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Magnetic Properties of Some Iminoxyl Polyradicals. II. TEMPOP Triradical and TEMPOS Tetraradical

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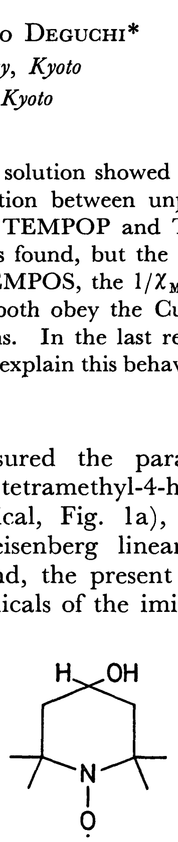
The EPR spectra of the TEMPOP triradical and the TEMPOS tetraradical in solution showed seven and nine absorption lines respectively, which were interpreted as the hyperfine interaction between unpaired electron and ^{14}N nuclei in the case of $|J_{\rm in}| \gg A$. The paramagnetic susceptibilities of TEMPOP and TEMPOS were measured. In the case of TEMPOP, no typical short-range ordering effect was found, but the $1/\chi_{\rm M}-T$ curve deviated from the Curie-Weiss law at very low temperatures. In the case of TEMPOS, the $1/\chi_{\rm M}-T$ curve was divided into four regions. In the first and third regions, the $1/\chi_{\rm M}-T$ curves both obey the Curie-Weiss law. The second region is the intermediate region between the first and third regions. In the last region, $1/\chi_{\rm M}-T$ shows a slight deviation from the Curie-Weiss law of the third region. In order to explain this behavior, some spin-cluster models with three and four spins were applied.

Recently, the magnetic properties of many organic stable free radicals have been investigated very actively.[1–5] It has been reported that many of these organic radicals exhibit some effects of the coupling of magnetic spins—for example, spin cluster or low-dimensional spin array—caused by an exchange interaction between unpaired electrons.

Among these, the iminoxyl radicals are the most interesting group, since they are very stable and many derivatives can be synthesized.[6,7]

Karimov and Rozantsev reported the EPR studies of some solid stable iminoxyl radicals and interpreted them in terms of the effect of the exchange interaction between unpaired electrons belonging to different radicals.[4b] Yamauchi *et al.*[5b] and Karimov[4c,4d] independently measured the paramagnetic susceptibility of 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl (TANOL radical, Fig. 1a), characterized as a one-dimensional Heisenberg linear chain.

On the other hand, the present authors had an interest in the polyradicals of the iminoxyl group as spin


a TANOL

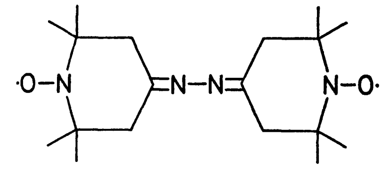
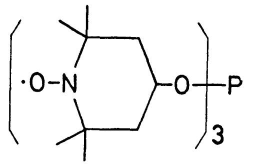

b TEMPAD

Fig. 1. Molecular structures of TANOL radical (a) and TEMPAD biradical (b).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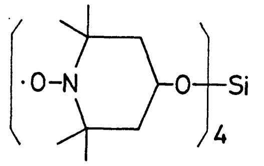
b TEMPOS

Fig. 2. Molecular structures of TEMPOP triradical (a) and TEMPOS tetraradical (b).

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clusters. In a previous work, we reported the paramagnetic susceptibility of bis(2,2,6,6-tetramethylpiperidine-4)azine-1,1′-dioxyl (TEMPAD biradical, Fig. 1b) and explained it as a pairing caused by an intra-molecular exchange interaction,[5a] but recent study has made it clear that the inter-molecular interaction is only the origin of the short-range ordering in the TEMPAD biradical.[8]

In this paper, we shall report the magnetic properties of two polyradicals, tris(2,2,6,6-tetramethylpiperidine-1-oxyl-4)phosphate (the TEMPOP triradical, Fig. 2a) and the tetrakis(2,2,6,6-tetramethylpiperidine-1-oxyl-4)silicate (the TEMPOS tetraradical, Fig. 2b), and will discuss them on the basis of some spin-cluster models.

Experimental

The TEMPOP triradical was prepared from the TANOL radical obtained by the oxidation of the corresponding amine by hydrogen peroxide, following the method of Neiman *et al.*[9] The TEMPOS tetraradical was also prepared from the same monoradical by the method of Rozantsev and Gulobev.[10] After purification by chromatography and recrystallization, the pure TEMPOP and TEMPOS (mps 143.5±0.5 and 160±1°C respectively) were obtained.

