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Synthesis and Magnetic Properties of Orthogonally Linked Phenothiazine Cation Radical Dimer and Tetramer

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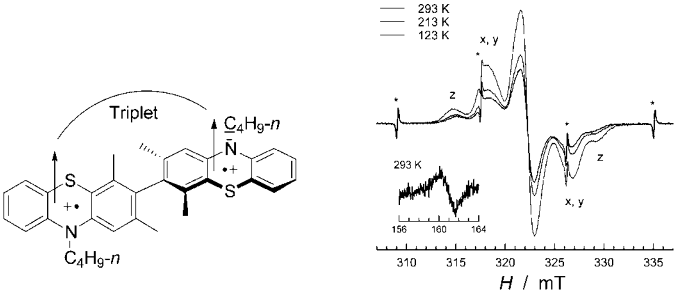
ABSTRACT



A 3,3′-orthogonally linked phenothiazine cation radical dimer with methyl substituents at the 2, 2′, 4, and 4′ positions was synthesized. The dimer was isolated as a stable product which exists in a triplet state due to a torsion angle of ca. 80° between the two phenothiazine units. The tetramer was also synthesized by linking the dimers using a 1,4-phenylene spacer.

High-spin organic polymers are important building blocks for producing organic molecule-based magnets;[1] therefore, a wide variety of organic polyradicals have been investigated.[2−10] The π-topological rule is an essential requirement to achieve high spin states in the ground state, as suggested, in studies on polycarbenes[2,3] and poly(triarylmethine radical)s[4] that have successfully achieved spin states with $10-10^3$ magnitudes. For practical use, polyradical spin sources should be air-stable organic radicals;[5−9] however, most stable radicals have partial spin density distributions. Therefore, through-bond spin coupling, which is very important for the π-topological rule, is often ineffective in stable polyradicals.

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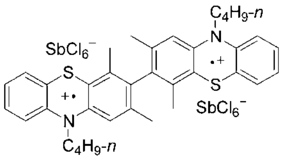
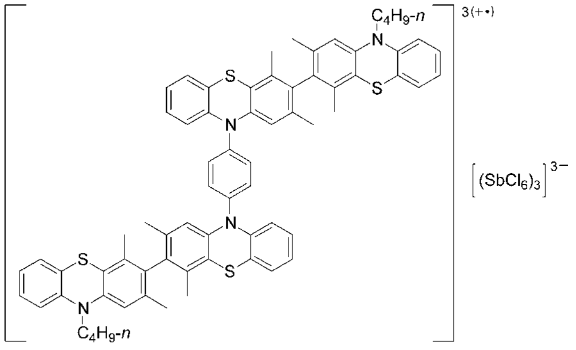
Triarylamine cation radicals are an exception and have successfully led to polymeric systems with high spin states.[5c−e,7] An orthogonal linkage between spin units like planar π-cation radicals is another requirement for intramolecular spin alignment. However, the requirement has not been actively pursued, probably due to difficult synthetic strategies. This requirement is occasionally more predominant than the π-topological rule when using stable radicals. Some orthogonally linked dimeric systems have been synthesized and isolated as stable products.[10] For example, the diradical dication of a spiro-fused triarylamine dimer formed a stable triplet molecule in the ground state.[10b] The diradical dication of a *meso*-β linked porphyrin dimer also existed in a triplet state with a small singlet−triplet energy gap of 2.1−12 cal mol^{-1} (1.1−6.0 K).[10c] Unfortunately, the development of polymeric systems from these dimers requires complex synthetic strategies.

In this work, a novel orthogonally linked dimeric system **1d(SbCl$_6$)$_2$**, which consists of a 3,3′-linked diphenothiazine **1d** coordinated to two SbCl$_6$ anions, was synthesized. Phenothiazine cation radicals are well-known stable radicals[11] but, suprisingly, have not been used as frequently as nitroxides, phenoxides, and triarylamine cation radicals. Complex **1d(SbCl$_6$)$_2$** was substituted by methyl groups at the 2, 2′, 4, and 4′ positions to generate an orthogonal conformation between the two phenothiazine units. Some reports have mentioned that diphenothiazines existed in the triplet state in sulfuric acid,[12] but the triplet species have not been isolated to date. On the other hand, **1d(SbCl$_6$)$_2$** was isolated as a stable product. Tetraphenothiazine **1t** was also synthesized using a 1,4-phenyelene spacer to evaluate the potential development of polymeric systems from **1d(SbCl$_6$)$_2$**. 10,10′-(1,4-Phenylene)diphenothiazine has been previously reported as a triplet ground-state molecule in sulfuric acid.[12b] Therefore, the complexation of **1t** with four SbCl$_6$ anions is expected to generate a quintet species. However, the complex obtained here, **1t(SbCl$_6$)$_3$**, contained three SbCl$_6$ anions instead of four. The synthesis and magnetic properties of **1d(SbCl$_6$)$_2$** and **1t(SbCl$_6$)$_3$** are reported here.

