded along the N–S axis. Nomenclature: tfd=(z)-1,2-bis(trifluoromethyl)-1,2-ethylenedithiolate, PMDA=1,2:4,5-benzenetetracarboxylic dianhydride(pyromellitic dianhydride), TCNQ=7,7,8,8-tetracyanoquinodimethan, TNB=1,3,5-trinitrobenzene, DNBA=3,5-dinitrobenzoic acid.

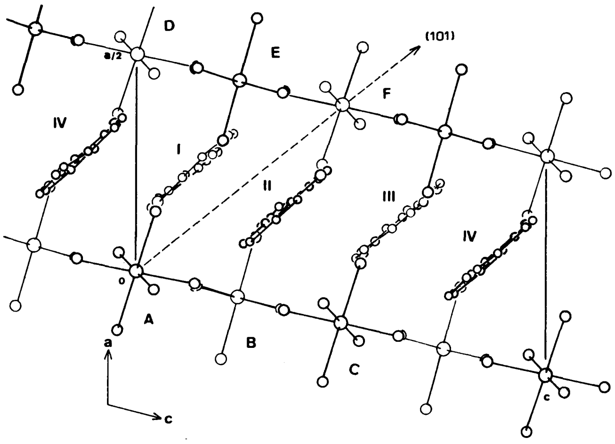

Fig. 2. The packing arrangements in the crystal lattice projected along the b axis. The numbering from I to IV correspond to PT$^{+\bullet}$'s, and those from A to F correspond to $(SbCl_6^-)$'s. The same notations are employed in Figs. 3 and 4. The broken line indicates the direction of [101] together with the intersection of (010) and $(10\bar{1})$ planes.

Symmetry code

PT$^{+\bullet}$:	I	x,	y,	z			
	II	$1/2-x$,	$1/2+y$,	$1/2-z$			
	III	x,	$-y$,	$1/2+z$			
	IV	$1/2-x$,	$1/2-y$,	$1-z$			
	IV′	$1/2-x$,	$1/2-y$,	$-z$			
$Sb(1)Cl_6^-$:							
	B	x,	y,	z;	$-x$,	y,	$1/2-z$
	E	$1/2-x$,	$1/2+y$,	$1/2+z$;	$1/2+x$,	$1/2+y$,	z
$Sb(2)Cl_6^-$:							
	A	x,	y,	z;	$-x$,	$1/2-y$,	$-z$
	C	x,	$-y$,	$1/2+z$;	$-x$,	y,	$1/2-z$
	D	$1/2+x$,	$1/2+y$,	z;	$1/2-x$,	$1/2-y$,	$-z$
	F	$1/2+x$,	$1/2-y$,	$1/2+z$;	$1/2-x$,	$-1/2+y$,	$1/2-z$

does not always accompany the shortened C–S bond, namely the delocalization of the central ring.

Anthonj *et al.*[21] cited some disorder of PT in the PT–PMDA CT complex: approximately one in fifty molecules has the positions of the S and N atoms reversed. Their basis for disorder was an asymmetrical peak around the N atom, which they interpreted as a twin peak of the H(N) and the disordered S atoms. In the case of the present crystal, however, all the S, N, and H(N) atom peaks were symmetric within the errors. So, the positional disorder was not considered for the PT$^{+\bullet}$ moiety in PT$^{+\bullet}$$SbCl_6^-$.

Figures 2 and 3 give the packing arrangement in the crystal projected along the b axis and onto the $(10\bar{1})$ plane, respectively. Figure 2 shows that all the Sb atoms exist on (200) planes, and that the PT$^{+\bullet}$ cation radicals put their molecular planes almost parallel to $(10\bar{1})$. However, the four PT$^{+\bullet}$ cation radicals, numbered from I to IV in Fig. 2, do not have any overlap, as illustrated in Fig. 3. In other words, a strong CT interaction is not expected between the PT$^{+\bullet}$ cation radicals in this crystal.

