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Resonance Raman and ^{129}I Mössbauer Spectroscopic Study of Phenothiazine-Iodine Complexes

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Resonance Raman and ^{129}I Mössbauer spectroscopy have been applied to the phenothiazine-iodine (PT-I_n) complexes, which exhibit relatively low electrical resistivities. It is shown from the resonance Raman spectra that the two iodine species in the PT-I_3 and PT-$I_{2.6}$ complexes are present in essentially the same chemical form, consisting of a distorted I_3^- unit and an I_2 unit strongly coordinated to the I_3^- unit. The ^{129}I Mössbauer spectrum, consistent with the results of the Raman spectra, suggests that the PT-$I_{2.6}$ complex can be approximately formulated as $(PT)_5^{3+}[(I_3)_3(I_2)_2]^{3-}$, in which about three electrons per five PT molecules are transferred to the iodine and the transferred electrons are delocalized on the thirteen iodine atoms. The radical salt is recognized as a partially oxidized mixed-valence compound. The formation of the complex is quite similar to that of the perylene-I_3 complex, which has a low electrical resistivity.

The phenothiazine–iodine (PT-I_n) complex is known to be a typical radical salt, exhibiting a relatively low electrical resistivity.1) The electrical properties, such as the electrical resistivity, the activation energy, the Seebeck coefficient, and the electromotive force, of the semiconducting complex have been examined in detail as a function of the composition n by Gutmann and Keyzer,2) Doi et al.,3) and Matsumoto and Matsunaga.4) According to their works, anomalous behavior of the electrical properties is observed between n=2.5 and 3: Drastic decreases in the electrical resistivity and in the activation energy, a change in sign of the Seebeck coefficient, and a step-by-step increase in the electromotive force. The vibrational spectrum of the complex at n=3, which exhibits the minimum resistivity of 20 Ωcm at room temperature, indicates that the phenothiazine (PT) exists as a complex radical cation where two PT molecules share a unit positive charge and are equivalent in the time scale of infrared spectroscopy.1,5) The results of the electrical properties and the vibrational spectrum suggest that the complex with a composition of n=3 is a nonstoichiometric compound, whereas that with the composition of n=2.5 is a stoichiometric one, probably formulated as $(PT)_2^+(I_5)^-$. The latter complex exhibits an electrical resistivity of about 800 Ωcm at room temperature. The crystal structure of the complex has not yet been established because of the difficulty of preparing a good single crystal. Recently, however, Uchida et al.6,7) have revealed the crystal structures of several phenothiazine complexes with antimony (V) chloride, in which PT forms a segregated stacking column. Generally the structures of iodine complexes with low electrical resistivities consist of stacking columns of partially oxidized donor molecules and reduced iodine acceptor counterions.8) One might expect the formation of a segregated stacking column of the PT in the present iodine complex because of its low electrical resistivity. However, there is no information on the chemical form and the charge density for the iodine atoms of the complex.

It is important to clarify the chemical form and the electronic structure of iodine in order to understand the electrical properties of the complex. Resonance Raman and ^{129}I Mössbauer spectroscopy are powerful methods for this purpose, and both have been successfully applied to iodine complexes with low electrical resistivities.9–13) In this paper we wish to report on our resonance Raman and ^{129}I Mössbauer studies of the phenothiazine–iodine complex.

Experimental

Materials. Commercially available phenothiazine was recrystallized from benzene. The PT-I_3 complex was precipitated by mixing PT and I_2, separately dissolved in hot benzene, in a prescribed mole ratio. A complex with a composition of n=2.5 was prepared by the use of a large excess of PT. The iodine contents were determined by elemental analysis and iodometry: Found; C, 24.31; H, 1.55%. Calcd for PT-I_3: C, 24.85; H, 1.56%. Found; C, 26.88, H, 1.72%. Calcd for PT-$I_{2.5}$: C, 27.90; H, 1.76%. By iodometry: Found; I, 65.8%. Calcd for PT-I_3: I, 65.64%. Found; I, 63.9%. Calcd for PT-$I_{2.5}$: I, 61.42%. The elemental analysis and iodometry of the sample prepared by the use of an excess of PT indicated that the composition was approximately PT-$I_{2.6}$. The composition of a precipitate appears to depend on the mole ratio of each component and on the concentration used in the preparation. However, when an excess of PT is used for the preparation, a good crystalline precipitate is obtained with the iodine content of n=2.6. The radioactive ^{129}I-labeled complex used for the measurement of the Mössbauer spectrum was prepared from Na^{129}I in an Na_2SO_3 solution. After the iodide had been oxidized with 3 mol dm^{-3} H_2SO_4 and 10% H_2O_2, the resulting molecular iodine was extracted with benzene. The iodine solution was thoroughly washed with water and passed through a Teflon filter to eliminate any slight amount of water. The hot solution was then added to the hot benzene solution with an excess of PT. The precipitate was identical to that obtained with the natural iodine (PT-$I_{2.6}$). The PT-$^{129}I_3$ complex could not be prepared because of the uncertainty as to the iodine content in the benzene solution. The sample thickness for the Mössbauer measurement was about 20 mg ^{129}I cm^{-2}.

