Magnetic Susceptibility and Low-field ESR of an Organic Ion-radical Salt, Tri-*p*-tolylaminiumyl Chloroantimonate

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The static magnetic susceptibility and the low-field ESR spectra (33.6 and 135 MHz) of powder samples of tri-*p*-tolylaminiumyl chloroantimonate were measured above 1.7 K. A broad maximum in the susceptibility, which indicates an antiferromagnetic interaction, was observed at 6.0 K; this is consistent with the results of the proton NMR measurements. In the low-field ESR spectra, broadening of the $g=2$ absorption line and distinct appearance of the $g=4$ absorption line were observed in the temperature region below T_m, the temperature at which the susceptibility is maximum. The results are interpreted by assuming that the magnetic behavior is due to antiferromagnetic Heisenberg linear chains. An abrupt decrease in the $g=2$ absorption intensity and a rapid increase in the $g=2$ absorption linewidth were also found in the temperature range from 3.5 to 2.5 K, while a slight rise in the susceptibility was observed below 2.5 K. These anomalies may imply a magnetic-phase transition in the vicinity of 2.5 K.

There have been many investigations regarding the magnetic properties of the stable organic free radicals. A deviation from the Curie-Weiss law and a broad maximum in the susceptibilities of some ion-radical salts with plate-like structures have been observed above the temperature of liquid nitrogen.[1] The anomalous behavior arises from the strong interaction between adjacent radicals and has been interpreted in terms of the exchange-coupled pair model or the linear Ising model. The mechanism of such a strong interaction is considered to be the charge-transfer stabilization. However, the magnetic behavior of ion-radical salts which have small Weiss constants had never been studied in the low-temperature region.

In triarylaminiumyl radical salts, the cations are considered to have propeller-like structures similar to those of triarylmethylium salts,[2] so that the exchange interaction between adjacent radicals is expected to be small compared with that of plate-like ion-radical salts. The static magnetic susceptibilities from 77 to 300 K and the proton NMR spectra from 1.5 to 77 K have been measured on powder samples of some triarylaminiumyl radical salts by the present author and his co-workers.[3] The static magnetic susceptibilities of tri-*p*-tolylaminiumyl chloroantimonate (TTA·$SbCl_5$) obeyed the Curie-Weiss law, with a Weiss constant of $\theta=-10$ K, and a broad maximum in the paramagnetic shift of its proton NMR spectra was found in the vicinity of 6.0 K. The broadening of the shifted lines was also observed below 4.2 K. This behavior cannot be explained by the anisotropic broadening.[3,4] In order to clarify the magnetic behavior of TTA·$SbCl_5$ at low temperatures, the static magnetic susceptibility and low-field ESR (33.6 and 135 MHz) measurements were carried out for temperatures above 1.7 K. Precise and absolute values of susceptibility can be obtained from the static magnetic measurements. Information concerning the dynamical behavior of the spin system near the zero field can be obtained from the low-field ESR (LF-ESR) measurements. In this paper the author will report the results of these measurements and discuss the exchange interaction, spin correlation, and abnormal ESR behavior in the TTA·$SbCl_5$ salt. The tri-*p*-tolylaminiumyl cation, TTA, has the molecular structure shown in Fig. 1.

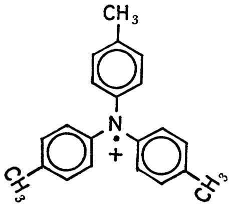

Fig. 1. Molecular structure of the tri-*p*-tolylaminiumyl cation, TTA.