Figure 4 illustrates the relation between the nearest neighbor species viewed down the [101] direction, which is horizontal in Fig. 3. In the figure, the shortest distances between neighboring species are also exhibited.

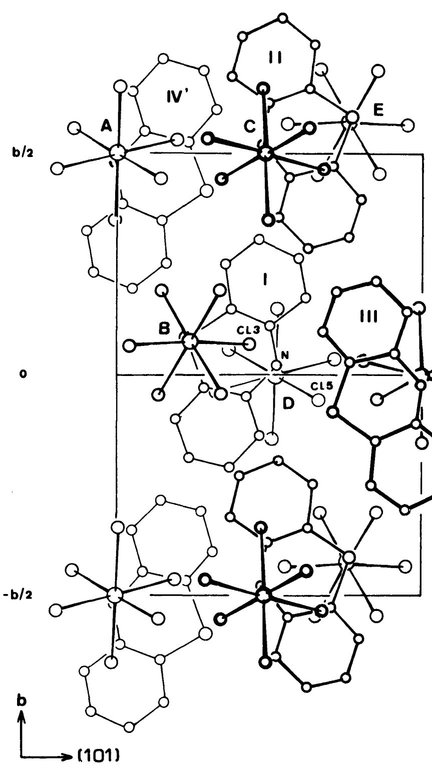

Fig. 3. The packing arrangements in the crystal lattice projected onto the $(10\bar{1})$ plane.

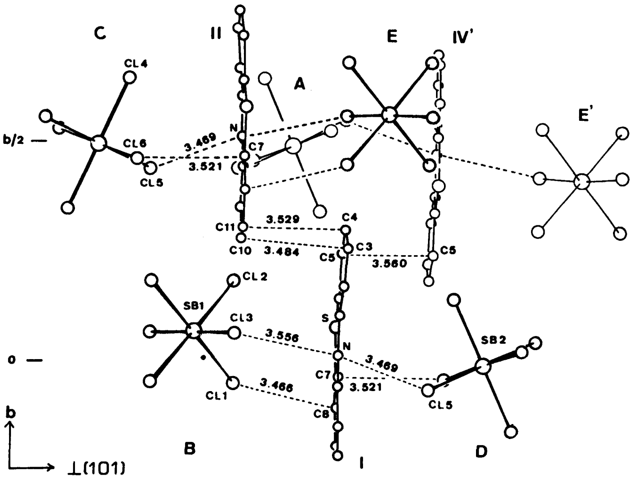

Fig. 4. Perspective relation between the cations and the anions viewed down the [101] direction. Intermolecular atomic distances (Å), less than 3.6 Å, are shown.

It is interesting that the slightly elongated two Sb–Cl bonds, namely Sb(1)–Cl(3) and Sb(2)–Cl(5), are pointed at the N atom of PT$^{+\bullet}$ from both sides of the cation, though the N···Cl intermolecular distances do not suggest considerable shortened contacts of them. Nevertheless the structure implies an appropriate charge deviation in each ion.

Polarized Absorption Spectra. Figure 5(a) shows polarized absorption spectra for the cases parallel to and perpendicular to [101] on the (010) face of a single

