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The Magnetic Properties of Some Iminoxyl Polyradicals. IV. The Paramagnetic Susceptibilities of the Diluted Crystals of the TEMPAD Biradical

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The paramagnetic susceptibilities of the diluted crystals of bis(2,2,6,6-tetramethylpiperidine-4)azine-1,1′-dioxyl (the TEMPAD biradical) have been measured from 1.8 to 77.3 K. The χ_M-T curves obey the Curie-Weiss law in the high and low temperature regions, and two kinds of the Weiss constant were found. The Weiss constant in the high-temperature region, which is caused by the strong inter-molecular exchange interaction, varies with the radical concentration from -8.5 to -15 K. The Weiss constant in the low-temperature region is of the order of magnitude of -1 K and reveals the existence of a weak intra-molecular exchange interaction. We can assume that the TEMPAD biradicals are distributed randomly in the matrix of the diamine and that they form either an isolated portion in which the weak intra-molecular exchange interaction exists only, or a clustering portion coupled by a strong inter-molecular exchange interaction besides the intra-molecular one. Then, the concentration dependence of the χ_M-T curves can be explained as the superposition of the contributions from these two portions. The curves caluclated on the assumption of the random distribution agreed with the experimental results.

There are many works concerned with the magnetic properties of organic stable free radical solids, which were introduced in Part II of the present series.[1] In these works some short-range ordering effects caused by exchange interaction among the unpaired electron spins were observed, and the linear chain or the spin-cluster model was applied. These two models are based on the localized spin treatment as in the case of the transition-metal ion salts. In iminoxyl radicals the unpaired electron is localized around the N–O bond, so they can also be treated as localized spin systems.

Previously the present author and his colleagues reported on these magnetic study of bis(2,2,6,6-tetramethylpiperidine-4)azine-1,1′-dioxyl (the TEMPAD biradical) and bis(2,2,6,6-tetramethylpiperidine-4)sulfite-1,1′-dioxyl (the sulfite biradical), and concluded that the strong inter-molecular exchange interaction has a

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[1] A. Nakajima, H. Ohya-Nishiguchi, and Y. Deguchi, This Bulletin, **44**, 2120 (1971). Please refer the added two works. J. Yamauchi, This Bulletin, **44**, 2301 (1971). W. Duffy, Jr., J. F. Dubach, P. A. Pianneta, J. F. Deck, D. L. Strandburg, and A. R. Miedema, *J. Chem. Phys.*, **56**, 2555 (1972).

short-range ordering effect in both biradicals.[2,3]

In this paper the author will report on the paramagnetic susceptibilities of the diluted crystals of the TEMPAD biradical and will discuss the intra- and inter-molecular exchange interactions in these systems.

Experimental

The TEMPAD biradical and bis(2,2,6,6-tetramethylpiperidine-4)azine (the diamine corresponding to the TEMPAD biradical), shown in Fig. 1, were prepared from 2,2,6,6-tetramethyl-4-piperidone supplied by the Aldrich Chemicals Co.; this substance was introduced in a previous paper.[3]

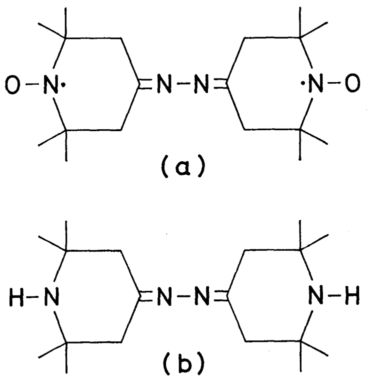

Fig. 1. Molecular structure of the TEMPAD biradical (a) and the corresponding diamine (b).

The space groups and the lattice constants of the TEMPAD biradical and the corresponding diamine listed in Table 1 are nearly equal to each other, so the diluted crystals of the TEMPAD biradical in its diamine can be prepared in various concentration ratios. The diluted crystals with 75, 50, and 25 mol% were crystallized from their ether solutions, and their elementary analyses agreed with the calculations.