Experimental

The tri-*p*-tolylamine was prepared by the method of Walter and was purified by repeated recrystallization.[5] The TTA·$SbCl_5$ was prepared according to the method of Wieland.[6] To a solution of the tri-*p*-tolylamine in benzene was added a chloroform solution of $SbCl_5$ under cooling. By addition of benzene a deep blue crystalline product with a metallic luster was obtained from the solution. After filtration, the product was quickly washed with benzene and dried *in vacuo*, mp 114—116 °C. The results of the elementary analysis were described in the previous paper.[3]

The static magnetic susceptibilities were measured for powder samples of 70—90 mg in a field of 8.8 kG from 1.7 to 100 K by means of the torsion balance described elsewhere.[7] No ferromagnetic impurities were found in samples by checking the field dependence of magnetization up to 12 kG at 4.2 K. The temperatures were measured with an AuCo–Cu thermocouple and a carbon resistor calibrated by measuring not only the magnetic susceptibility of Mn-Tutton salt, but also the vapor pressures of liquid helium, liquid hydrogen, and liquid nitrogen. The LF-ESR spectra (33.6 and 135 MHz) were observed using a Robinson type spectrometer[8] and a Benedek-Kusida type spectrometer,[9] respectively. Details of the apparatus for the LF-ESR measurements have been described elsewhere.[10] The sensitivity of the Robinson type spectrometer with respect to temperature variations was checked by measuring the absorption intensity of the proton NMR, which is inversely proportional to the temperature. A conventional cryostat was used, and tem-

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Table 1. Results from susceptibility measurements

	χ_d / 10^{-4} emu·mol^{-1}	θ / K	T_m / K	χ_m / 10^{-4} emu·mol^{-1}	p	J/k / K
TTA·SbCl$_5$[a]	−3.4	−10	6.0	188	0.94	−4.7
TANOL[b]	−1.1	−6	6.5	226	1.00	−5.0
p-Cl-BDPA[b]	−2.8	−6	5.6	196	1.00	−4.4

a) This work. b) Ref. 12.

peratures were determined using an Allen-Bradley carbon resistor calibrated against the vapor pressures of liquid helium, hydrogen, and nitrogen.

Results and Discussion

Susceptibility. The diamagnetic correction was made using Pascal's constant. The diamagnetic susceptibility, χ_d, is listed in Table 1. In the temperature range above 15 K, the paramagnetic susceptibility, χ_p, of TTA·SbCl$_5$ follows the Curie-Weiss law, with a Weiss constant of $\theta=-10$ K and a spin concentration of $p=0.94$. As the temperature is lowered below 15 K, it deviates from the Curie-Weiss law and reaches a broad maximum at 6.0 K, as is shown in Fig. 2. After passing through the maximum, it decreases comparatively slowly down to 2.5 K. However, below 2.5 K it increases slightly as the temperature is lowered. In the region from 3.0 to 77 K, the behavior of the susceptibility is consistent with that of the relative susceptibility obtained from the proton paramagnetic shift.[3]

The g-value of TTA·SbCl$_5$ is nearly isotropic, so that it is not appropriate to discuss its magnetic properties on the basis of the linear Ising model. Therefore, the susceptibility data have been analyzed using the pair model and the one-dimensional Heisenberg model based on Bonner and Fisher's calculation.[11] The kT_m/J ratio is 1.28 for the one-dimensional Heisenberg model and 1.25 for the pair model, where T_m is the temperature at which the susceptibility reaches its maximum value and J is the exchange coupling constant. The J value for each model can be estimated from the T_m value obtained experimentally. In Fig. 2, the paramagnetic susceptibility is compared with the theoretical curves for the one-dimensional Heisenberg model of $J=-4.7$ K and for the pair model of $J=-4.9$ K, which are fitted at the temperature T_m. It can be seen from Fig. 2 that the observed value above 2.5 K fits the one-dimensional Heisenberg model better than the pair model. However, the maximum value of the observed susceptibility, $\chi_m=188\times10^{-4}$ emu/mol, is 20% lower than the former theoretical $\chi_m=225\times10^{-4}$ emu/mol; it is 40% lower than the latter theoretical $\chi_m=296\times10^{-4}$ emu/mol. The difference between the experiment and the theory is not due to a poor spin concentration, but to the some other effect, for the spin concentration is equal to 0.94 in the temperature range above 15 K. The one-dimensional Heisenberg interaction has not been observed in ion-radical salts. It is interesting that the ion-radical salt, TTA·SbCl$_5$, studied here exhibits a one-dimensional Heisenberg interaction. In the crystalline state, the cation radicals with a propeller-like configuration may form chain-like arrays of molecules. The propeller-like structure of the cation radical, TTA, may restrict pairing of electron spins and dimerization of molecules in the crystalline state compared with a plate-like structure. The resulting parameters are summarized in Table 1, together with those of one-dimensional Heisenberg antiferromagnets typical of organic neutral radicals, 2,2,6,6-tetramethyl-4-hydroxy-1-piperidinyloxyl (TANOL) and 9-(α-fluorenylidene-p-chlorobenzyl)-9-fluorenyl (p-Cl-BDPA).[12] The exchange parameter J for TTA·SbCl$_5$ is as large as that for the organic neutral radicals. The mechanism of such a weak interaction may be attributable to the overlap of π-orbitals occupied by the unpaired electron rather than to the charge-transfer stabilization. The slight rise in the susceptibility below 2.5 K may be attributable to a magnetic-phase transition rather than to paramagnetic impurities. Such a slight rise in the susceptibility has also been found near a magnetic-phase transition into an antiferromagnetic state in the case of some organic neutral radicals.[12,13] This will be discussed below on the basis of the LF-ESR results.