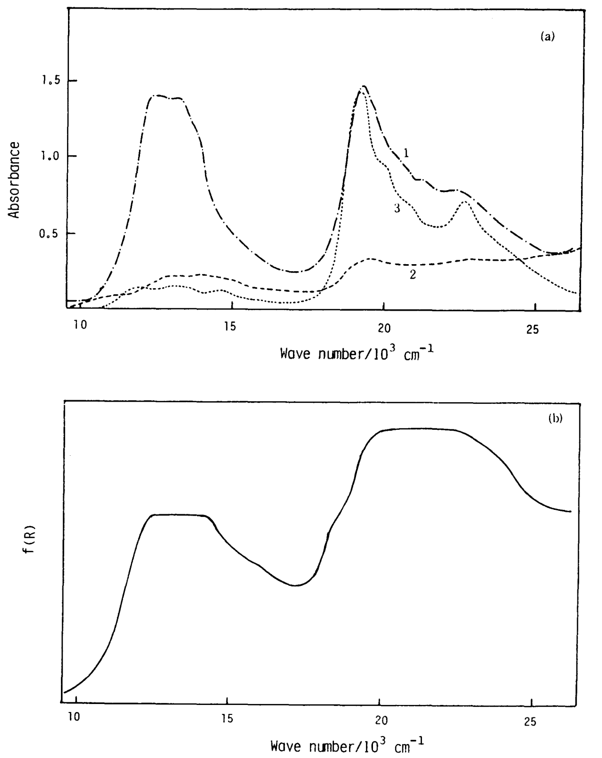

Fig. 5. (a) Polarized absorption spectrum of a single crystal, 1 (—·—·): //[101], 2(------): ⊥[101], and 3 (······): solution spectrum in 1,2-dichloroethane. (b) Polycrystalline reflection spectrum.

crystal of PT$^{+\cdot}$SbCl$_6^-$, as well as its solution spectrum. As mentioned in the previous section and shown in Fig. 3, [101] direction is very close to the short axis in the PT$^{+\cdot}$ molecular plane. The polycrystalline reflection spectrum of monoclinic(I) crystals is shown in Fig. 5(b). They lack the absorption band at 10×10^3 cm^{-1} (1000 nm) that was found in "PT$^+$(SbCl$_5$)$^-$" polycrystalline spectra and assigned as the CT band between PT$^{+\cdot}$ radicals by Sato *et al.*[8] Since the monoclinic(I) crystal is a simple salt, as mentioned in the previous section, it is reasonable that the CT band between cation radicals does not appear in the absorption spectra. However, crystals of other forms still have the possibility of being "PT$^+$(SbCl$_5$)$^-$" described by Sato *et al.*[8]

Curve 1 in Fig. 5(a), //[101] spectrum, is essentially similar to the polycrystalline reflection spectra of monoclinic(I) (Fig. 5(b)), PT$^{+\cdot}$Br$^-$,[3,25] PT$^{+\cdot}$HSO$_4^-$·H$_2$O and PT$^{+\cdot}$ picrate;[3] it consists of two intense bands around (12—14)$\times10^3$ cm^{-1} and (19—23)$\times10^3$ cm^{-1}. The latter band well agrees with the solution spectrum (Curve 3), in which the absorption maxima at 19.2 and 22.6×10^3 cm^{-1} are characteristic to PT$^{+\cdot}$.[2,3] On the other hand, the former band at (12—14)$\times10^3$ cm^{-1} is intense only in the solid state. If this band is attributed to cation-anion interaction, it should be weaker in the [101] direction than the other direction according to the structural consideration. Since Curve 2 has no intense band, the lower frequency band at (12—14)$\times10^3$ cm^{-1} is possibly assigned to the PT$^{+\cdot}$ intramolecular electronic transition, the intensity of which is enhansed in the solid state. As a result, in the range of wave numbers measured, there exist only local excitation bands of PT$^{+\cdot}$ cation radical.