Table 1. The space groups and the lattice constants for the diamine and the TEMPAD biradical

Name	Diamine	TEMPAD
Space-group	Monoclinic C_c	Monoclinic C_c or $C_{2/c}$
a	29.0 Å	29.1 Å
b	12.6	12.8
c	10.4	10.5
β	~90°	~90°

The paramagnetic susceptibility measurements were carried out using a torsion balance with powder samples from 77.3 to 1.8 K, the details of which have been described in the previous paper.[3] The diamagnetic contributions of the TEMPAD biradical and the diamine were calculated at -2.37×10^{-4} and -2.33×10^{-4} emu/mol respectively. The diamagnetic contributions of the diluted crystals were estimated as the sum of the aforementioned two values multiplied by each concentration ratio.

Results and Discussion

The inverse paramagnetic susceptibilities of the 100, 75, 50, and 25 mol% TEMPAD biradicals versus the temperature are shown in Fig. 2. Each curve obeys the Curie-Weiss law above 30K and below 4K except for the 100% case. The paramagnetic Curie constants and the Weiss constants of each concentration in these temperature regions are listed in Table 2.

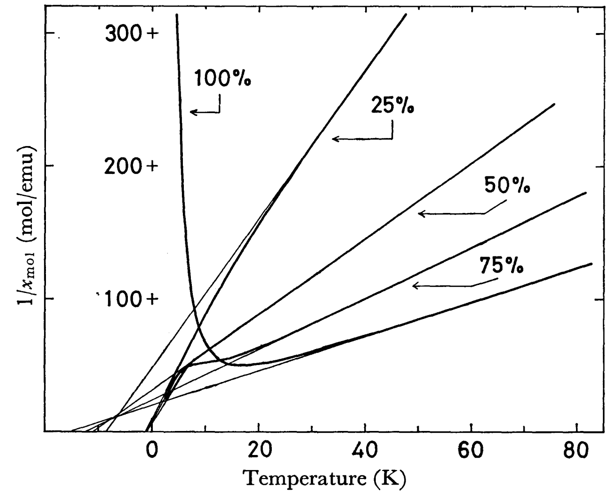

Fig. 2. Temperature dependence of the inverse paramagnetic susceptibilities of the diluted crystals of the TEMPAD biradical for 100, 75, 50, and 25 mol %.

Table 2. The experimental and the theoretical magnetic constants for each concentration. The latters are in the case of $|J_1|/k=12.8\text{K}$ and $\alpha=1/20$.

n (%)	Experimental				Calculation	
	C_L	C_H	θ_L	θ_H	C_H	θ_H
25	0.131	0.181	−1.0	−8.5	0.189	− 3.20
50	0.158	0.368	−1.0	−11.0	0.378	− 5.25
75	0.146	0.537	−1.1	−12.5	0.574	− 7.95
100	—	0.770	—	−15.0	0.772	−10.8

C_H and C_L: the paramagnetic Curie constants
θ_H and θ_L: the Weiss constants (K).

The Weiss constant generally indicates the magnitude of the exchange interaction among the coupled magnetic spins. In the diluted crystals of the TEMPAD biradical, two kinds of Weiss constant were found, in the high- and in the low-temperature regions. The Weiss constant in the high-temperature region, which is of

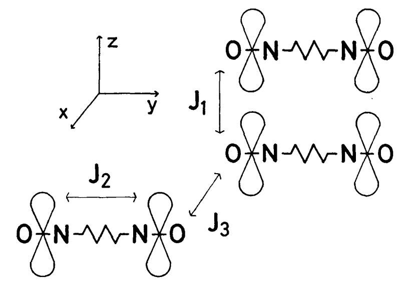

Fig. 3. Simplified molecular stack model for the TEMPAD biradical.

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2) A. Nakajima, H. Nishiguchi, and Y. Deguchi, *J. Phys. Soc, Jap.*, **24**, 1175 (1968).

3) A. Nakajima, H. Ohya-Nishiguchi, and Y. Deguchi, This Bulletin, **45**, 713 (1972).

the order of magnitude of -10K, must be caused by the strong exchange interaction. On the other hand, the Weiss constant in the low-temperature region is of the order of magnitude of -1K.