The electron paramagnetic resonance absorptions were measured using two 100 kHz modulated X-band spectrometers, JEOLCO's JES-3BX and JES-P-10.

The static magnetic susceptibility was measured with about 50—100 mg powder samples over the temperature range of 1.8—273°K and at a magnetic field strength of about 8—9 kOe, using a torsion balance described elsewhere.[11] All the data were corrected for the diamagnetic contribution calculated by the Pascal method (-3.57×10^{-4} emu/mol for the TEMPOP triradical and -4.82×10^{-4} emu/mol for the TEMPOS tetraradical).

Results and Discussion

TEMPOP Triradical. The EPR spectrum of the TEMPOP triradical in a tetrahydrofuran (THF) solution shows seven lines, all caused by the hyperfine interaction between three unpaired electrons and three ^{14}N nuclei, the splitting of which is 5.18 gauss and the g-value of which is 2.0060 (Fig. 3).[12] The spin Hamiltonian of this system is:

$$\mathscr{H} = -g\beta\mathrm{H}\cdot(\boldsymbol{S}_1+\boldsymbol{S}_2+\boldsymbol{S}_3) + A\sum_{i=1}^{3}\boldsymbol{I}_i\cdot\boldsymbol{S}_i + J_{\mathrm{in}}\sum_{\langle i,j\rangle}\boldsymbol{S}_i\cdot\boldsymbol{S}_i, \qquad (1)$$

where A is the hyperfine interaction parameter and where J_{in} is the intra-molecular exchange interaction. When $|J_{\mathrm{in}}|\gg A$, the theoretical spectrum shows seven lines with an intensity ratio of 1 : 3 : 6 : 7 : 6 : 3 : 1. The experimental spectrum does not correspond accurately to this extreme case. We must pay attention to the fact that the line-widths of the inner three lines are fairly broad even in a very dilute solution. One may be able to explain them in terms of the dipole-dipole interaction between three unpaired electrons and/or some effects caused by the exchange interaction, which is not very large compared with the hyperfine interaction.[13] Taking account of this explanation, one can conclude that $A\leq|J|\ll kT$.

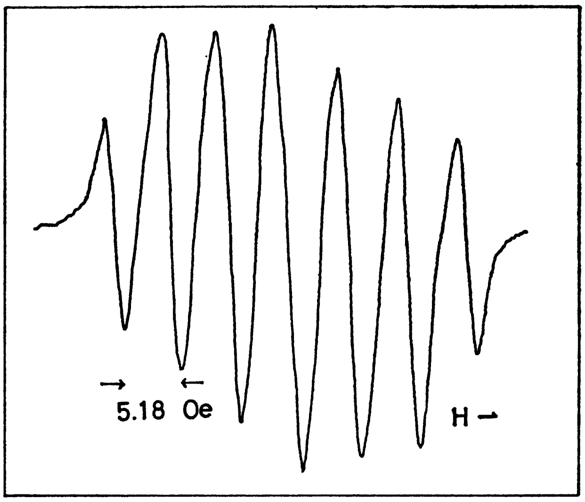

Fig. 3. The EPR spectrum of TEMPOP triradical in THF solution.

The inverse paramagnetic susceptibility of the powder TEMPOP triradical *versus* the temperature is shown in Fig. 4. The curve obeys the Curie-Weiss law except in the very low temperature region. The Curie constant, the effective Bohr magneton, and the Weiss constant, corresponding to a molecule with three unpaired electrons, are listed in Table 1. The devi-

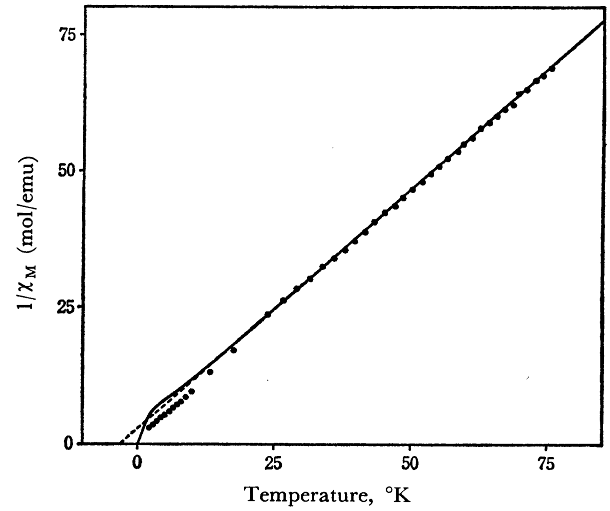

Fig. 4. The inverse paramagnetic susceptibility of powdered TEMPOP triradical *versus* temperature (truncated for clarity showing susceptibity between 1.8 and 77°K). The solid curve is that of the spin cluster with three spins of Eq. (3) as $J=-2.7$°K.

