BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 2539—2543 (1967)

Magnetic Susceptibilities of Crystalline Phenothiazine, *N*-Methylphenothiazine and Thianthrene Radical Salts with Antimony Pentachloride

Yoichiro SATO, Minoru KINOSHITA, Mizuka SANO and Hideo AKAMATU

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo

(Received May 23, 1967)

Phenothiazine, *N*-methylphenothiazine and thianthrene are oxidized with antimony pentachloride, and give the corresponding monopositive ion radicals. These aromatic positive ions form crystalline salts with the complex negative ion of antimony pentachloride or tetrachloride. The paramagnetism for these salts is attributed to the aromatic ion radicals, and follows the Curie-Weiss law at higher temperatures, and deviates from it at lower temperatures. This behavior has been interpreted by assuming the linear chain model being applicable, which suggests a remarkable spin exchange interaction in the crystalline salt of phenothiazine·$SbCl_4$, of J/k ~395°K.

Recent investigations have indicated that π-electron compounds can give ion radicals which in some cases are stabilized in the formation of crystalline salts. There are evidences to believe in these crystalline salts a remarkable interaction between molecules, which will be reflected onto the paramagnetic behaviors of these salts. The salts of anion radical of tetracyanoquinodimethane (TCNQ) give the typical examples.[1-3] We have reported previously the formation of solid complexes of antimony pentachloride which involved cation radicals of aromatic compounds.[4,5]

Phenothiazine and thianthrene form stable paramagnetic crystalline complexes when they are combined with antimony pentachloride. ESR spectra of these complexes have revealed that the origin of the paramagnetism is due to the aromatic cation radicals which are produced through oxidation with antimony pentachloride, a strong Lewis acid, and crystalline cation radical salts are formed. For further studies on the paramagnetic behavior of these crystalline salts, the magnetic susceptibilities have been observed the static method. The accurate values of paramagnetic susceptibility and its variation with temperature will provide useful information about the interaction between molecules in these crystalline radical salts.

Experimental

Apparatus. A susceptibility microbalance of the Faraday type was constructed, as shown schematically in Fig. 1. The balance has a sensitivity of 0.01 dyne. The basic design is same as that of an analytical balance by Mauer,[6] only with some modifications which facilitate the measurement of susceptibility at lower temperatures. The main modifications are: (1) the whole balance was set in a stainless-steel bell jar which could be evacuated. (2) A solenoid was suspended from a balance beam and positioned in the field of about 2 kgauss of a pot type magnet so that the influence of stray field would be negligible. (3) A pre-amplifier was used to magnify the susceptibility signal. (4) An X-Y recorder was used to record continuously the change in susceptibility as a function of temperature.

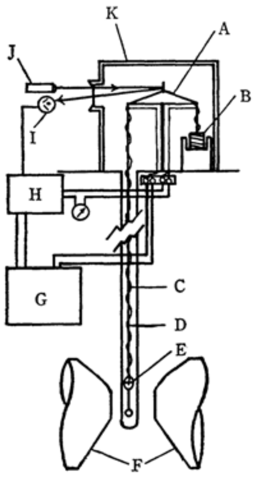

Fig. 1. The susceptibility balance of the Faraday type.

A	Balance	B	Solenoid
C	Thermocouple	D	Quartz rod
E	Quartz bucket	F	Pole pieces
G	X-Y recorder	H	Amplifier
I	Phototube	J	Light source
K	Bell jar		

---

[1] D. B. Chesnut and W. D. Phillips, *J. Chem. Phys.*, **35**, 1002 (1961).

[2] R. G. Kepler, *ibid.*, **39**, 3528 (1963).

[3] M. Kinoshita and H. Akamatu, *Nature*, **207**, 291 (1965).

[4] M. Kinoshita and H. Akamatu, This Bulletin, **35**, 1040 (1962).

[5] M. Kinoshita, *ibid.*, **35**, 1137 (1962).

[6] F. A. Mauer, *Rev. Sci. Instr.*, **25**, 598 (1954).