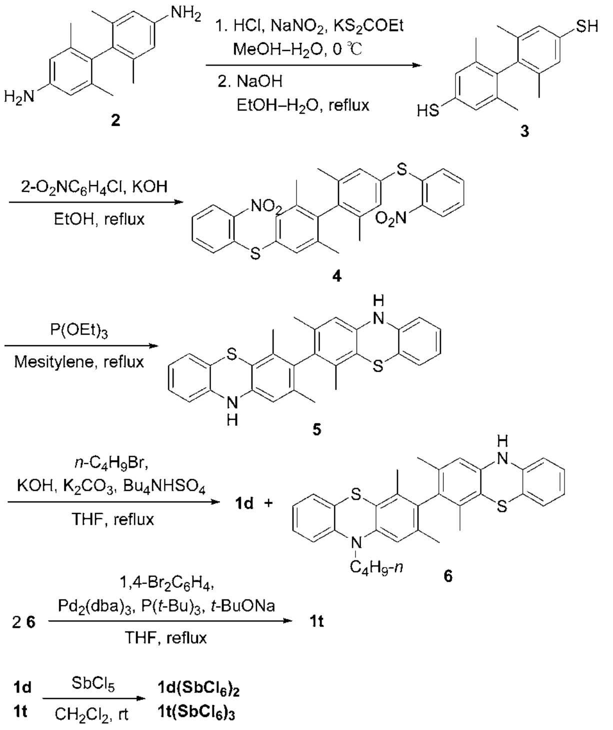


1d(SbCl$_6$)$_2$



1t(SbCl$_6$)$_3$

Scheme 1. Synthetic Route of **1d(SbCl$_6$)$_2$** and **1t(SbCl$_6$)$_3$**



Phenothiazines **1d** and **1t** were synthesized from 4,4′-diamino-2,2′,6,6′-tetramethylbiphenyl (**2**) which was prepared by benzidine rearrangement (Scheme 1).[13] The reaction of a diazonium salt prepared from **2** with potassium ethyl xanthate and the susequent hydrolysis in the presence of solium hydroxide formed dithiol **3**. The reaction of **3** with 2-chloronitrobenzene in the presence of potassium hydroxide produced **4** in 32% yield from **2**. The reaction of **4** with triethyl phosphite resulted in 3,3′-linked diphenothiazine **5**. This reaction is one of the methods to prepare phenothiazines and involves a rearrangement through a nitrene intermediate.[14] Because of low solubility except for THF, crude **5** was directly reacted with 1-bromobutane in the presence of bases to give **1d** and **6** in 5% and 10% yields from **4**, respectively. Pd-catalyzed amination of 2 equiv of **6** with 1,4-dibromobenzene in the presence of tri-*tert*-butylphoshine and sodium *tert*-butoxide produced **1t** in 73% yield.

The reaction of **1d** with excess pentachloroantimony formed **1d(SbCl$_6$)$_2$** which was purified by recrystallization from a dichloromethane−benzene mixture which was evaporated slowly. The isolated yield was 31%, and the experimental values obtained by elemental analysis were in agreement with the calculated values for **1d(SbCl$_6$)$_2$**. In addition, ESR experiments in dichloromethane indicated that the spin concentration amounted to 1.90 spins per molecule. On the other hand, the reaction of **1t** with excess pentachloroantimony formed **1t(SbCl$_6$)$_3$** in 56% yield, instead of a

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complex carrying four $SbCl_6$ anions. Elemental analysis of **1t(SbCl$_6$)$_3$** gave 40.11%, 3.56%, and 2.37% for C, H, and N, respectively, in agreement with the calculated values (C = 40.13%, H = 3.18%, and N = 2.67%). A spin concentration of 2.24 spins per molecule was determined by ESR in dichloromethane for **1t(SbCl$_6$)$_3$**.