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Table 1. Some magnetic constants of TEMPOP triradical at the high temperature range compared with the calculated values of three spins with $S=1/2$ and $g=2.00$

Constant	Experimental	Calculation
C	1.14	1.141
μ_{eff}	3.01	3.000
θ	−3.5°K	—

C: the Curie constant
μ_{eff}: the effective Bohr magneton
θ: the Weiss constant

ation from the Curie-Weiss law in the very low temperature region probably suggests a short range ordering effect caused by the exchange interaction between spins belonging to different molecules.

The spin-cluster Hamiltonian with three spins, involving the exchange and Zeeman terms, is given by:

$$\begin{aligned}\mathscr{H} &= -2(J_{12}\boldsymbol{S}_1\cdot\boldsymbol{S}_2+J_{23}\boldsymbol{S}_2\cdot\boldsymbol{S}_3+J_{31}\boldsymbol{S}_3\cdot\boldsymbol{S}_1)\\ &\quad - g\beta\mathrm{H}\cdot(\boldsymbol{S}_1+\boldsymbol{S}_2+\boldsymbol{S}_3) \qquad (2)\end{aligned}$$

with the following eigen values:

a. *Quartet State*:

$$E_q = -(J_{12}+J_{23}+J_{31})/2 - g\beta\mathrm{H}m \qquad (m = 3/2,\ 1/2,\ -1/2,\ -3/2)$$

b. *Doublet State*:

$$\begin{aligned}E_{d\pm} &= (J_{12}+J_{23}+J_{31}) - g\beta\mathrm{H}m\\ &\quad \pm [2\{(J_{12}-J_{23})^2 + (J_{23}-J_{31})^2 + (J_{31}-J_{12})^2\}]^{1/2}\\ &\quad (m = 1/2,\ -1/2)\end{aligned}$$

The paramagnetic susceptibility is given from the Van Vleck formula,[24] and when $J_{12}=J_{23}=J_{31}=J$ (negative), the theoretical susceptibility is given by:

$$|J|\chi_{\mathrm{M}}/N(g\beta)^2 = (x/4)(5+\mathrm{e}^{3x})/(1+\mathrm{e}^{3x}) \qquad (x = |J|/kT). \qquad (3)$$

This curve is shown in Fig. 4 as $J=-2.7$°K.

As for the TEMPOP triradical one can conclude from Fig. 4 that the exchange interaction appearing in the static susceptibility is fairly weak compared with kT, and no typical short-range ordering effect can be found.

TEMPOS Tetraradical. The EPR spectrum of the TEMPOS tetraradical in the THF solution shows nine lines, all of them caused by the hyperfine interaction between four unpaired electrons and four ^{14}N nuclei, the splitting of which is 3.94 gauss and the g-value of which is 2.0058 (Fig. 5).[12] The spin Hamiltonian of this system is:

$$\mathscr{H} = -g\beta\mathrm{H}\cdot\sum_{i=1}^{4}\boldsymbol{S}_i + \mathrm{A}\sum_{i=1}^{4}\boldsymbol{I}_i\cdot\boldsymbol{S}_i + J_{\mathrm{In}}\sum_{\langle i,j\rangle}\boldsymbol{S}_i\cdot\boldsymbol{S}_j \qquad (4)$$

When $|J_{\mathrm{In}}|\gg A$, $g\beta$H, the theoretical spectrum shows nine lines with the intensity ratio of 1 : 4 : 10 : 14 : 19 : 14 : 10 : 4 : 1; the experimental results just agree.

