Electrical Properties and Constitution of the Phenothiazine–Iodine and Related Complexes[1)]

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The electrical properties of the phenothiazine–iodine complex were examined in detail as a function of the composition. A shoulder in the resistivity-composition isotherm, a decrease in the activation energy for semiconduction by a factor of two, and a change in the sign of the Seebeck coefficient from negative to positive were observed at a composition of two molecules of phenothiazine to five atoms of iodine. These observations and the spectral behavior reported earlier indicate the formation of a complex cation radical salt, (phenothiazine)$_2^+$I$_5^-$, which exhibits a resistivity of about 800 ohm cm at room temperature. By the incorporation of a half mole of iodine into this salt, the resistivity reaches a minimum of about 20 ohm cm at room temperature. Similar singularities in the resistivity-composition isotherms were observed with the complexes of the benzo[*a*]-, benzo[*c*]-, and *N*-methyl-derivatives.

Since Akamatu, Inokuchi, and Matsunaga reported anomalously low electrical resistivities exhibited by some polycyclic aromatic hydrocarbon–halogen complexes,[2,3)] a large number of halogen complexes, mostly iodine complexes, have been studied by various workers. For example, the organic component compounds so far examined include such hydrocarbons as pyrene,[4)] perylene,[2,4,5)] and violanthrene,[3,6)] such diamines as *p*-phenylenediamine,[7)] benzidine,[8)] and their derivatives,[9,10)] carotene,[11)] pyridazine,[12)] phenothiazine,[13–16)] its *N*-methyl derivative,[13,17–19)] and phenoselenazine.[16)] However, only relatively few works have been published on the nature of low-resistivity halogen complexes.

The vibrational spectrum of the phenothiazine–iodine complex of a mole ratio of 2: 3 has been shown to be clearly different from that of the parent organic compound, but nearly identical with that of the cation radical bromide.[13)] Later, we found two patterns rather similar to each other for the latter,[20)] and demonstrated that one of them can be ascribed to the simple cation radical bromide, and the other, to the complex cation radical bromide of the 2: 1 type.[21)] The spectrum identical to that of the iodine complex is the latter. Thus, this iodine complex appears to be a kind of the complex cation radical salt; however, six atoms of iodine per two molecules of phenothiazine do not fit to the composition of any polyiodide. Labes *et al.* have found that the vibrational spectrum of the perylene–bromine complex with a mole ratio of 2: 7 is quite different from that of either the parent hydrocarbon or the reaction product, 3,9-dibromoperylene, indicating a significant decrease in symmetry.[22)] They have suggested the formation of a σ-type complex.

Undoubtedly, the analysis of the crystal and molecular structure is a powerful tool in solving the problem. However, the task becomes more and more difficult with an increase in the heavy halogen content. There are only a few works on low-resistivity complexes with relatively low iodine contents. Both of the following compounds have been reported to contain cation radicals: [4,4′-bis(dimethylamino)diphenylamine] I and [*N*,*N*′-diphenyl-*p*-phenylenediamine]$_5$I$_{12}$. The former salt, with a resistivity of the order of 10^5 ohm cm, is a simple iodide.[23)] The halogen atoms in the latter are arranged in columns in the form of triiodide ions.[24)] As the number of the diamine molecules exceeds that of the triiodide ions, the salt contains both the cations and formally neutral molecules. This complex cation radical salt is known to exhibit a resistivity of about 3 ohm cm.[10)] More recently, the structure of highly conducting tetrathiafulvalene (TTF) halides with a deviation from the 1: 1 composition has been clarified.[25–27)] The halogen atoms are in the form of simple halide ions, and the stack of organic molecules consists of neutral and fully charged molecules or fractionally charged molecules. All the available results agree on the points that the low-resistivity halogen complexes are actually cation radical salts and that the resistivities are particularly low when the compositions are complex.