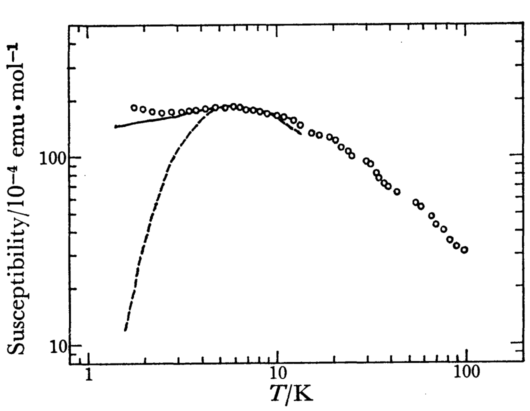

Fig. 2. Magnetic molar susceptibility of TTA·SbCl$_5$. The open circles represent the experimental values. The solid line and the dashed line are the theoretical curves for the one-dimensional Heisenberg model of $J=-4.7$ K and for the pair model of $J=-4.9$ K, respectively, which are fitted at $T_m=6.0$ K.

LF-ESR. The LF-ESR absorption spectra of TTA·SbCl$_5$ exhibit a single line which has an exchange-narrowed Lorentzian shape at room temperature. The temperature dependences of the 33.6 MHz ESR and 135 MHz ESR spectra are shown in Figs. 3 and 4, respectively. The linewidth, which was taken to be the peak-to-peak linewidth of the first derivative of the $g=2$ absorption spectrum, started to increase as the temperature was decreased below T_m, where the susceptibility went through a broad maximum. The

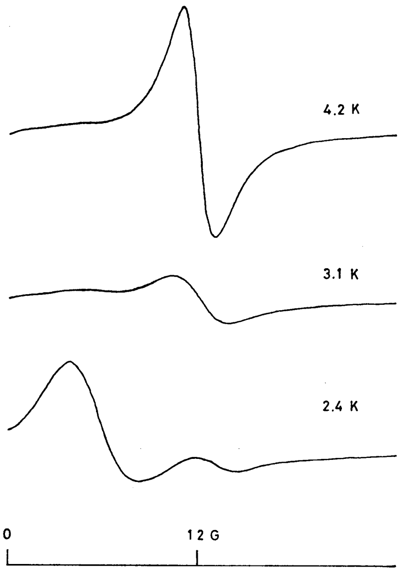

Fig. 3. The LF-ESR spectra of TTA·$SbCl_5$ measured at 33.6 MHz. The 2.4 K signal is amplified thirty three times compared with the 4.2 and 3.1 K signals.