The inverse paramagnetic susceptibility of the powder TEMPOS tetraradical *versus* the temperature is shown in Fig. 6. It is appropriate to divide the curve into four regions (Region I: above 25°K, II: from 15 to 25°K, III: from 5 to 15°K, and IV: below 5°K). In the I and III regions, the $1/\chi_{\mathrm{M}}$-T curve obeys the Curie-Weiss law. The magnetic constants of these two regions are listed in Table 2. The II region is the intermediate region between I and III. The temperature dependence of the χ_{M} in these three regions suggests the formation of a spin

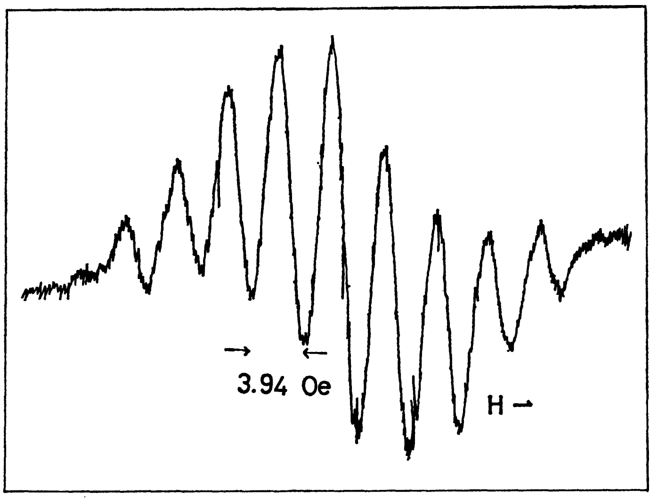

Fig. 5. The EPR spectrum of TEMPOS tetraradical in THF solution.

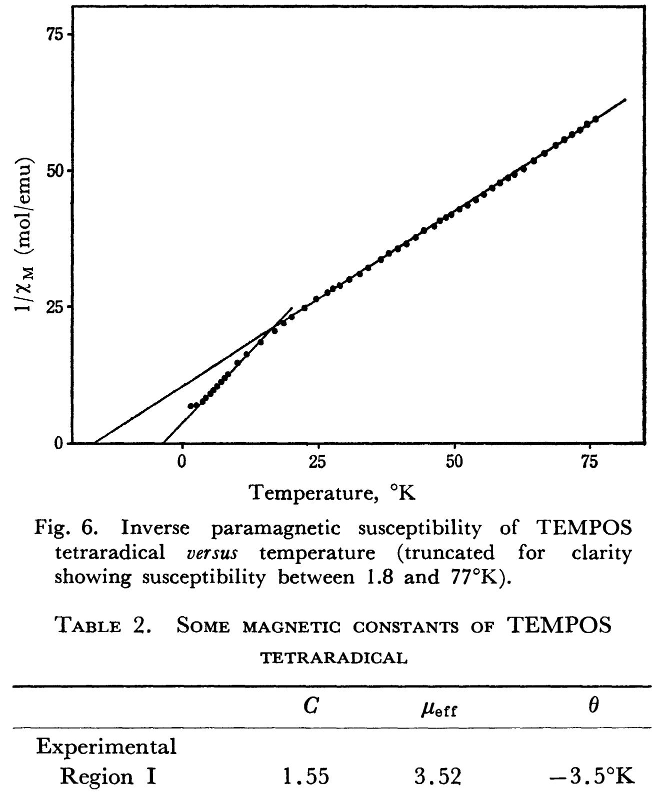

Fig. 6. Inverse paramagnetic susceptibility of TEMPOS tetraradical *versus* temperature (truncated for clarity showing susceptibility between 1.8 and 77°K).

Table 2. Some magnetic constants of TEMPOS tetraradical

	C	μ_{eff}	θ
Experimental			
Region I	1.55	3.52	−3.5°K
Region III	0.98	2.80	−16°K
Calculation			
$S_{\mathrm{total}}=1$	1.01	2.83	—
Four spins with $S=1/2$	1.51	3.46	—

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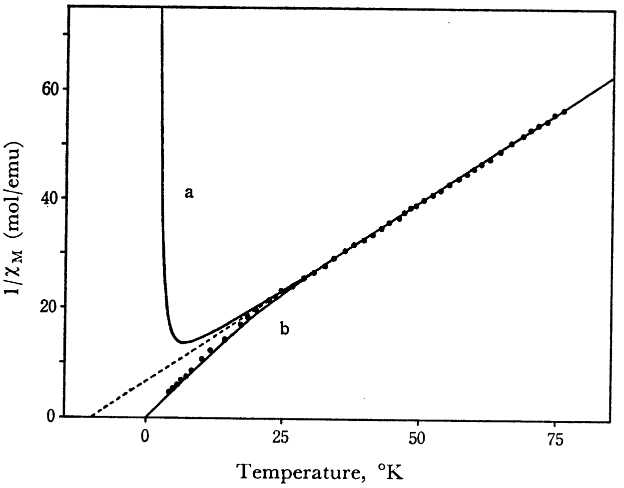