Until now, resistivity-composition isotherms have been prepared for the following systems: violanthrene–iodine,[3)] phenothiazine–iodine,[14)] and phenothiazine bromide–iodine.[20)] In these works, the resistivity minimum has been assumed to correspond to the composition of a distinct compound. This simple assumption is, however, good only for the systems in which two coexisting phases are stoichiometric and mechanically mixed without interaction. If the incorporation of a marked stoichiometric imbalance is conceivable, the electrical behavior should depend quite differently upon the composition. As conduction electrons or holes are introduced by incorporating an excess of one of the components to a pure, accurately stoichiometric compound, the composition must be indicated by a maximum or a shoulder in the resistivity-composition isotherm. On the other hand, the minimum, if any, may be indicative of the limit of the deviation from stoichiometry. Furthermore, we may expect a change in the sign of the Seebeck coefficient at the composition of this stoichiometric compound. No such singularity has been noted in the published isotherms; however, the Seebeck coefficient in the phenothiazine–iodine complex has been reported to change its sign somewhere between two and six iodine atoms per thiazine molecule.[15)] Thus, the careful examination of

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the electrical properties as functions of the composition seemed to be a tool more powerful than has been supposed for elucidating the constitution of semiconducting organic compound–iodine complexes. Accordingly, we decided to initiate the present series of works with the four thiazine–iodine complexes.

Experimental

Materials. Samples were prepared by the following three methods, and the iodine contents were determined by microanalysis.

a) Thiazine–iodine complexes with a mole ratio of 2 : 3 were precipitated by mixing the organic component and iodine separately dissolved in hot benzene or ether.[13,16,17] The preparation of samples of other mole ratios was carried out by the careful grinding of the weighed complex and the thiazine or iodine in the presence of a small amount of the solvent.

b) An equimolar mixture of the thiazine and its *S*-oxide was thoroughly ground in an agate mortar. The fine powder was spread in a beaker and moistened with concentrated hydroiodic acid. The reaction mixture was then dried in a vacuum desiccator containing potassium hydroxide pellets.[28] The "iodide" thus prepared was mixed with the thiazine or iodine in order to adjust the composition.

c) The weighed thiazine and iodine were directly ground in an agate mortar in the presence of a small amount of benzene or ether.

Measurements. The electrical resistivities and Seebeck coefficients of compactions were recorded as functions of the temperature by the procedures described in the paper by Kan and Matsunaga.[17]

Results and Discussion

Phenothiazine–Iodine In Fig. 1, the electrical resistivity values at 20 °C are plotted against the number of iodine atoms per phenothiazine molecule, *n*. The samples made by Method a are indicated by shaded circles, while those made by Method b are indicated by open circles. The "iodide" gave the following analytical results: C, 38.61; H, 2.77; I, 46.09%. Calcd for $C_{12}H_9NSI_{1.35}$: C, 38.81; H, 2.43; I, 46.33%. A shoulder appears at $n=2.5$ in the resistivity-composition isotherm, the value at this composition being about 800 ohm cm. Then the resistivity reaches a minimum of about 20 ohm cm at $n=3$. The latter is the composition of the iodine complex deposited from the solution. The temperature dependence of the resistivity, ρ, follows the typical semiconductor behavior: $\rho=\rho_0\exp(E/kT)$. As is shown in Fig. 2, the activation energy for semiconduction, *E*, is about 0.3 eV up to $n=2.5$; it then suddenly decreases to about 0.15 eV. For the above-mentioned reason, one may postulate that a distinct compound is formed at a composition of $n=2.5$. In conjunction with our earlier observation that the vibrational spectrum of the complex agrees well with that of the complex cation radical bromide of the 2 : 1 type,[21] the compound may be identified as $(C_{12}H_9NS)_2{}^+I_5{}^-$. The two thiazine molecules are equivalent in the time scale of infrared spectroscopy. A deviation of as much as a half mole of iodine is allowed in this formula. This iodine plays a crucial role in the significant decrease in the activation energy. Thus, the very sharp decrease in the electrical resistivity arises undoubtedly from a drastic increase in the charge-carrier concentration. Above $n=3$, the resistivity increases as the iodine content becomes higher. As the vibrational spectrum of phenothiazine mixed with a large amount of iodine resembles that of the simple cation radical bromide, the increase may be attributed to the coexistence of a high-resistivity simple salt rather than free iodine. The rapid increase in the activation energy in this composition range appears to be consistent with the observed high resistivity. Although a resistivity minimum is located at $n=3$ in the isotherm reported by Gutmann and Keyzer, their value, 350 ohm cm, is considerably higher than ours.[14] Moreover, the change observed by them in the composition range from $n=1$ to 4 is merely about one order of magnitude.