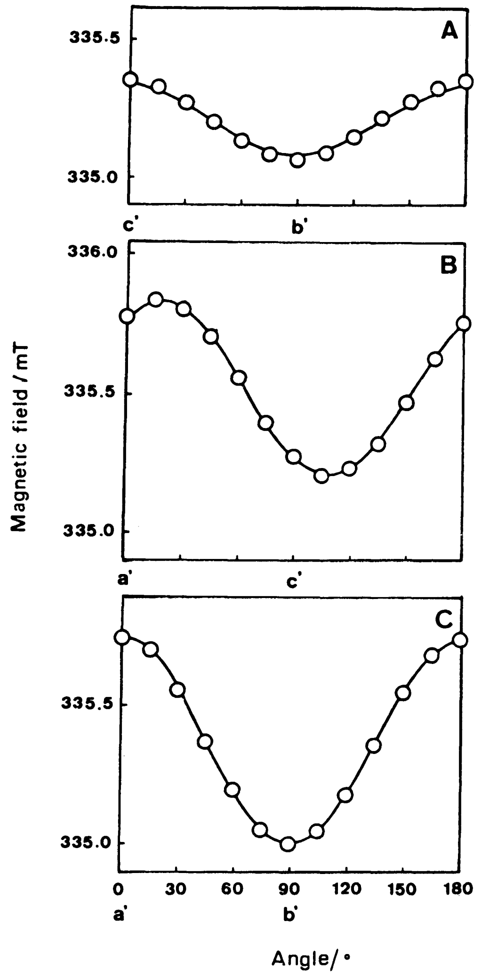

Fig. 6. Angular dependence of the resonance field for rotation about the A: a′ axis, B: b′(=b) axis, and C: c′ axis, where the orthogonal axes a′, b′, and c′ are defined in the text. Circles are experimental, and solid lines are calculated ones.

Electron Spin Resonance. The ESR spectra of polycrystalline samples at room temperature showed anisotropy of *g*-factor without hyperfine structure. At 77 K, neither the line-splitting nor any large change of line-shape occurred.

The single crystal spectra consisted of a line corresponding to a unique arrangement of PT$^{+\cdot}$ radicals in the crystal lattice. Namely, all the eight PT$^{+\cdot}$ radicals in a unit cell are geometrically parallel and magnetically equivalent to each other. The line width, ΔH_{msl}, was slightly changed from 0.09 to 0.17 mT with the orientation of the crystal to the magnetic field. The observed angular dependencies of the spectra, as shown in A and C of Fig. 6, are symmetrical around the b axis, which is also the crystallographically unique axis. The calculated direction cosines of the magnetic field with respect to the a′, b′, and c′ axes are presented in Table 6, together with the three principal *g*-values. The g_1 value is close to that of free electron, and is directed normal to the molecular plane of the PT$^{+\cdot}$ within the experimental error($\pm3°$). The direction of g_2 is in accord

Table 6. Principal g values and their direction cosines with respect to the a′, b′, and c′ axes

	g	Direction cosine		
		a'	b'	c'
g_1	2.003(1)	±0.96(2)	0.00(5)	∓0.29(5)
g_2	2.008(1)	0.00(5)	±1.00	0.00(5)
g_3	2.007(1)	±0.29(5)	0.00(5)	±0.96(2)

with the crystal b axis, and the g_3 approximately coincides with the [101] direction (see Fig. 3). Both g_2 and g_3 are in the molecular plane of $PT^{+\cdot}$. The anisotropic difference between the principal values of g_1 and g_2 is not so large as in the case of the unpaired electron localized at S atom.

Many authors have observed the hyperfine structures of $PT^{+\cdot}$ in solution.[26-29] Malrieu and Pullman calculated the spin density distribution in the ring system of $PT^{+\cdot}$ with a simple MO method, and estimated the same order of the spin density for both N and S atoms (0.244 and 0.217, respectively), provided the radical was assumed to be planar.[27] Chiu *et al.* obtained values similar to those of Malrieu and Pullman by the observation of hyperfine splitting from H, N, and ^{33}S atoms of $PT^{+\cdot}$ in solution.[28] Their experimentally estimated spin density distributions are 0.234 and 0.218 for N and S atoms, respectively. Since the orbital states occupied by unpaired electron of $PT^{+\cdot}$ in solid state should not be much different from that in solution, it is reasonable to conclude for the present crystal that the unpaired electron of $PT^{+\cdot}$ is delocalized in the ring system including hetero-atoms.

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11) It is not clear what kind of reaction occurred in the mixture solution, since $SbCl_5$ is a very active reagent not only for phenothiazine but also for solvent molecules or traces of water.

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