Measurements. The laser Raman spectra were measured with Ar$^+$ (514.5 nm) excitation by using a JEOL-JRS-400T triple monochromator. The data were obtained at room temperature with compressed pellets of the powdered complexes (PT-I_3 and PT-$I_{2.6}$) by the front-surface-reflection method, using 60 mW of laser power and a spinning cell. No decomposition was observed with this laser power.

The ^{129}I Mössbauer measurements were carried out in a transmission geometry by cooling the source and the absorber sample (PT-$I_{2.6}$) at 16 K with a closed-cycle helium refrigerator. The Mössbauer source, ^{66}Zn^{129}Te ($t_{1/2}$=70 min), was prepared by the neutron irradiation of 140 mg of a ^{66}Zn^{128}Te compound at a fluence rate of 2×10^{13} neutrons cm^{-2} s^{-1} for 1 h in the Kyoto University Reactor (KUR). The source activity produced by the ^{128}Te(n,γ)^{129}Te reaction was initially about 10 mCi. The constant-acceleration Mössbauer drive was calibrated with a six-line spectrum of an Fe foil.

Results and Discussion

Resonance Raman Spectra. In Fig. 1 are presented the resonance Raman spectra of the (a) PT-I_3 and (b) PT-$I_{2.6}$ complexes excited by the Ar$^+$ 514.5 nm line. Interestingly, the two spectra (107 s, 143 w, 167 m, cm^{-1}) are essentially identical, suggesting that the iodine species exist as an identical chemical form in both complexes. The strong scattering Raman band at 107 cm^{-1} is characteristic of the symmetric stretching vibration of a linear triiodide anion (I_3^-). The isolated and symmetrical I_3^- ions in methanol[14] and $(C_6H_5)_4As^+I_3^-$[9,11] show the strong Raman bands at 112 and 113 cm^{-1} respectively, whereas the corresponding bands are observed at 107—108 cm^{-1} for successive I_3^- chains in (benzamide)$_2$H$^+$$I_3^-$[9] and (*N*,*N*′-diphenyl-*p*-phenylenediamine)$(I_3^-)_{0.8}$[13] complexes. In I_3^- units in polyiodides containing I_3^- and I_2, the transition bands are observed in the 105 to 120 cm^{-1} region, depending upon the interaction of the I_3^- and I_2 units.[9,11] The latter distorted I_3^- units give rise to a second, weak Raman band near 145 cm^{-1}; this band has been assigned to the antisymmetric stretching vibration. Therefore, the strong and weak Raman bands at 107 and 143 cm^{-1} observed for the PT-I_n complexes suggest the presence of a distorted I_3^- unit in these complexes.

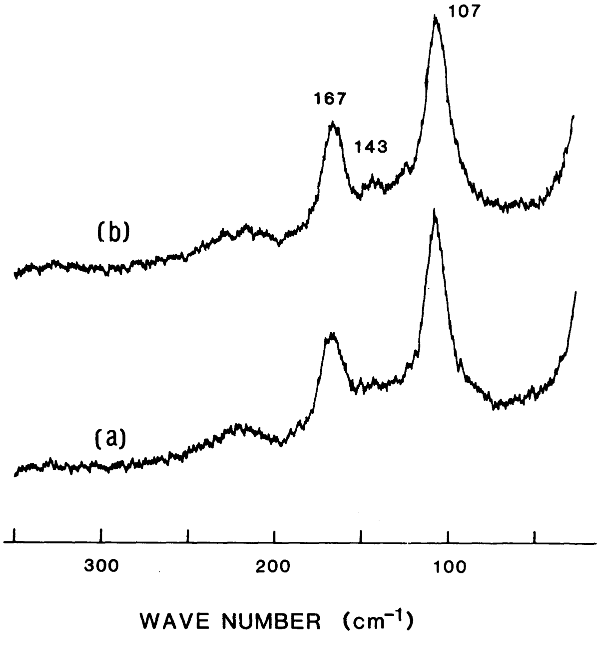

Fig. 1. Resonance Raman spectra excited by the Ar$^+$ 514.5 nm line of (a) PT-I_3 and (b) PT-$I_{2.6}$ complexes.