By the dilution of the monoradical the inter-molecular exchange interaction can generally be eliminated, thus leading to the disappearance of the broad maximum in the χ_M-T curve. In the TEMPAD biradical two kinds of exchange interaction exist (see Fig. 3);[4] one is the strong inter-molecular exchange interaction (J_1), which causes the short-range ordering effect in the 100% case.[2] The other is the weak intra-molecular exchange interaction (J_2), which affects the hyperfine structure of the EPR in the dilute solution.[3] In the diluted crystals of the TEMPAD biradical, we can assume that the biradicals are distributed randomly in the matrix of the diamine and that they form two portions magnetically different in microscopical scale; one is the isolated portion in which the weak intra-molecular exchange interaction exists alone, and the other is the clustering portion coupled by the strong inter-molecular exchange interaction besides the intra-molecular one. Then the paramagnetic susceptibility of the diluted crystals may be considered to the superposition of the contributions from these two portions. If we adopt the pair model for the clustering portion and apply the Weiss molecular-field approximation for the weak intra-molecular exchange interaction, the theoretical susceptibility can be calculated on the assumption of the following random distribution:

$$|J_1|\chi_M/N_0(g\beta)^2 = 2[n^2x/(3+e^{2x})+n(1-n)x/4]/(1+\alpha x),$$

where $x=|J_1|/kT$; $\alpha=|J_2/J_1|$; N_0 is the Avogadro number; g, the g-value (2.0060 for the TEMPAD biradical[5]); β, the Bohr magneton, and n, the mole concentration of the biradical. The first term is the susceptibility of the pair model (the clustering portion), and the second term is that of the isolated portion. The theoretical $1/\chi_M-T$ curves for $|J_1|/k\simeq 12.8$K and $\alpha=1/20$ are shown in Fig. 4, while the theoretical paramagnetic Curie constants and the Weiss constants are listed in Table 2. They are in good qualitative agreement with the experimental results.

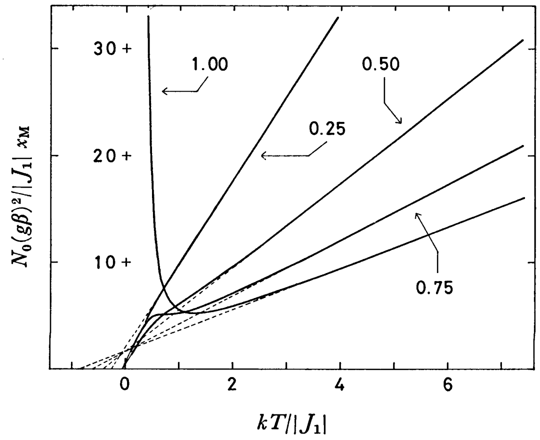

Fig. 4. Theoretical curves of the inverse paramagnetic susceptibility of the diluted systems for $n=1.0$, 0.75, 0.50, and 0.25 in the case of $\alpha=|J_2/J_1|=1/20$.

The exchange energy estimated from the Weiss constants in the low-temperature region is still larger than the value estimated from the EPR spectra in the dilute solution.[3] This is possibly caused by the difference in magnitude of the intra-molecular exchange interaction (J_2 in Fig. 3), which results from the distinction of the molecular conformation between the solid state and the dissolved state, and by the existence of another inter-molecular exchange interaction, *e.g.*, J_3 in Fig. 3.

The pair model was applied to the clustering portion on the basis of the random distribution, but the experimental results are different from those calculated—the value of χ_M deviates from the pair model near T_{max} ($=16.5$K) in the 100% case[2] and the' Weiss constants of the high-temperature region are different from the calculated values (Table 2). If the TEMPAD molecules are distributed randomly enough in the diamine host, we must consider the higher-order clusters (trimers, tetramers, and so on) besides the pairs. As the data were explained qualitatively by the pair-model at so high a concentration, it may be suggested that the systems are fairly uniform.

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[4] From the crystal structure, the distance between unpaired electrons in x-, y-, and z-directions are thought to be nearly equal to each other. Then the overlap integral will be the largest in the z-direction, namely $|J_1|>|J_2|$, $|J_3|$. The study of the dipolar interaction in ESR spectra also support this assumption.[5]

[4] A. Nakajima, to be published.