A quartz sample bucket was suspended from the balance with a quartz rod. The position of a sample was adjusted for the maximum magnetic force on the sample. All measurements were made at a current of 90 A, which generated $H \cdot dH/dx$ of 1.57×10^7 gauss^2/cm. The leads of a thermocouple ran along the quartz rod and the balance beam, and were taken out from the bell jar through a hermetic seal.

Preparation. Phenothiazine (PT) and thianthrene (TA) were purified from reagent-grade starting materials by repeated solvent recrystallizations and by sublimation *in vacuo*. *N*-Methylphenothiazine (MPT) was prepared by the methylation of phenothiazine with methyliodide and purified by recrystallization and sublimation.

PT·$SbCl_4$ (I): To a solution of 0.2 g of phenothiazine in chloroform was added 10 m*l* of a chloroform solution of antimony pentachloride (containing 0.28 g $SbCl_5$). The solution was stirred for several minutes after completion of antimony pentachloride addition, and then a brown powder precipitated. After filtration, the powder was quickly washed with a small amount of chloroform and dried *in vacuo*. The composition of the product was determined by an elementary analysis to be $C_{12}H_9NS \cdot SbCl_4$.

PT·$SbCl_5$ (II): The brown product of $C_{12}H_9NS \cdot SbCl_5$ was formed, when an excess amount (2.5 to 4 equiv.) of antimony pentachloride was added to a solution of phenothiazine.

MPT·$SbCl_5$ (III): The reddish brown product of $C_{13}H_{11}NS \cdot SbCl_5$ was obtained by addition of a chloroform solution of antimony pentachloride (1 to 4 equivs.) to a chloroform solution of *N*-methylphenothiazine.

TA·$SbCl_5$ (IV): The brownish purple needles of $C_{12}H_8S_2 \cdot SbCl_5$ were obtained by the similar method with thianthrene in place of *N*-methylphenothiazine.

These products, III and IV, had a component of $SbCl_5$ rather than $SbCl_4$, independently of an added amount of antimony pentachloride. The infrared absorption spectrum confirmed the existence of an NH group in the products, I and II, indicating that the hydrogen atom bound to the nitrogen atom in phenothiazine was neither lost nor replaced in the process of oxidation with antimony pentachloride, for both cases.

Measurements. The balance was calibrated referring to distilled, oxygen-free water, the susceptibility of which was taken to be -0.720×10^{-6} emu/g at room temperature. Several measurements at room temperature on zone-refined anthracene and naphthalene powders gave the susceptibilities of $(-0.742 \pm 0.003) \times 10^{-6}$ and $(-0.728 \pm 0.003) \times 10^{-6}$ emu/g, respectively. The paramagnetic susceptibility of crystalline diphenylpicrylhydrazyl (DPPH), which was recrystallized out of carbon disulfide, obeyed the Curie-Weiss law with the Weiss constnat of -20 ± 4°K. The value is in agreement with that of Duffy.[7)]

A sample of 100 mg or more was used for each measurement, and a little less for that at lower temperatures. A powder sample was sealed in a thin-wall spherical pyrex-glass container so that the sample was not exposed to high vacuum during the evacuation of the apparatus. The container was filled with helium gas so that the contribution of paramagnetic oxygen to the measured value would be negligible, and the decomposition of the sample by the evaporation of antimony pentachloride would be prevented.

Susceptibilities were measured in the temperature range from 48 to 300°K. A sample was suspended from the balance inside a long glass tube which was placed in a glass dewar. The glass tube was filled with 10 to 20 mmHg helium as a heat-transfer gas. Liquid nitrogen was introduced into the dewar so carefully that the cooling rate of the sample was sufficiently slow. The temperature of the sample was controlled by the amount of liquid nitrogen added in the dewar. The temperatures between 48 and 77°K were obtained with solid nitrogen which was formed around the sample by pumping of the liquid nitrogen-filled dewar. In this temperature range, however, the susceptibility readings were made only with the increase in temperature. The temperature rise was slow, about 1°K per three minutes. Temperatures were read with a platinum *vs.* gold-cobalt thermocouple, whose junction part was attached to the sample container.

ESR measurements were carried out at 9400 Mc/s with a Hitachi MPS-1 spectrometer. The *g*-value was determined by comparison with crystalline DPPH, for which the *g*-value was taken to be 2.0036.