On the other hand, the Raman band observed at 167 cm^{-1} can be assigned to a linear pentaiodide anion (I_5^-) or to an I_2 unit coordinated to the I_3^- unit. The resonance Raman spectra of (trimesic acid $H_2O)_{10}$-H$^+$$I_5^-$ and starch-iodine complexes, in which the iodine atoms exist as linear I_5^- ions, exhibit a strong scattering at 162—163 cm^{-1} and a weaker band at 104—109 cm^{-1}.[9,15] Raman bands for I_2 units in polyiodides are observed at 172—173 cm^{-1} for Cs_2I_8[11] and (α-CD)$_2$LiI$_5$·8H$_2$O (α-CD, α-cyclodextrin).[15] If the I_2 unit strongly coordinates to the I_3^- unit, close to the I_5^- ion, the I-I stretching band shifts to a lower frequency. The band at 167 cm^{-1} observed for the present complexes is just intermediate between those of the I_5^- ion and the I_2 unit coordinated to the I_3^- unit. It may, therefore, be concluded from the resonance Raman spectra that the iodine atoms in the phenothiazine-iodine complexes exist as a polyiodide consisting of a distorted I_3^- unit and an I_2 unit strongly coordinated to the I_3^- unit.

Site 2 1 3 Site 2′ 1′ 3′ 4 5
I—I···I I—I···I···I—I
1: distorted I_3^- unit **2**: I_2 unit coordinated to the I_3^- unit

Undoubtedly resonance Raman spectroscopy is a powerful method for the identification of the chemical form of the iodine species in the iodine complexes, but there is a limitation with respect to the quantification of the relative amounts of iodine species, because the relative intensities of the Raman bands are strongly dependent on the excitation wavelength. The ^{129}I Mössbauer spectroscopy can provide complementary information on the relative amounts of iodine species and the presence of an isolated I$^-$ ion. Furthermore, the electronic structure of each iodine atom (Sites 1 to 5) can be directly derived from the Mössbauer spectrum.

Mössbauer Spectra. The ^{129}I Mössbauer spectrum of the PT-$I_{2.6}$ complex at 16 K is shown in Fig. 2. The spectrum consists of roughly three different quadrupole octets (A, B, and C), indicating the presence of three distinct iodine sites in the complex. In the analysis of the spectrum, a broadening of the line-width is observed. The line-width of the ^{129}I Mössbauer spectra is usually found with our apparatus to be about 1.0 mm s^{-1}.[13] In particular, the quadrupole octets B and C show considerable line-broadening, enhanced in the higher Doppler-velocity region. This broadening is attributable to an overlap of the spectra originating from iodine atoms with slightly different charge densities. The spectrum clearly rules out the presence of the isolated I^- ion and the molecular iodine (I_2). The former ion, inactive and undetectable by Raman spectroscopy, would show a single absorption peak at -0.5 mm s^{-1} in the spectrum. The latter molecular iodine, which has not been observed in the Raman spectra, would indicate a slightly smaller quadrupole splitting ($e^2Qq=-2255\pm$ 30 MHz, $\delta=0.94$X0.05 mm s^{-1})[16] than that of the quadrupole octet A. The obtained Mössbauer parameters, such as the quadrupole coupling constant (e^2Qq), the asymmetry parameter (η), the isomer shift (δ), the line-width (2Γ), and the relative area, are summarized in Table 1.

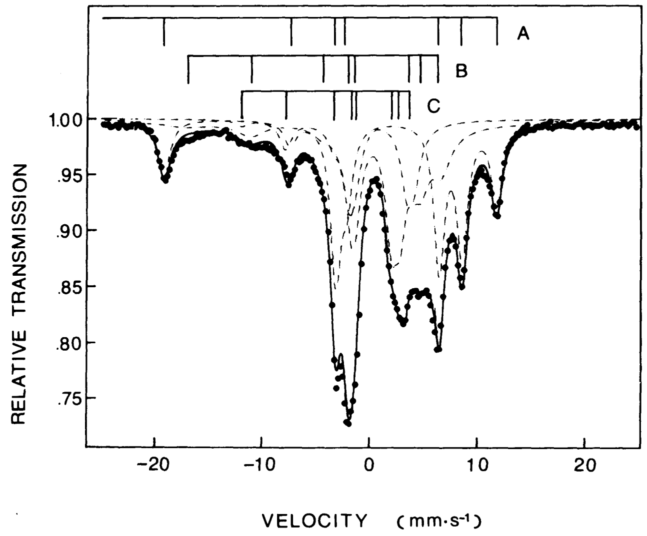

Fig. 2. ^{129}I Mössbauer spectrum at 16 K of the PT–$I_{2.6}$ complex.

