CHEMISTRY LETTERS, pp. 999-1002, 1986.

THE STRUCTURE AND PROPERTIES OF TWO POLYMORPHIC FORMS OF PHENOTHIAZINE-TETRACHLOROANTIMONATE

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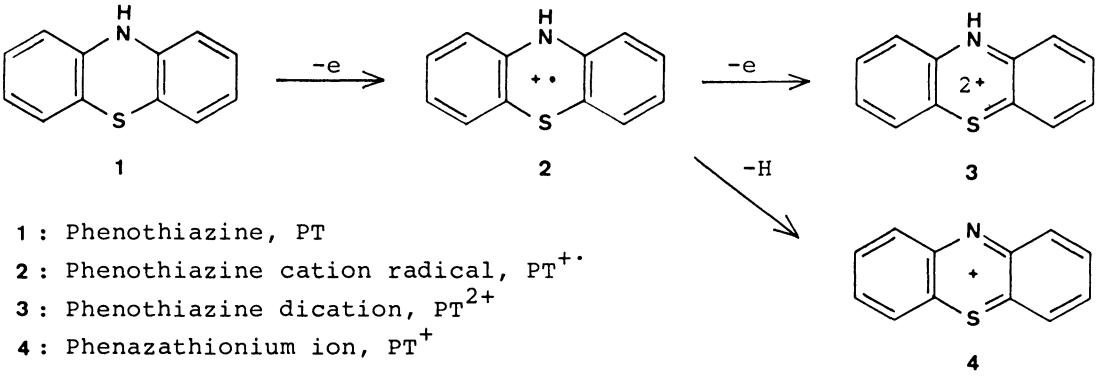
The crystal structure of two polymorphic forms of phenothiazine-tetrachloroantimonate, triclinic and monoclinic forms, was determined. The monoclinic crystal consists of one-dimensional stacking columns of phenothiazine cation radicals and infinite chains of $(SbCl_4^-)_n$. Its single crystals are semiconductors with an activation energy of 0.3 eV, and possess anisotropic behavior.

Phenothiazine (PT) is famous for possessing many oxidation states as shown below.$^{1-3)}$ Since its cation radical ($PT^{+\cdot}$) is stable even in the solid state, many works were published on the solid state properties of cation radical salts of PT or substituted PT.$^{3-11)}$ (In this report, PT denotes phenothiazine species as well as neutral phenothiazine molecule.) However, there have been few structural studies about them.$^{10-14)}$



1 : Phenothiazine, PT
2 : Phenothiazine cation radical, $PT^{+\cdot}$
3 : Phenothiazine dication, PT^{2+}
4 : Phenazathionium ion, PT^{+}

We obtained two polymorphic forms of PT-tetrachloroantimonate as single crystals: triclinic form and monoclinic form. Though the structure of them was not able to be satisfactorily refined owing to their poor crystallinity, the layered stacking structure of cationic PT species was found in both forms as well as the characteristic features of polyanions. Especially in the monoclinic form, $PT^{+\cdot}$'s stack to give the one-dimensional columns. This report concerns with the crystal structure of the two forms of PT-$SbCl_4$, and with the electronic spectra and electrical resistivity of the monoclinic form.

Both forms of crystals grew in the same solution of 1,2-dichloroethane containing PT and $SbCl_3$ at the mole ratio 1 : 2. The monoclinic crystals could be also obtained by mixing PT and $SbCl_5$ at the mole ratio 2 : 1. Table 1 shows the crystal data of both forms of PT-$SbCl_4$. X-Ray data collection was carried out with a Rigaku four-circle diffractometer (Mo Kα radiation) by the θ-2θ scan method up to 2θ ≤ 55°. The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method. All the calculations were carried out at the Computer Centre of the University of Tokyo with the UNICS program system.[15]