Results

The susceptibilities of PT·$SbCl_5$, MPT·$SbCl_5$ and TA·$SbCl_5$ increased with the decrease in temperature, while the susceptibility of PT·$SbCl_4$ changed little with temperature.

Diamagnetic contribution was estimated from the value of diamagnetic susceptibility of components, on the assumption that the value for a neutral organic molecule may be used in place of the value for the molecular ion.[*1] The value of -129.8×10^{-6} emu/mol for TA was determined by the Gouy method.[5)] The values of -124×10^{-6} for PT and -132×10^{-6} emu/mol for MPT were calculated from Pascal's constants. The value of 120.6×10^{-6} emu/mol for $SbCl_5$ was taken from the values which were determined experimentally by Kido[8)] and Pascal.[9)] The value for $SbCl_4^-$ was calculated to be -109×10^{-6} emu/mol by Kainer and Hausser.[10)] The corrected (paramagnetic) susceptibilities at room temperature, χ_p (per mole) are given in Table 1, together with the assumed values of the diamagnetic susceptibility.

When the inverse susceptibility, $1/\chi_p$ was plotted against temperature, straight lines were obtained for PT·$SbCl_5$, MPT·$SbCl_5$, and TA·$SbCl_5$ at higher temperatures, as shown in Fig. 2. The susceptibility obeys the Curie-Weiss law, $\chi_p = C/(T-\theta)$, for which θ is negative. The values of

---

7) W. Duffy, Jr., *J. Chem. Phys.*, **36**, 490 (1962).

[*1] When the neutral organic molecule is changed to the ion, the molecular form may be changed toward coplanar, which would result in a little increase in diamagnetic susceptibility.

8) K. Kido, *Sci. Rep. Tohoku*, [I] **21**, 872 (1923).

9) P. Pascal, *Compt. Rend.*, **152**, 863 (1912), *Bull. Soc. Chim. France*, [4] **11**, 201 (1912).

10) H. Kainer and K. H. Hausser, *Chem. Ber.*, **86**, 1563 (1953).

Table 1. The magnetic susceptibilities and radical concentrations

	Molecular weight	Observed susceptibility (at 296°K) $\times 10^4$ emu/mol	Assumed diamagnetic susceptibility $\times 10^4$ emu/mol	Paramagnetic susceptibility (at 296°K) $\times 10^4$ emu/mol	Weiss constant θ °K	Curie constant emu·°K/mol	Radical concentration %
PT·$SbCl_4$	463	1.63	−2.33	3.96	—	—	—
PT·$SbCl_5$	498	7.99	−2.45	10.44	-20 ± 10	0.327	87
MTP·$SbCl_5$	512	8.66	−2.53	11.19	-5 ± 10	0.342	91
TA·$SbCl_5$	515	9.09	−2.51	11.60	0 ± 4	0.343	92

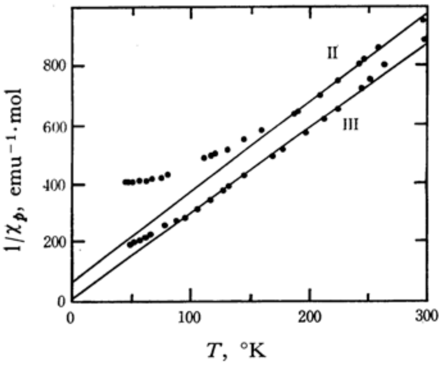

Fig. 2a. The inverse paramagnetic susceptibilities of (II) PT·$SbCl_5$, and (III) MPT·$SbCl_5$.

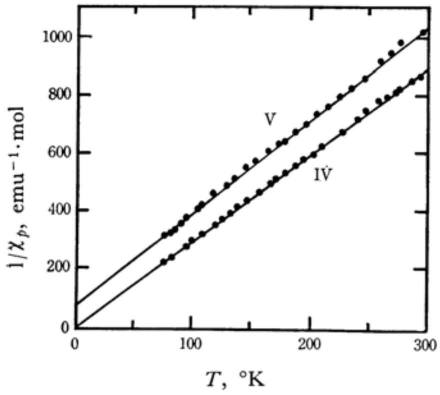

Fig. 2b. The inverse paramagnetic susceptibilities of (IV) TA·$SbCl_5$ and (V) DPPH.

the Curie constant C, and the Weiss constant θ, were calculated from the slope of the line, and its intersection on the temperature axis. Radical concentrations were calculated from the Curie constant, on the assumption that each radical possessed a spin quantum number of 1/2.