The e^2Qq and δ values of the quadrupole octet A, larger than those for the free iodine molecule in inert matrices, indicate that the iodine atom (I_A) corresponding to the octet A has a slightly positive charge density. Such iodine atoms are observed in the central iodine of linear I_3^- ions[12,13] and the intermediate iodines of linear I_5^- ions.[9,15] In addition, when an I_2 unit is strongly coordinated to an I_3^- unit, as is to be expected from the Raman spectra, the iodine atom coordinated to the I_3^- unit has a positive charge density.[11,17] Therefore, it is reasonable to assign the iodine atom I_A to those of Sites 1, 1′, and 4 in the **1** and **2** iodine species. This is the reason for the broadening of the line-width in the sub-spectrum A. Because of the poor resolution of the Mössbauer spectrum of ^{129}I, any distinction among them may be difficult.

The e^2Qq values of the two terminal iodines of the distorted I_3^- ion in CsI_3 are, from the ^{127}I NQR[18] and ^{129}I Mössbauer measurements,[19] found to be about -1440 MHz and -820 MHz. These e^2Qq values are close to those for the quadrupole octets B and C. That is, the iodine atoms, I_B and I_C, corresponding to the B and C octets can be assigned to the iodines of Sites 2 and 3 respectively in the distorted I_3^- species **1**. Since the charge density localized on each iodine of the I_3^- unit is expected to be perturbed by the coordination of the I_2 unit, the e^2Qq and δ values for the iodines of Sites 2′ and 3′ in the **2** species are slightly different from those of Sites 2 and 3 in the **1** species. This difference causes the line-broadening of the quadrupole octets, B and C. The charge density on the iodine of Site 5 may be close to that of Site 2′, because the I_2 unit is strongly coordinated to the I_3^- unit. The spectrum of the iodine Site 5 is included in the broad sub-spectrum B.

The terminal iodine atoms of Sites 2 and 3 in **1** probably interact with the terminal iodines of the other iodine species, **2**. If the interaction is perpendicular to the molecular axis, a large η value must be observed for the iodine atom. The quite large η value observed for the quadrupole octet B suggests that the iodine atoms are, on the average, present in the complex as a polyiodide with the following structure (Fig. 3):

Table 1. Mössbauer Parameters for the Phenothiazine-Iodine (PT–$I_{2.6}$) Complex

		e^2Qq a) / MHz	η / %	δ b) / mm s^{-1}	2Γ / mm s^{-1}	Area c) Ratio	U_p d)	h_p e)
PT–$I_{2.6}$	I_A	-2381 ± 25	0	1.34 ± 0.05	1.20 ± 0.10	1.4	1.04	1.25
	I_B	-1414 ± 25	29 ± 10	0.66 ± 0.05	$1.30+\alpha$ f)	1.0	0.62	0.80
	I_C	-918 ± 25	0	0.08 ± 0.05	$1.36+\beta$ f)	1.0	0.40	0.41

a) The e^2Qq values are converted to the ^{127}I nucleus. b) The δ values are relative to the ZnTe source. c) The ratios are normalized with respect to the I_C atom. d) $U_p=-e^2Qq_{\mathrm{obsd}}/e^2Qq_{\mathrm{atom}}$, $e^2Qq_{\mathrm{atom}}=2292.7$ MHz. e) $\delta=1.5\,h_p-0.54$ (mm s^{-1}). f) The values are of the line-widths at zero Doppler velocity. The errors quoted in this work include estimated systematic errors.

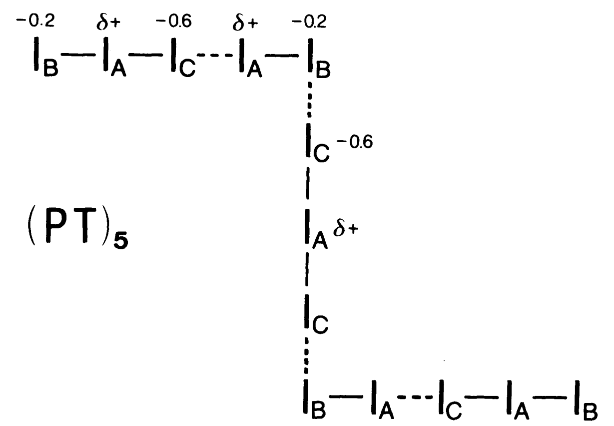

Fig. 3. The speculated structure of the iodine atoms in the PT–$I_{2.6}$ complex.