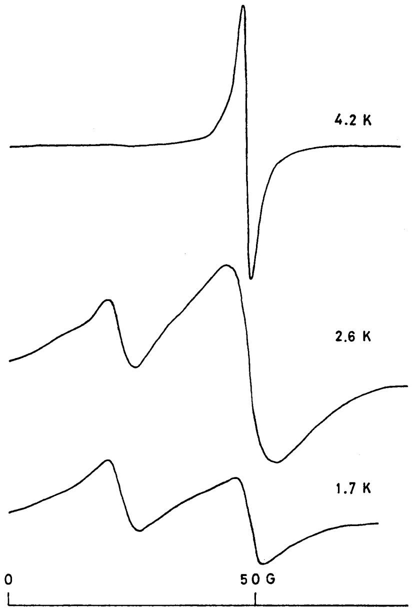

Fig. 4. The LF-ESR spectra of TTA·$SbCl_5$ measured at 135 MHz.

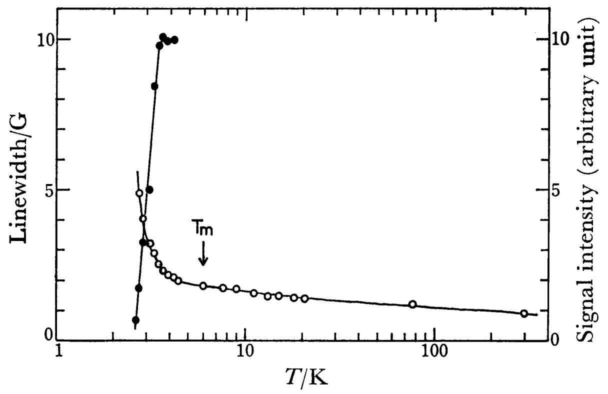

Fig. 5. Temperature dependence of the LF-ESR linewidth (-○-) and signal intensity (-●-) measured at 33.6 MHz.

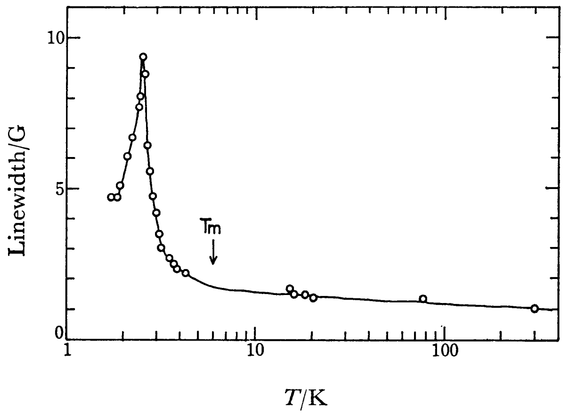

Fig. 6. Temperature dependence of the LF-ESR linewidth measured at 135 MHz.

signal intensity, which was defined as the product of the square of the linewidth and the amplitude of the first derivative of the $g=2$ absorption line, measured at 33.6 MHz, was almost constant in the region from 4.2 to 3.5 K. In the temperature range from 3.5 to 2.5 K, an abrupt decrease in the signal intensity and a rapid increase in the linewidth were found. The temperature dependence of the linewidth and signal intensity measured at 33.6 MHz is shown in Fig. 5. Below 2.5 K the linewidth measured at 135 MHz decreased rapidly, as is shown in Fig. 6. The $g=4$ absorption could not be observed at room temperature or at liquid nitrogen temperature. Below the temperature at which the susceptibility deviated from the Curie-Weiss law, the $g=4$ absorption was detected as the temperature was lowered. At fixed temperature, the ratio of the intensity of the $g=4$ resonance absorption to that of the $g=2$ absorption was larger in the 33.6 MHz ESR spectrum than in the 135 MHz ESR spectrum.