TA·$SbCl_5$ gave the largest value in radical concentration, and the smallest value of $|\theta|$. The molar susceptibility of the salt at 296°K is in good agreement with the value obtained by the Gouy method.[5)]

As the temperature was lowered, the susceptibilities for PT·$SbCl_5$ and MPT·$SbCl_5$ deviated from the Curie-Weiss law. The susceptibility for PT·$SbCl_5$ reached nearly a maximum around 49°K,

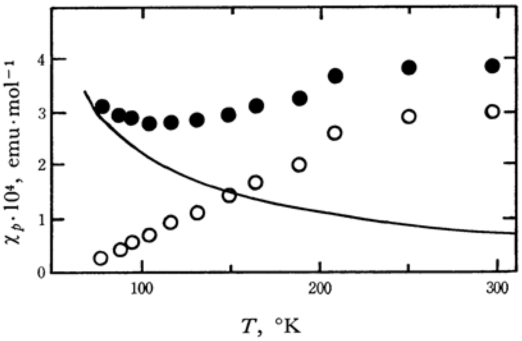

Fig. 3. The paramagnetic susceptibility of PT·$SbCl_4$.

● Observed
— The assumed susceptibility for impurity
○ The difference between observed and impurity susceptibilities

though the temperature for the maximum would be determined distinctly by the measurement at still lower temperatures. The susceptibility at 49°K is 25.3×10^{-4} emu/mol.

PT·$SbCl_4$ gave the smallest value of paramagnetism, which changed little with temperature. The paramagnetism, however, was not caused by ferromagnetic impurities because the susceptibility was found to be independent of the strength of magnetic field in the temperature range.

The ion radical salts were stable in air: Over a period of a month, X-ray diffraction gave a distinct crystalline pattern, the molar susceptibility was constant with time, and no change of color was recognized.

Discussion

The radical concentrations of about 90% obtained from the Curie constants for PT·$SbCl_5$, MPT·$SbCl_5$ and TA·$SbCl_5$ indicate that each ion radical complex has one unpaired electron. It is reasonable to ascribe the unpaired electron to the monopositive ion radical produced by the oxidation of the aromatic compound with $SbCl_5$. The initial reaction is believed to involve a one-electron transfer from the aromatic molecule to $SbCl_5$.[11)]

---

11) I. C. Lewis and L. S. Singer, *J. Chem. Phys.*, **43**, 2712 (1965).

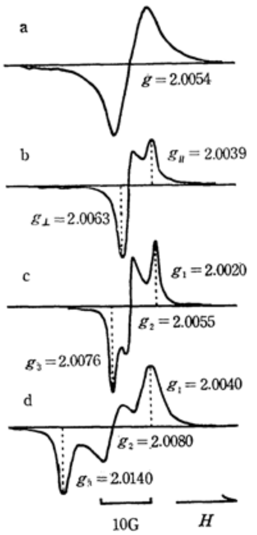

Fig. 4. The derivative curves of ESR absorption for powder samples.
a PT·$SbCl_4$ b PT·$SbCl_5$
c MPT·$SbCl_5$ d TA·$SbCl_5$

The positive ion radicals have been studied by an electron spin resonance absorption.[12,13] The ESR spectra for these solid complexes showed asymmetrical patterns, consisting of two or three peaks due to the *g*-factor anisotropy.[5] The principal *g*-values obtained by the approximation according to Kneubühl[14] are shown in Fig. 4. An average of these principal values of each complex is in good agreement with the *g*-value reported for the corresponding compound in a concentrated sulfuric acid solution. The spectra of PT·$SbCl_5$ and TA·$SbCl_5$ in a nitrobenzene solution exhibited the identical hyperfine structures with those observed in a sulfuric acid solution of phenothiazine, and thianthrene.[12,13] Further, the spin concentrations obtained from the ESR measurements of the solid complexes were in fairly good agreement with those obtained from the susceptibility measurements. This result ensures that there is no paramagnetic species in the solid complexes which could not be observed in the ESR absorption spectra. A diamagnetic form of antimony pentachloride in the complexes is not known. Kainer and Hausser, however, suggested a formula of $(SbCl_4^- + SbCl_6^-)/2$ in the case of the complexes of diphenylamine derivatives.[10] It is, therefore, plausible to conclude that the paramagnetism of the complexes observed in the susceptibility measurements originates entirely from the monopositive aromatic ion radical, rather than from the part of antimony pentachloride.