In Fig. 3 the intermolecular bond (···) between the I_C and I_A atoms implies the strong interaction previously described, whereas the bond (····) between the I_B and I_C atoms indicates a weak intermolecular interaction. The proposed structure with relative populations of 1.25:1.0:1.0 for I_A:I_B:I_C of the iodine species satisfies the relative absorption areas (1.4:1.0:1.0) of the sub-spectra corresponding to I_A, I_B, and I_C. The slight increase in the area of I_A can be explained in terms of the difference in the recoilless fraction. That is, the recoilless fraction of I_A can be expected to be larger than those of I_B and I_C, for the I_A atom is strongly bound to two neighboring atoms. This effect is also found in the other I_3^- ions, where the central atom indicates a stronger absorption intensity than each terminal atom.[12,13]

The charge density localized on each iodine atom is calculated from the values of e^2Qq, η, and δ as follows:[13]

$$U_p = -e^2Qq_{\text{obsd}}/e^2Qq_{\text{atom}} = -N_z + (N_x+N_y)/2,$$

$$\eta = 3(N_x-N_y)/2U_p,$$

$$\delta = 1.5\,h_p - 0.54 \quad (\text{mm s}^{-1}, \text{ for the ZnTe source}),$$

$$h_p = 6 - (N_x+N_y+N_z),$$

where U_p is the number of unbalanced p-electrons; e^2Qq_{atom}, the atomic iodine quadrupole coupling constant, is equal to 2292.7 MHz for ^{127}I, and h_p is the number of 5p-electrons removed from the $5s^25p^6$ (I^-) configuration. N_x, N_y, and N_z are the populations of 5p-electrons in the x, y, and z directions respectively. When the bonding of iodine is formed by only $5p_\sigma$-electrons, one expects the relationship $U_p=h_p=1\pm i$ to be valid, where i is the ionic character. The U_p and h_p values obtained for each iodine atom are presented in Table 1.

It can be seen that the h_p value is larger than the U_p value for the I_A atom. This phenomenon, also found in the central iodine of linear I_3^- ions,[12,13] can be explained in terms of the contribution of $4d_\sigma$-electrons to the bond formation, in addition to the delocalized three-center four-electron bonding of 5p-electrons.[13] Consequently, the I_A atom has, on the average, a slight positive charge (δ+), less than the +0.04 e$^-$ obtained from the U_p value. The disagreement of h_p and U_p values for the I_B atom is attributable to the intermolecular interaction in the x or y direction. This result is supported by the large η value of the atom. The charge density localized on the I_B atom is, on the average, estimated from the h_p value to be −0.2 e$^-$. For the I_C atom, the h_p value is close to the U_p value, suggesting that the bonding of the atom is mainly caused only by $5p_\sigma$-electrons. The charge density on the I_C atom is roughly estimated to be −0.6 e$^-$ from the h_p and U_p values. The charge densities obtained from the Mössbauer parameters are indicated on the respective iodine atoms in Fig. 3. It should be noted that the charge densities are the averaged values because of the broadening of the line-widths in all sub-spectra.

It is concluded from the results of the resonance Raman and ^{129}I Mössbauer spectra that the present complex with a composition of n=2.6 can be approximately formulated as $(PT)_5^{3+}[(I_3)_3(I_2)_2]^{3-}$. That is, about three electrons per five PT molecules are transferred to a polyiodide, consisting of a distorted I_3^- unit and an I_2 unit strongly coordinated to the I_3^- unit. This complex is apparently not a stoichiometric compound formulated as $(PT)_2^+(I_5)^-$. From the similarity of the resonance Raman spectra, it might be reasonable to speculate that the PT–I_3 complex can be formulated as $(PT)_5^{3+}[(I_3)_3(I_2)_3]^{3-}$ in a manner similar to that used for PT–$I_{2.6}$. The difference in the electrical resistivities of the two complexes is probably the result of a structural factor, such as the stacking of the PT molecules and/or the packing of the polyiodides. These complexes are recognized as partially oxidized mixed-valence compounds. The formation of these complexes is quite similar to that of the perylene–$I_{2.92}$ complex, exhibiting a low electrical resistivity of about 10 Ωcm at 300 K.[11]

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