It is well-known that the signal intensity of the ESR absorption line is proportional to the magnetic susceptibility in the paramagnetic state. The relative susceptibility, obtained from the signal intensity, agrees qualitatively with the static magnetic susceptibility for temperatures above 3.5 K. In Fig. 7, the relative susceptibility, obtained from the signal intensity, is compared with the static magnetic susceptibility and the theoretical curves for the one-dimensional Heisenberg model of $J=-4.7$ K and the pair model of $J=-4.9$ K, which are normalized at 4.2 K. In a one-dimensional Heisenberg system, a rapid decrease in the signal intensity is not observed below the temperature of maximum susceptibility.[14] In a pair-like system, the signal intensity decreases in direct proportion to the static magnetic susceptibility below the temperature of maximum susceptibility. The observed deviation from the static magnetic susceptibility below 3.5 K, consisting in an abrupt decrease in the signal intensity of the ESR line, indicates the occurrence of a reorganization of the energy spectrum involving a decrease in the number of

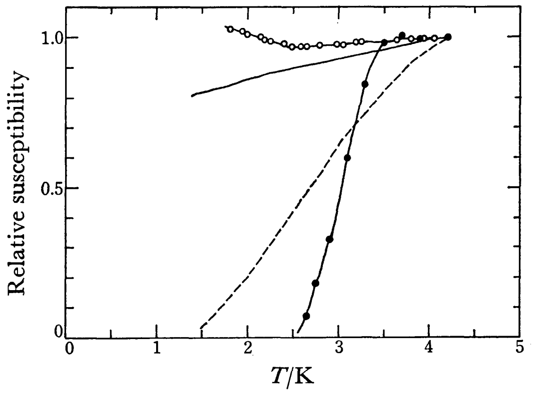

Fig. 7. Comparison between the static magnetic susceptibility (-○-) and the relative susceptibility obtained from the LF-ESR signal intensity (-●-). The solid line and the dashed line represent the theoretical curves for the one-dimensional Heisenberg model of $J=-4.7$ K and the pair model of $J=-4.9$ K, respectively. The experimental plots and the theoretical curves are normalized at 4.2 K.

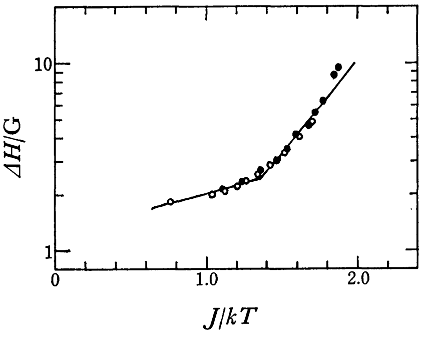

Fig. 8. LF-ESR linewidth (ΔH) *versus* J/kT. ○: 33.6 MHz, ●: 135 MHz.

spins possessing a paramagnetic property. Recent magnetic resonance measurements revealed that some organic neutral radicals go into a long-range ordered antiferromagnetic state in a sufficiently low temperature region.15) The abrupt decrease in the signal intensity of the ESR line of TTA·SbCl$_5$ may imply a magnetic-phase transition from the short-range ordered state to the long-range ordered state in the vicinity of 2.5 K. In the temperature range from 3.8 to 3.2 K, such an abrupt decrease in the signal intensity of 33.6 MHz ESR line has also been observed for *p*-Cl-BDPA,16) which undergoes a magnetic-phase transition to an antiferromagnetic state at 3.25 K.17) Delocalization of the unpaired electron on the three *p*-tolyl rings or the chloroantimonate anion with a diamagnetic formula3) may play some role in an exchange interaction leading to a long-range ordered state, such as the interchain exchange interaction.

In the case of LF-ESR, precise linewidth data can be obtained even in powder samples, because any contribution to the linewidth from the anisotropy of the *g*-values is excluded. The LF-ESR line is narrowed by the strong exchange interaction in the high-temperature region. It has been reported that, in several organic neutral radicals, the LF-ESR linewidth *versus* temperature below T_m of maximum susceptibility can be fitted to the following empirical relation:14)