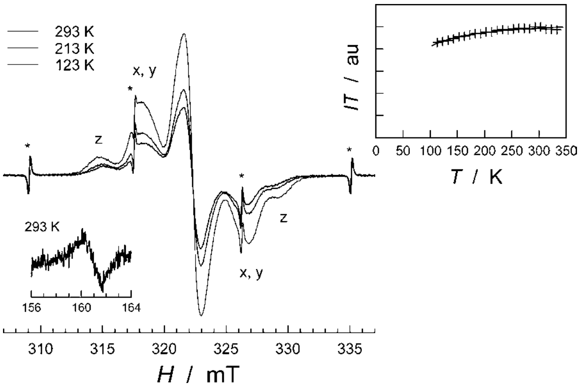

Figure 1. Temperature dependence of ESR spectra of **1d(SbCl$_6$)$_2$** in PMMA matrix (3 wt % content). Asterisks denote signals due to the Mn^{2+} standard. The $IT-T$ plot was obtained by monitoring the triplet signal at 318 mT. The solid line in the $IT-T$ plot represents the least-squares fit using eq 1.

Rigid media ESR spectra of **1d(SbCl$_6$)$_2$** were acquired in poly(methyl methacrylate) (PMMA) matrix in the temperature range of 113−333 K (Figure 1). The ESR spectra clearly showed the triplet signals with the zero-field splitting constants of $|D| = 7.2$ and $|E| \approx 0$ mT. The $\Delta M_S = \pm 2$ forbidden transition was also observed at ca. 160 mT. The D value is larger than the value (3.8 mT) calculated using the point dipole approximation based on the distance between the centers of two phenothiazine units (ca. 9.0 Å). This may be due to delocalization of unpaired electrons around the bond linking two phenothiazine units. The intensity of the triplet signals increased with decreasing temperature. In the $IT-T$ plot in Figure 1, the IT value gradually decreased with decreasing temperature, showing that the triplet state exists in the thermally excited state. The $IT-T$ behavior was analyzed using the Bleaney−Bowers singlet−triplet model (eq 1) to estimate the intramolecular exchange coupling constant (J).

$$IT = C\frac{3}{3 + \exp(-2J/kT)} \qquad (1)$$

The least-squares fit led to a J/k value of −38.5 K ($|R| = 0.977$).

The torsion angle between the two phenothiazine units in **1d(SbCl$_6$)$_2$** was examined using an MO calculation of the J value. Energies of singlet and triplet states were calculated in consideration of the broken-symmetry (BS) problem for the lowest spin state. Spin projection was then performed using eq 2 to eliminate spin contamination effects on the BS lower spin state from higher spin states.[15]

$$J = \frac{E_S - E_T}{\langle S^2\rangle_T - \langle S^2\rangle_S} \qquad (2)$$

The input geometry for MO calculation was constructed from the X-ray crystallographic data of the recently synthesized 3,7-diphenyl-10-*n*-octylphenothiazine cation radical (Figure 2, left).[9e] Because J strongly depends on the torsion angle between the two phenothiazine units, the methyl groups were not needed. MO calculations were performed at the UB3LYP/6-31G(d) level using Gaussian 03.[16] The dihedral angle dependence (∠C5−C4−C4′−C3′) of J is shown in Figure 2 (right). From the J/k value of −38.5 K estimated above, the torsion angle was found to be ca. 80° in **1d(SbCl$_6$)$_2$**, consistent with the corresponding torsion angle in 2,2′,6,6′-tetramethyl-substituted biphenyls (80−97°).[17]

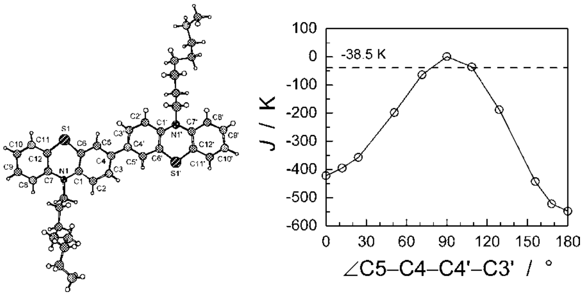

Figure 2. Input geometry for MO calculation (left) and intramolecular exchange coupling constant as a function of dihedral angle (right). C4−C4′ = 1.49 Å and ∠C5−C4−C4−C3′ = 24.2°.

The ESR spectrum of **1t(SbCl$_6$)$_3$** in PMMA matrix showed a single line but did not exhibit signals characterizing high spin states. Spins may be far from each other because of the low spin concentration.

