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METAL-NITROXYL SPIN EXCHANGE INTERACTION OBSERVED FOR THE IMINOXYL LABELED Co(II)- TETRAPHENYLPORPHYRIN

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A typical AB type featured to spin-spin exchange interaction was observed for the ESR of the iminoxyl adduct of the low spin tetraphenylporphyrin-Co(II) complex. A scalar spin-spin exchange interaction (J) between the nitroxide and the metal site was successfully extimated from the line separation in the observed AB type doublet splitting.

The spin-spin exchange interaction between the biogenic radical intermediate and the low spin Co(II) site of coenzyme B_{12} has been extensively studied by ESR.[1-4] In these cases, however, the geometrical structure of the radical adduct has not been well documented. In order to compile the fundamental views on the ESR hyperfine structure arised from electron spin-spin exchange or dipole-dipole interaction, which varies as a function of the separating distance (r) between the metal and the radical site, the iminoxyl spin adduct of the low spin Co(II) complex with a fixed distance (r) was synthesized, and the ESR of the spin adduct was investigated using tetraphenylporphyrin(TPP) as a model ligand.

In this paper, we wish to report the first example of AB type ESR, where the spin-spin interaction between the Co(II) low spin site ($3d^7$, S=1/2) and the axially coordinated label was clearly detected. The TPP-Co(II) complex was prepared as previously reported.[5,6] The spin labeled ligand used here is a Schiff base

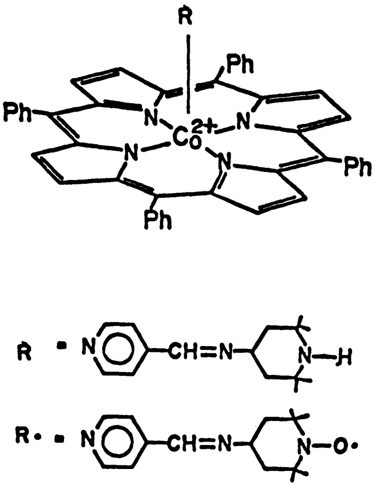

Fig. 1.. Structure of TPP-Co(II) adducts.

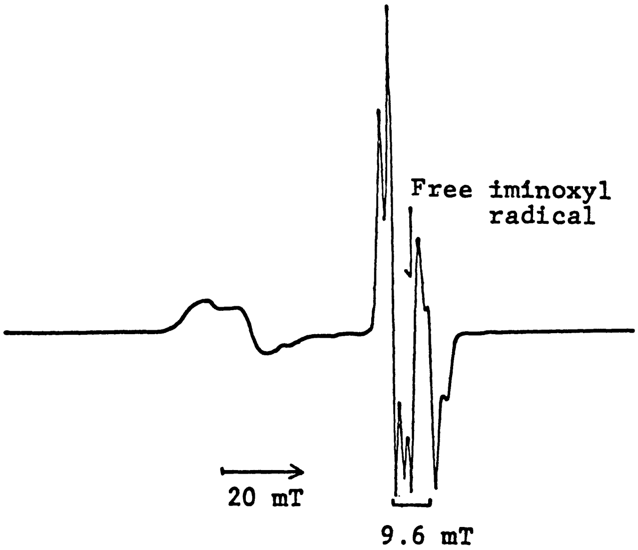

Fig. 2. ESR spectrum of TPP-Co(II)-R· adduct observed in toluene at 77 K.

Table 1. ESR parameters of TPP-Co(II)-R adducts. (A: $\times 10^{-4}$ cm^{-1})

	$\lvert A_{\parallel}\rvert$	$\lvert A_{\perp}^{R}\rvert$	$\lvert A_{0}\rvert$	$g_{\parallel}$	$g_{\perp}$	g_{0}	$\lvert A_{N}\rvert$	
Pyridine	78.7	11	35	2.027	2.236	2.226	15.7	Ref. 8)
R	81.4	11	36	2.025	2.321	2.222	16.1	This work

synthesized from pyridine-4-aldehyde and 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl.[7)] A purity of the material was checked by the melting point, IR and ^{1}H-NMR indices. The ESR measurements were carried out for the toluene solution containing the TPP-Co(II) complex and the spin label in the equimolar ratio. The ESR parameters obtained for TPP-Co(II) complex ligated by the radical precursor (R), 4-[(2,2,6,6-tetramethyl-4-piperidyl)iminomethyl]pyridine (Table 1), were very close to those reported for TPP-Co(II)-pyridine complex taking the square pyramidal geometry with the pyridine residue R at the apical position[8)] (Fig. 1).

The ESR spectrum of the spin adduct, TPP-Co(II)-R• is given in Fig. 2. At the lower field side, one will see that the hyperfine structure of the Co(II) site with axially symmetric g-component, further split into a doublet structure due to the spin-spin exchange interaction J. On the other hand, at the higher field side, a pair of triplet structure composed of the anisotropic electron-nuclear hyperfine splitting of the iminoxyl nitrogen atom is clearly separated by $|J|=9.6$ mT. The averaged value $\bar{g}_0=2.114$ obtained from the isotropic g_0 value of each paramagnetic site ($g_0^{Co}=2.222$, $g_0^{R}=2.006$) is actually equal to that ($\bar{g}_0=2.110$) estimated from the center of the AB system, when the J splitting is taken into account. The ESR is thus adequately analyzed in terms of the following spin Hamiltonian;

$$\hat{H} = g_0^{Co}\beta\hat{S}_1\cdot\vec{H} + g_0^{R}\beta\hat{S}_2\cdot\vec{H} + hJ\hat{S}_1\cdot\hat{S}_2 .$$

The expected line intensity ratio (I) can be calculated as a function of J, that is,

$$I = \frac{(g_0^{Co}\sin\theta + g_0^{R}\cos\theta)^2}{(g_0^{Co}\sin\theta - g_0^{R}\cos\theta)^2}, \quad \tan 2\theta = \frac{J}{(g_0^{Co} - g_0^{R})(\beta H/h)} \qquad 9)$$

By substituting the experimental J value into the equation, the expected intensity ratio calculated is very close to that observed (2:1). A distance (r) estimated from the molecular model of this spin adduct is about 12 Å. The estimated value of r is reasonable, when it is compared with the reported value for nitroxyl biradical.[10)]

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