Table 1. Crystal Data of Two PT-$SbCl_4$

	$(PT^{+\cdot}PT^{+})_2(Sb_4Cl_{16})^{4-}$	$PT^{+\cdot}SbCl_4^{-}$
F. W.	1851	462.8
Crystal system	Triclinic	Monoclinic
a (Å)	12.148(3)	12.13(2)
b (Å)	13.040(3)	18.17(2)
c (Å)	11.768(3)	7.50(2)
α (°)	108.61(2)	90.0
β (°)	107.76(2)	108.5(1)
γ (°)	104.67(2)	90.0
V ($Å^3$)	1550(1)	1568(6)
Space group	$P\bar{1}$	$P2_1/c$
D_o (g cm^{-3})	1.93	1.98
D_x (g cm^{-3})	1.98	1.96
Chemical unit	1	4
μ(Mo Kα) (cm^{-1})	26.1	26.1
No. of reflection (used/measured)	3125/7106	811/4736
Present R	0.10	0.19

In the triclinic crystals, both PT's and $SbCl_4$'s exist as centrosymmetric tetramers as shown in Fig. 1. In the anion, each Sb atom is octahedrally surrounded by six Cl atoms. The $(PT_4)^{4-}$ tetramer consists of almost parallel four PT's, and the average C-S distance of 1.67 Å in the outer PT is significantly shorter than that in the inner one, 1.76 Å. This fact suggests that outer and inner PT's are in different electronic states. We propose that outer PT is **4**, and inner one is **2** on the basis of C-S distances.

In the case of monoclnic crystals, both the cations and anions form "one-dimensional" structure. Figure 2, (010) projection,

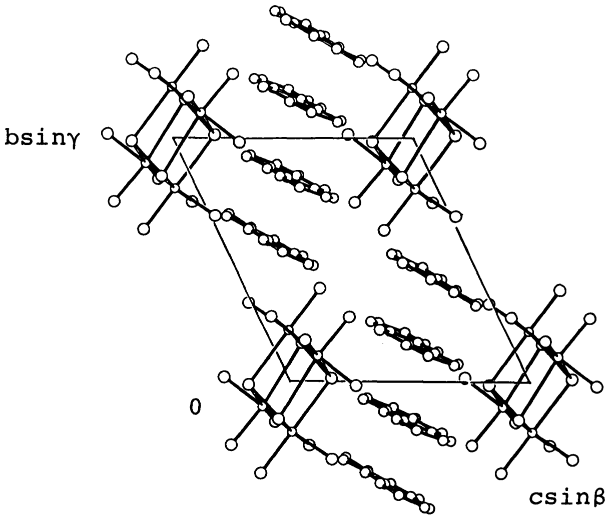


Fig. 1. Crystal structure of triclinic PT-$SbCl_4$ projected along the a axis.

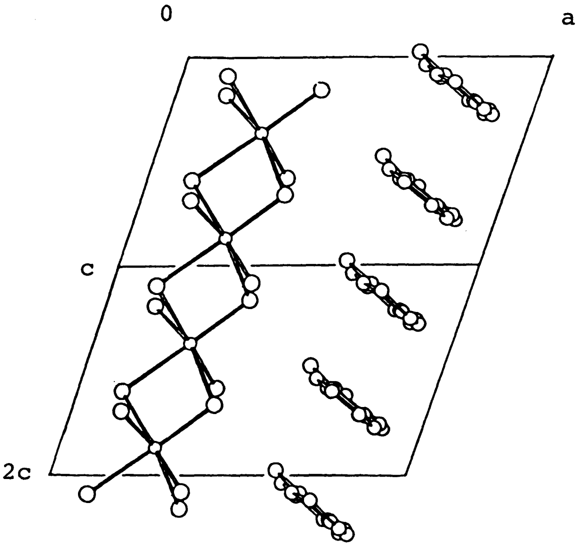


Fig. 2. Crystal structure of monoclinic PT-$SbCl_4$ projected onto (010).

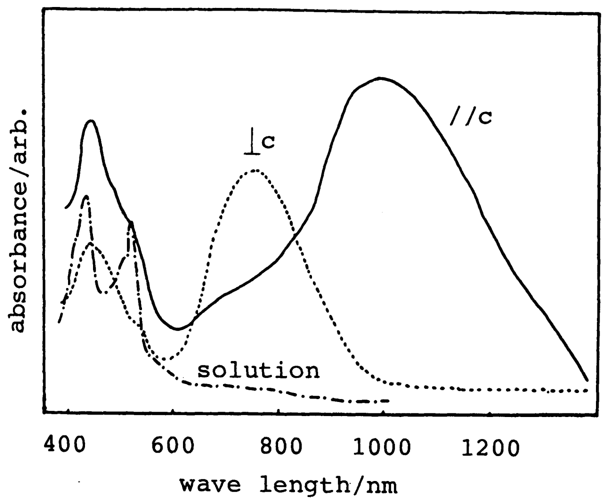


Fig. 3. Single crystal and solution spectra of monoclinic PT-$SbCl_4$.