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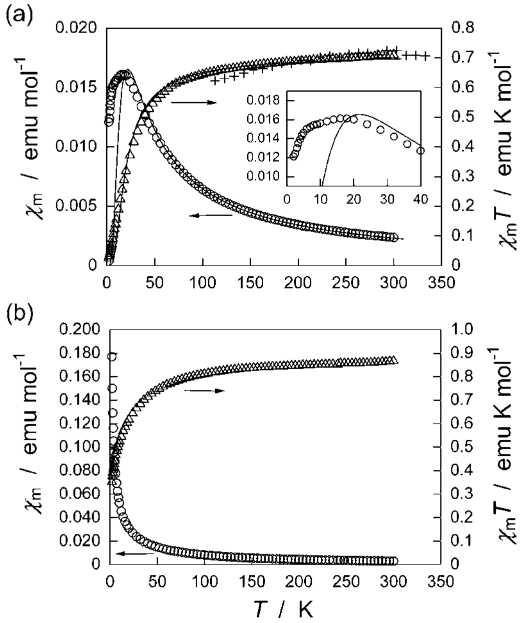

Figure 3. Temperature dependence of magnetic susceptibility of (a) **1d(SbCl$_6$)$_2$** and (b) **1t(SbCl$_6$)$_3$** in bulk solid state. Open circles and triangles correspond to χ_m and $\chi_m T$ data, respectively. Crosses are IT data obtained through ESR measurements in PMMA matrix. The solid line in Figure 3(a) represents the least-squares fit using eq 3.

The magnetic susceptibilities (χ_m) of **1d(SbCl$_6$)$_2$** and **1t(SbCl$_6$)$_3$** were measured at various temperatures in bulk using a SQUID magnetometer (Figure 3). The χ_m value for **1d(SbCl$_6$)$_2$** increased with decreasing temperature up to 20 K. It decreased gradually from 20 to 6 K and then rapidly decreased below 6 K. From 300 to 100 K, the $\chi_m - T$ behavior was in good agreement with the $IT - T$ behavior observed by ESR measurements in PMMA matrix. ESR signal intensity is proportional to magnetic susceptibility. The $\chi_m - T$ behavior up to around 6 K was probably mainly due to an intramolecular singlet–triplet behavior. The $\chi_m - T$ behavior below 6 K arose from intermolecular antiferromagnetic interactions. The $\chi_m T - T$ behavior above 10 K was analyzed the Bleaney–Bowers singlet–triplet model (eq 3).[18]

$$\chi_m T = f\frac{2Ng^2\beta^2}{k}\frac{1}{3 + \exp(-2J/kT)} \tag{3}$$

The least-squares fit resulted in values of 0.963, 1.99, and −17.4 K for f, g, and J/k, respectively ($|R| = 0.994$).

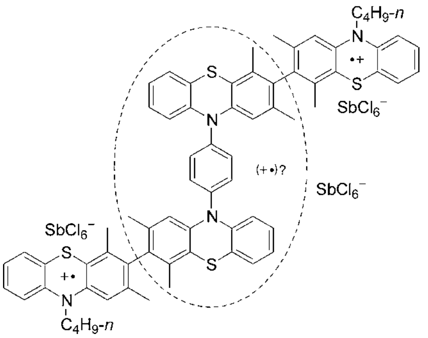

Figure 4. Potential structure of **1t(SbCl$_6$)$_3$**.

The $\chi_m T$ value for **1t(SbCl$_6$)$_3$** at 300 K was 0.867 emu K mol^{-1}. This value is in good agreement with the value (0.840) calculated from a spin concentration of 2.24 spins per molecule and 0.375 emu K mol^{-1} for a species with $S = 1/2$. This suggests that there are two isolating $S = 1/2$ species in **1t(SbCl$_6$)$_3$**. A potential structure for **1t(SbCl$_6$)$_3$** is shown in Figure 4. In this structure, one SbCl$_6$ anion is positionned at the center two phenothiazine units containing the 1,4-phenylene spacer, while each of the other SbCl$_6$ anions are at each phenothiazine extremity. Only 0.24 spins may be generated at the center two phenothiazines circled by the dotted line in Figure 4. The 3,7-bis(di-4-anisylamino)-10-*n*-octylphenothiazine–SbCl$_5$ complex, which was synthesized previously, displayed only a spin concentration of 0.15 spins per molecule.[9d] This low spin concentration may be due to unexpected oxidation at the 1,4-phenylenediamino moieties. A similar unexpected oxidation may occur at the 1,4-phenylenediamino moiety in **1t(SbCl$_6$)$_3$**. The $\chi_m T$ value decreased with decreasing temperature, consistent with antiferromagnetic interactions.

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Supporting Information Available: Synthetic procedure, ESR spectra, and MO calculation results. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) The least-squares fit to the $\chi_m T$-T plot gave better fitting than that to the $\chi_m - T$ plot. The solid line to the $\chi_m - T$ plot in Figure 3a is artificially drawn using parameters estimated in the least-squares fit.