Fig. 7. Inverse paramagnetic susceptibility of TEMPOS tetraradical which was corrected for the inter-cluster interaction by multiplying $T/(T+3.5)$ with $1/\chi_M$. The solid curves are the theoretical $1/\chi_M-T$ of the spin cluster models with for spins: a) Tetrahedral model ($J=-5.55$°K), b) Trigonal model ($J=-15.9$°K).

cluster caused by the exchange interaction. In the IV region, the $1/\chi_M-T$ shows a slight deviation from the Curie-Weiss law of the III region, with $\theta=-3.5$°K; this suggests the existence of an inter-cluster interaction, but in this paper, treating the exchange interaction in a cluster, we will not discuss the inter-cluster interaction further.

Now let us come back to our discussions of the I, II, and III regions. For the analysis of the results, two essential experimental parameters are taken into account. One is the μ_{eff} of the III region, which will give the total spin of the ground state; the other is the ratio of the Curie constants between the I and III regions ($\rho=C_I/C_{III}$), which indicates the relation of the spin states between the high- and low-temperature regions. In our case, $\mu_{\text{eff}}=2.80$—which corresponds to the total spin, S=1—and $\rho=1.58$.

As the TEMPOS tetraradical has four spins in a molecule, some spin-cluster models with four spins are applicable.[15] The spin Hamiltonian of the cluster models is:

$$\mathscr{H} = -2\{J_{12}\boldsymbol{S}_1\cdot\boldsymbol{S}_2 + J_{13}\boldsymbol{S}_1\boldsymbol{S}_3 + J_{14}\boldsymbol{S}_1\cdot\boldsymbol{S}_4 + J_{23}\boldsymbol{S}_2\cdot\boldsymbol{S}_3 + J_{24}\boldsymbol{S}_2\cdot\boldsymbol{S}_4 + J_{34}\boldsymbol{S}_3\cdot\boldsymbol{S}_4\} \quad (5)$$
$$(\text{all } \boldsymbol{S}_i = 1/2)$$

Table 3. Some spin cluster models with four spins

Model	$\lvert J\rvert\chi_M/N(g\beta)^2$	ρ	J
Tetrahedral	$\dfrac{2\times(5+e^{4x})}{5+9e^{4x}+2e^{6x}}$	—	−5.55°K
Rhombus	$\dfrac{2\times(5+e^{2x}+2e^{4x})}{5+3e^{2x}+7e^{4x}+e^{6x}}$	—	—
Trigonal	$\dfrac{2\times(5+e^{x}+2e^{4x})}{7+3e^{x}+6e^{4x}}$	1.50	−15.9°K

$S=1/2$ for all spins and $x=|J|/kT$. ρ is the ratio of the Curie constants between high and low temperature ranges. J was determined from the experimental Weiss constant, $\theta=-10$°K.

and the paramagnetic susceptibilities of each model, which is derived from the Van Vleck formula,[14] are listed in Table 3. The theoretical $1/\chi_M-T$ curves of two typical models (tetrahedral and trigonal) are shown in Fig. 7 in comparison with the experimental result corrected for the inter-cluster interaction by multiplying $T(T+3.5)$ by $1/\chi_M$; the latter trigonal model ($\mu_{\text{eff}}=2.83$, $\rho=1.50$) agrees exactly with the experimental result, as $J=-15.9$°K. In our further discussions, we must proceed to a structural study of these polyradicals.

Summary

The paramagnetic susceptibilities of the TEMPOP triradical and the TEMPOS tetraradical have been measured; we have found some deviations from the Curie-Weiss law caused by an exchange interaction between electron spins. Though we could not make clear whether or not the exchange interaction occurs in a molecules, we adopted some spin-cluster models with three and four spins as one step to interpreting the experimental phenomena.

In TEMPOP triradical, we could find no suitable model, for this radical did not indicate any typical ordering phenomenon at any measuring temperature used so far. On the other hand, in the TEMPOS tetraradical, we found a short-range ordering effect and applied the spin-cluster models with four spins. The trigonal model best fit the experimental results.

The authors are very much obliged to Professor H. Takaki for his continuing guidance and encouragement through this work. The authors are also deeply indepted to Professor M. Mekata, Mr. J. Yamauchi and their collaborators for their helpful advice and discussions.

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[15] Of course we cannot say definitely that the exchange interaction occurs exclusively in a molecule, and the probability of the inter-molecular interaction will not be ommitted. Here we must understand that the above-mentioned models will be only practical ones.[8]