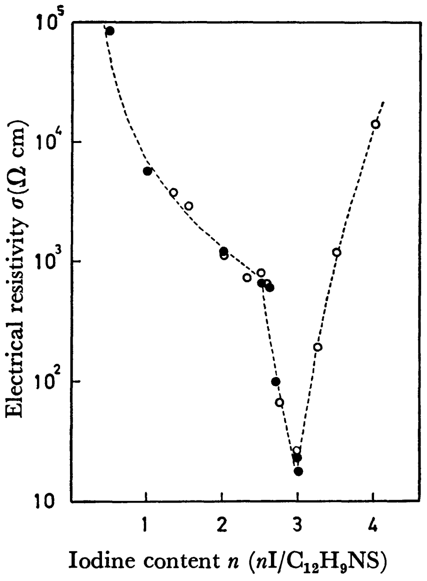

Fig. 1. Electrical resistivity at 20 °C plotted against the iodine content (*n* iodine atoms/thiazine molecule) in the phenothiazine–iodine system.

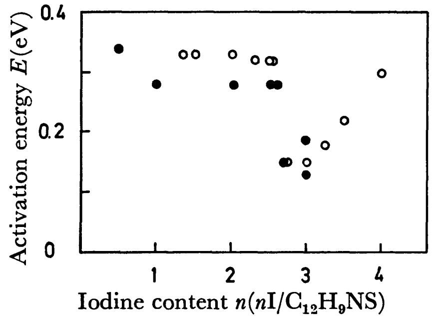

Fig. 2. Activation energy for semiconduction plotted against the iodine content in the phenothiazine–iodine system.

In Fig. 3, the variation in the Seebeck coefficient with the temperature for some representative samples made by Method b is presented. The coefficient depends remarkably upon the composition. Up to $n=2.5$, a linear relationship with the reciprocal temperature is observed near room temperature. Such a range is wider when the composition becomes closer to $n=2.5$. This behavior implies that the compound expressed by the

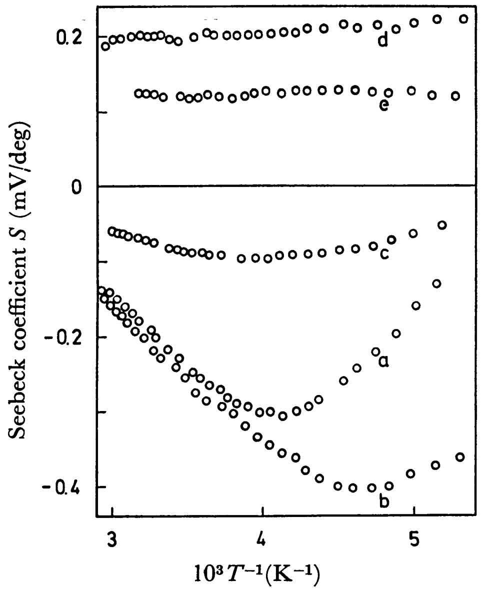

Fig. 3. Seebeck coefficient of the phenothiazine–iodine complexes; a) $n=1.35$, b) 2.50, c) 2.55, d) 2.75, and e) 4.00.

$(C_{12}H_9NS)_2{}^+I_5{}^-$ formula exists in these samples. In other words, the solubility of phenothiazine into the compound is rather small and the samples examined in this composition range are not homogeneous. The shape of the resistivity-composition isotherm does seem to be in accord with this view. The linear part appears to fit in with the expression for the thermoelectric motive force of an intrinsic semiconductor; therefore, we attempted to estimate the ratio of the electron mobility, μ_e, to the hole mobility, μ_h, tentatively assuming the applicability of the band model to the present compound. It is given by:

$$b = \mu_e/\mu_h = \left[\frac{E_G}{2} - \frac{\Delta S}{\Delta(10^3/T)}\right]\left[\frac{E_G}{2} + \frac{\Delta S}{\Delta(10^3/T)}\right]^{-1},$$

provided that S is measured in mV/deg.[29] E_G is the width of the forbidden band and is assumed to be twice the observed activation energy for semiconduction. With samples of $n=2.00$, 2.30, and 2.50, the above ratio is found within 4 and 6. Then, the conductivity, σ, is given by:

$$\sigma = \frac{1}{\rho} = e\mu_e\left(\frac{b+1}{b}\right)N\exp\left(-E/kT\right),$$

where N is taken to be equal to the number of phenothiazine molecules per cm^3 of the compaction; that is, $(2.6—2.9)\times10^{21}$. Employing the resistivity and the activation energy presented in Figs. 1 and 2, the electron mobility is estimated to be 0.6—0.9 cm^2/Vs. This value is a little smaller than those estimated similarly for the *N*-methylphenothiazine complex, 2.3 cm^2/Vs,[17] and for the phenoselenazine complex, 2.6 cm^2/Vs.[16,30]