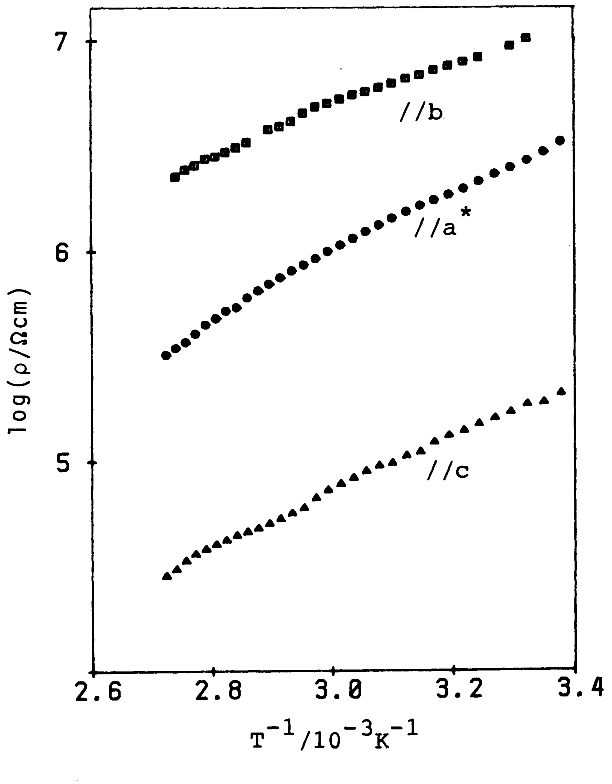


Fig. 4. Temperature dependence of electrical resistivity of single crystals of monoclinic form.

illustrares an infinite chain of the anions and a stacking column of PT's. In the anionic chain, each Sb is surrounded by six Cl atoms similar to the anion in the triclinic form. Since an asymmetric unit contains only one PT, the electronic states of PT must be crystallographically unique. However, precise discussion about the atomic distances is difficult due to the poor convergency of this crystal. The plane to plane spacing of PT's in a cation column is approximately 3.4 Å, which is comparable as PT interplanar distance of 3.38(1) Å in the dimeric pair of chloropromazine-$CuCl_4$ complex.[13)]

Figure 3 shows polarized absorption spectra for the cases parallel to and perpendicular to the c axis on the (010) face of a single monoclinic crystal as well as its solution spectrum, which gives characteristic features of $PT^{+\cdot}$.[2,3,10)] By comparing Fig. 2 with Fig. 3, the broad absorption band around 1000 nm can be assigned to the CT band between $PT^{+\cdot}$

radicals which was ever noted in the "$PT^+(SbCl_5)^-$" polycrystalline spectra by Sato et al.[6] There is a possibility that the "$PT^+(SbCl_4)^-$" was polycrystalline mixture of monoclinic PT-$SbCl_4$ and monoclinic PT-$SbCl_6$.[10]

Measurement of the electrical resistivity was tried with single crystals of the monoclinic form. As shown in Fig. 4, they are semiconductors with anisotropic resistivity: ρ(25 °C, //c) = 2 X 10^5 Ω cm, E = 0.3 eV. In spite of its one-dimensional structure, the resistivity is rather high. That is because the amount of charge transfer is considered to be very close to 1.0 in this complex.

The author express their hearty thanks to Mr. Teruyuki Kodama of the University of Tokyo and Mrs. Midori Goto of National Chemical Laboratory for Industry for the X-ray data collection. The authors are also indebted to Professor Haruo Kuroda and Assistant Professor Kyuya Yakushi of the University of Tokyo for the use of the microspectrophotometer. The present work was partially supported by a Grant-in-Aid for Scientific Research No. 60540296 from the Ministry of Education, Science and Culture.

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(Received April 3, 1986)