The Weiss constants obtained are -20 ± 10, -5 ± 10, and 0 ± 4°K for PT·$SbCl_5$, MPT·$SbCl_5$, and TA·$SbCl_5$, respectively, indicating that the spin exchange interaction in the complexes decreases in this sequence. At lower temperatures, the susceptibilities for the former two deviate from the Curie-Weiss law, as shown in Fig. 2, and the deviation starts at a higher temperature for the complex of a larger $|\theta|$ value. The susceptibility of PT·$SbCl_5$ reaches its maximum at 49°K. The deviation and an appearance of a maximum are expected to occur in the temperature range where the magnitude of a spin exchange interaction is comparable with that of $\boldsymbol{k}T$. The similar kinds of magnetic behaviors were observed in a number of crystalline organic free radicals, such as TCNQ anion radical salts, DPPH, 1, 3-bis-(diphenylene)-2-phenyl-allyl, *N*-picryl-9-aminocarbazyl, *etc.*

According to the recent development in experimental and theoretical treatments, the magnetic behavior of these crystalline organic free radicals can be reasonably interpreted by an exchange-coupled linear chain model.[15-17] The corresponding Hamiltonian is given by

$$\mathscr{H} = \sum_{i}^{N/2} (2J\vec{\boldsymbol{S}}_{2i-1}\vec{\boldsymbol{S}}_{2i} + 2J'\vec{\boldsymbol{S}}_{2i}\vec{\boldsymbol{S}}_{2i+1}), \qquad (1)$$

where J and $J'(|J|\geq|J'|)$ are the exchange coupling constants between the $(2i-1)$th and the $(2i)$th radicals, and between the $(2i)$th and the $(2i+1)$th radicals in a chain with N radicals, respectively. Positive values of J and J' correspond to antiferromagnetic coupling. The exact solution of this Hamiltonian has not been obtained except for the extreme cases: (1) $J=J'=0$, (2) $J\neq J'=0$, and (3) for the case of $\vec{\boldsymbol{S}}_i\vec{\boldsymbol{S}}_j = S_i^z S_j^z$, $J=J'\neq0$. Case (1) simply gives the Curie law, case (2) corresponds to the singlet-triplet model, and case (3) to the linear Ising model.

It is interesting to see the susceptibility of PT·$SbCl_5$ salt being explained either by the singlet-triplet or by the linear Ising model. In the singlet-triplet model, the susceptibility is expressed by

$$\chi_p = (2N'g^2\beta^2/\boldsymbol{k}T)[3+\exp(2J/\boldsymbol{k}T)]^{-1}, \qquad (2)$$

where $2J$ is the singlet-triplet energy separation, and N' is the number of spin pairs. In the linear Ising model, the susceptibility is given by

$$\chi_p = (Ng^2\beta^2/4\boldsymbol{k}T)\exp(-J/\boldsymbol{k}T) \qquad (3)$$

in the temperature range discussed.[18,19] N is

---

[12] L. D. Tuck and D. W. Schieser, *J. Phys. Chem.*, **66**, 937 (1962).
[13] J. Lhoste and F. Tonnard, *J. chim. Phys.*, **63**, 678 (1966).
[14] F. K. Kneubühl, *J. Chem. Phys.*, **33**, 1074 (1960).
[15] Z. G. Soos, *J. Chem. Phys.*, **43**, 1121 (1965).
[16] R. M. Lynden-Bell and H. M. McConnell, *ibid.*, **37**, 794 (1962).
[17] A. S. Edelstein, *ibid.*, **40**, 488 (1964).
[18] J. W. Stout and R. C. Chisholm, *ibid.*, **36**, 979 (1962).
[19] J. C. Bonner and M. E. Fisher, *Phys. Rev.*, **135**, A640 (1964).

the total number of spins, and J is taken to be positive for convenience. The temperature T_m, at which the susceptibility shows its maximum, corresponds to $1.25J/\boldsymbol{k}$ for Eq. (2) and to $J/\boldsymbol{k}$ for Eq. (3).