Above $n=2.5$, the Seebeck coefficient becomes less negative (see Curve c), and finally it changes its sign (see Curve d). A maximum value of about 0.2 mV/deg is observed near $n=3$. In Fig. 4, the coefficient at 20 °C is plotted against the iodine content. This physical quantity is apparently more sensitive to the preparation methods than the electrical resistivity. The values observed with samples made by Method a are appreciably more negative than those made by Method b in the composition range from $n=2$ to 2.5. Regardless of such disagreement, though, the formation of the $(C_{12}H_9NS)_2{}^+I_5{}^-$ compound is strongly supported by the sudden change in the sign near this composition. The behavior above $n=2.5$ suggests that the electrical conduction is extrinsic and that the major charge carriers are holes.

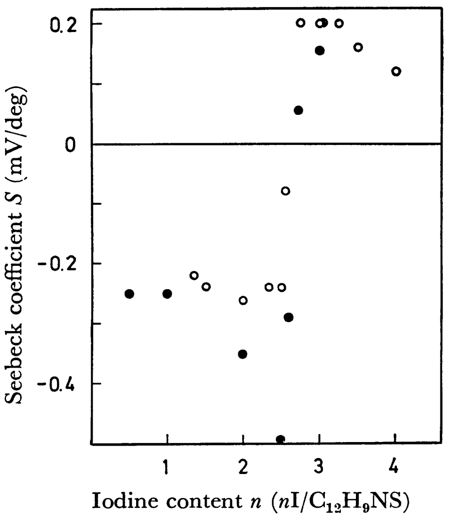

Fig. 4. Seebeck coefficient at 20°C plotted against the iodine content in the phenothiazine–iodine system.

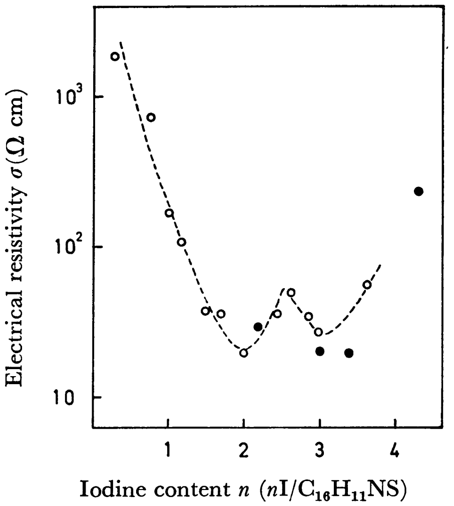

Fig. 5. Electrical resistivity at 20°C plotted against the iodine content in the benzo[*a*]phenothiazine–iodine system.

Benzo[a]*phenothiazine–Iodine.* The complex deposited from a benzene solution has a mole ratio of 2: 3 and exhibits a resistivity of about 20 ohm cm at room temperature.[13,16] For the present work, the samples were prepared by Methods a and c. The resistivity-composition isotherm at 20 °C is presented in Fig. 5. The shaded circles denote samples prepared from the 2: 3 complex, and the open circles those prepared by mixing the components. The maximum of about 50 ohm cm clearly observed near $n=2.5$ and the minima near $n=2$ and 3 make the formation of a complex cation radical salt, $(C_{16}H_{11}NS)_2{}^+I_5{}^-$, very plausible. The

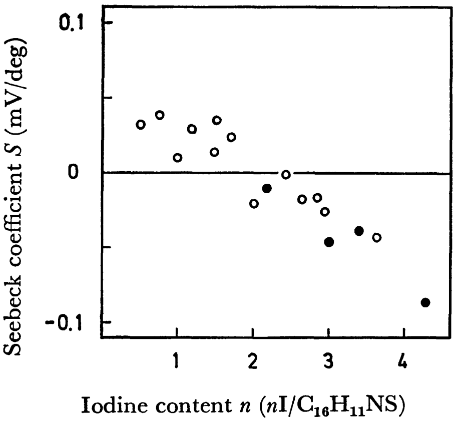

Fig. 6. Seebeck coefficient at 20 °C plotted against the iodine content in the benzo[*a*]phenothiazine–iodine system.