$$\Delta H = \alpha \exp(\beta J/kT), \tag{1}$$

where α and β are constant and where J means the absolute value of the exchange coupling constant. The parameters of temperature dependent LF-ESR linewidth for TTA·SbCl$_5$ are summarized in Table 2, together with those for some organic neutral radicals.14,16) The β values for TTA·SbCl$_5$ were determined to be 0.50 in the region from 6.0 to 3.5 K and to be 2.30 in the region from 3.5 to 2.5 K, by plotting the linewidth against the reciprocal of the temperature, as is shown in Fig. 8. The β value is considered to be associated with the correlation mechanism of exchange motion, which may be related to the magnetic interaction of the system. It is interesting that the first β value for TTA·SbCl$_5$ is nearly equal to the β value for TANOL, which has a one-dimensional Heisenberg interaction.12) The broadening of the resonance with the first β value is attributable to an increase in the correlation for exchange motion because of short-range magnetic ordering below the temperature of maximum susceptibility. Such a broadening was not found above 1.7 K in tri-*p*-tolylaminiumly perchlorate (TTA·ClO$_4$); its susceptibility obeyed the Curie-Weiss law with a Weiss constant of $\theta=-0.5$ K.3) The second β value for TTA·SbCl$_5$ is much larger than the β values for the radicals with one-dimensional Heisenberg or pair-like interaction. The rapid increase in linewidth with the second β value may be the result of the critical fluctuation of electron spins in the vicinity of the transition temperature, which may simultaneously cause the abrupt decrease in the signal intensity in the range from 3.5 to 2.5 K. It may be appropriate to use one parameter in place of $\beta J/k$ in Eq. 1, because the J parameter is considered to be insignificant in this temperature

Table 2. Parameters for temperature dependent LF-ESR linewidth and magnetic interaction

		α/G	β	J/k/K	Magnetic interaction
TTA·SbCl$_5$ a)	2.5—3.5 K	0.1	2.30	4.7	——
	3.5—6.0 K	1.2	0.50	4.7	one-dimensional Heisenberg interaction
TANOL b)		3.6	0.48	5.0	
Porphyrexide b)		3.0	0.95	5.9	pair-like interaction
Cl-porphyrexide b),c)		1.1	0.93	18.2	
Solvent-free DPPH d)		0.7	0.70	8.8	

a) This work. b) Ref. 14. c) Monochloroporhyrexide. d) α,α-Diphenyl-β-picryl hydrazyl recrystallized from ether. Refs. 16 and 18.

range. The behavior of the $g=2$ resonance can be related to the broadening of the shifted lines in the proton NMR spectra below 4.2 K. The residual resonance measured at 135 MHz below 2.5 K is probably due to paramagnetic impurities.

In the high-temperature region, the $g=4$ resonance, which is probably caused by a forbidden transition due to dipolar interaction, cannot be detected,[14,19] for the strong exchange interaction averages the dipolar coupling.[20] The appearance of the $g=4$ resonance at low temperatures can be explained by an increase in the correlation time for exchange motion, as is expected from the linewidth of the $g=2$ resonance and the susceptibility data. Below 3.5 K the behavior of the $g=4$ resonance was independent of the temperature in spite of the anomalies of the $g=2$ resonance. This cannot be explained now.

Conclusions

1. The static magnetic susceptibility of TTA·$SbCl_5$, as well as the relative susceptibility obtained from the paramagnetic shift, can be described by the one-dimensional Heisenberg model of $J/k=-4.7$ K in the temperature range above 2.5 K, although the maximum value of the observed susceptibility is 20% lower than the theoretical value.
2. The broadening of the $g=2$ absorption line and the distinct appearance of the $g=4$ absorption line in the LF-ESR spectra are attributable to the effects of short-range magnetic ordering below the temperature of the susceptibility maximum.
3. The following anomalies may imply a magnetic-phase transition in the vicinity of 2.5 K: 1) the rise of the susceptibility below 2.5 K, 2) the abrupt decrease in the $g=2$ absorption intensity and the rapid increase in the $g=2$ absorption linewidth in the temperature range from 3.5 to 2.5 K, 3) the broadening of the shifted lines in the proton NMR spectra below 4.2 K.

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