The quantity of $(\boldsymbol{k}T_m)(\chi_{max}/Ng^2\beta^2)$, which is theoretically independent of J-value, is a measure for the comparison between experimental and theoretical values. The experimental value of this quantity for PT·SbCl$_5$ is 0.0954, where T_m is taken to be 49°K and χ_{max} is normalized with respect to the radical concentration of 0.87, while its theoretical value for the singlet-triplet model is 0.1256, and that for the linear Ising model is 0.0920.*2 These figures indicate that the linear chain models give rather better fit to the observed susceptibility of PT·SbCl.$_5$ Assuming the linear Ising model, therefore, J=0.0042 eV for PT·SbCl$_5$.

The susceptibility of PT·SbCl$_4$, on the other hand, changes little with temperature. The nearly temperature-independent paramagnetism was reported for the TCNQ salts which had high electrical conductivity, and it was explained by Pauli spin paramagnetism.[2,20] However, the conductivity of PT·SbCl$_4$, which was measured with a compressed powder, was $3.8\times10^{-9}\,\Omega^{-1}\,\mathrm{cm}^{-1}$ at room temperature. Hence the paramagnetic susceptibility of PT·SbCl$_4$ might not be explained by the Pauli paramagnetism. If the small rise of the susceptibility on the lower temperature side is assumed to be dominated by a paramagnetic impurity, whose susceptibility follows the Curie law, we get a corrected intrinsic susceptibility, which decreases with the decrease in temperature. The theoretical curves are shown in Fig. 5, which were calculated either from Eq. (2) or Eq. (3) assuming some fixed values for J. One can see that the experimental points are most closely fitted onto the curve of the linear Ising model. Therefore the susceptibility of PT·SbCl$_4$ can be explained rather by the linear Ising model, but not by the singlet-triplet model. The spin exchange interaction of 0.034 eV, or 395°K in temperature scale for PT·SbCl$_4$ is found to be the greatest among these cation radical complexes.

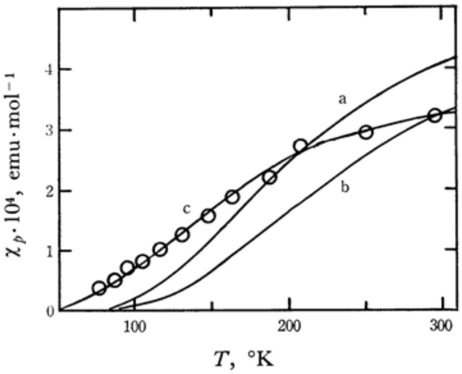

Fig. 5. The intrinsic paramagnetic susceptibility of PT·SbCl$_4$.
○ Experimental (corrected for impurity);
(a) Calculated from the singlet-triplet model for $2J$=0.056 eV and (b) for $2J$=0.064 eV; (c) calculated from the linear Ising model for J=0.034 eV.

The paramagnetic behaviors of PT·SbCl$_5$ and PT·SbCl$_4$ suggest that the spin exchange interactions in these solids are not restricted to those of bimolecular nature, but rather they are spread over a whole crystal domain or at least several molecules, probably through linear array of molecules.

The expense for constructing the magnetic susceptibility balance has been defrayed from a grant given by the Toyo Rayon Science Foundation, to which the authors' sincere thanks are due. The authors also wish to thank Dr. Akira Tasaki of Osaka University for his valuable advice to the design of the magnetic balance.

---

*2 When the regular Heisenberg linear chain model is used in place of the linear Ising model, it is calculated to be 0.0942.[19]

20) R. W. Tsien, C. M. Huggins and O. H. LeBlanc, Jr., *J. Chem. Phys.*, **45**, 4370 (1966).