presence of two resistivity minima suggests that the solubilities of both iodine and the thiazine into this salt are appreciable. In other words, the salt is highly nonstoichiometric. It must be noted that the resistivity of this salt is lowered by only a factor of two by the deviation. The values of the activation energy for semiconduction near room temperature are mostly in the range from 0.11 to 0.15 eV. Higher values, 0.18—0.20 eV, were obtained at $n=0.27$, 3.63, and 4.29. Contrary to the phenothiazine–iodine system, no abrupt change could be detected at the composition of the resistivity maximum. The Seebeck coefficient of this system depends only slightly upon the temperature and seems to be dominated by some impurities. The values are rather small and scattered (see Fig. 6). Nevertheless, they are consistently positive at low iodine contents and negative at high iodine contents. The composition at which $S=0$ appears to be $n \simeq 2.2$. Although the values at higher temperatures are more positive or less negative in all the samples, the shift of this composition by the temperature is inconsiderable. The impurities mentioned above may be the components present in excess; however, the change in the sign here is in the direction opposite to that found with unsubstituted phenothiazine. We earlier noted the similarity in the vibrational patterns of the 2: 3 iodine complex and the cation radical bromide.16) Now this observation suggests the difficulty in drawing a distinction on the basis of the vibrational spectrum between the simple benzophenothiazine cation radical salt and the complex one. Furthermore, the electronic spectrum of the "iodide" was found to be quite different from those of the other simple cation radical salts, but to resemble that of the low-resistivity iodine complex.28) In view of the present work, the "iodide" prepared earlier is probably a kind of complex cation radical salt. Even in the case of the bromide, the simple salt was found to convert easily into the complex salt at room temperature.21) As iodine is less electronegative than bromine, the simple thiazine cation radical "monoiodide" may be unstable or may not exist at all.

Benzo[c]*phenothiazine–Iodine.* A shoulder with a resistivity of about 20 ohm cm is observed at $n=2.5$ and a minimum is located near $n=2$ in the isotherm presented in Fig. 7. Here, the samples prepared by Method a are indicated by shaded circles. The rest were prepared starting from the "iodide" which had the following composition: C, 46.36; H, 2.74; N, 3.07; I 38.63%. Calcd for $C_{16}H_{11}NSI_{1.27}$: C, 46.82; H, 2.68; N, 3.41; I, 39.27%. No singularity is seen at $n=3$, which is the composition of the complex deposited from a benzene solution.13,16) Thus, the effect of excess thiazine is much larger than that of excess iodine on the electrical resistivity in this system. The activation energy for semiconduction increases gradually up to $n=2.5$ and sharply above this composition. The values at $n=0.5$, 2.5, and 4.0 are 0.09, 0.12, and 0.21 eV respectively. The thermoelectric behavior is similar to that of the isomeric thiazine–iodine system. As is illustrated in Fig. 8, the Seebeck coefficient at room temperature decreases nearly linearly with n and changes its sign near $n=2.3$. Even though the evidence is not so complete as in the case of the phenothiazine complex, one may conclude that the stoichiometric compound formed in this system has a composition of $(C_{16}H_{11}NS)_2{}^+I_5{}^-$.

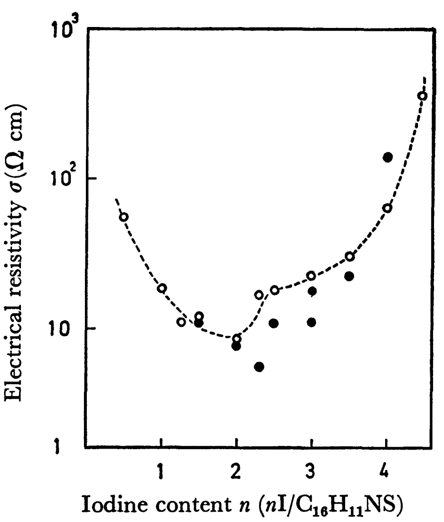

Fig. 7. Electrical resistivity at 20 °C plotted against the iodine content in the benzo[*c*]phenothiazine–iodine system.

N-*Methylphenothiazine–Iodine.* The complex deposited from ether has a mole ratio of 2: 3 and is

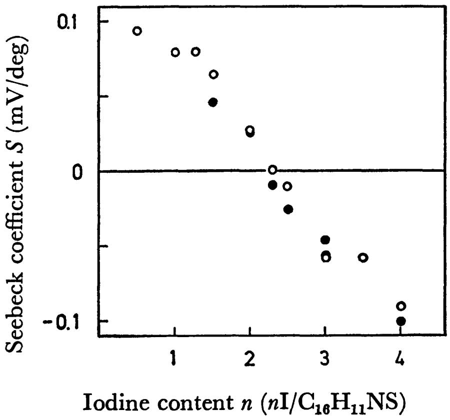

Fig. 8. Seebeck coefficient at 20 °C plotted against the iodine content in the benzo[*c*]phenothiazine–iodine system.

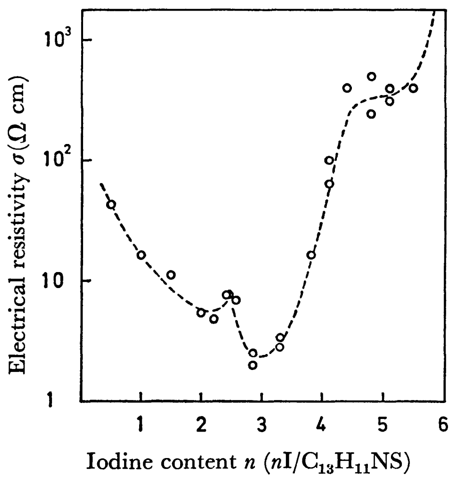

Fig. 9. Electrical resistivity at 20 °C plotted against the iodine content in the *N*-methylphenothiazine–iodine system.

more conductive by an order of magnitude than the unsubstituted phenothiazine complex.[13,17] The single crystal is known to be highly anisotropic. The principal conductivities at 23 °C, as measured by Dix, are as follows: 95, 0.96, and 0.022 ohm^{-1} cm^{-1}.[19] In addition to this complex, Dix has isolated two more, the 2: 5 and 2: 7 complexes. The resistivity-composition isotherm reported in Fig. 9 was derived from measurements of samples prepared by Method c. Clearly, the isotherm possesses a maximum of about 8 ohm cm at n=2.5, minima near n=2 and 3, and a shoulder around n=4.5. By analogy to the phenothiazine–iodine system, one may suggest the formation of the complex cation radical salt, $(C_{13}H_{11}NS)_2{}^+I_5{}^-$. The 2: 3 complex corresponds to a minimum at n=3. The low resistivity is, to some extent, due to the incorporation of a half mole of iodine into the above-mentioned salt. Because of the instability, the temperature-dependence is rather complicated and no obvious manifestation of the formation of the salt is apparent in the activation energy. The Seebeck coefficient of the 2: 3 complex depends markedly upon the temperature, as has been reported by Sano *et al.* and also by Kan and Matsunaga.[17,31] It is surprising to see that this feature is hardly modified by the composition change over the entire range examined here. The vibrational spectra of the samples with n>4.5 consist of sharp bands and are very different from both that of the parent compound and that of the 2: 3 complex. Therefore, the formation of a simple cation radical salt, $(C_{13}H_{11}NS)^+I_5{}^-$, seems to be likely. This composition agrees with the 2: 5 complex reported by Dix.

In conclusion, all the 2: 3 thiazine–iodine complexes studied may be expressed by $(\text{thiazine})_2{}^+I_5{}^- + 1/2I_2$. Their low electrical resistivities are more or less attributable to the charge carriers generated by the incorporation of extra iodine into the complex cation radical pentaiodide. Some years ago, Wakayama determined the lattice constants of the *N*-methylphenothiazine complex.[32] This complex is orthorhombic with a=11.4, b=21.4, and c=21.1 Å. The unit cell is so large that six formally neutral thiazine molecules, six positively charged thiazine radicals, six pentaiodide anions, and three iodine molecules are accommodated. The exact form of the last constituent remains to be clarified, however. It may exist as the molecule, the triiodide ion, or a part of polyiodide ion(s). No matter which is the exact form, all the species derived from iodine are diamagnetic.

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