CHEMISTRY LETTERS, pp. 131-132, 1974. Published by the Chemical Society of Japan

TRIPLET STATE ESR OF 1,10-PHENANTHROLINE AND 2,9-DIMETHYL-1,10-PHENANTHROLINE METAL CHELATES

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Triplet state ESR spectra of 1,10-phenanthroline and 2,9-dimethyl-1,10-phenanthroline metal chelates are reported with their zero-field splitting parameters.

During the course of the study of magnetic properties of organic free radicals,1) 1,10-phenanthroline and its methyl derivative metal chelates have been studied in their solutions and crystal solids. Weissman et al. reported the ESR study of triplet state of 1,10-phenanthroline derivative alkaline-earth metal chelates2,3) except for that of 1,10-phenanthroline metal chelate. The authors will report the ESR observation of the triplet states of 1,10-phenanthroline and its methyl derivative metal chelates.

1,10-phenanthroline and 2,9-dimethyl-1,10-phenanthroline metal chelates were reduced with the metal amalgum in 2-dimethyltetrahydrofuran(MeTHF) where the metals were lithium and calcium. Concentration of the sample was carefully adjusted so that the triplet state ESR spectra were intensely observed. The ESR spectra were measured at 77 K by an X-band ESR spectrometer(JEOL ME-3) equipped with 100kHz field modulation.

In Fig.1 the ESR spectrum of triplet state of 1,10-phenanthroline lithium chelate is shown as one of the examples. In our case, we may safely assume as E=0 in the triplet state spin Hamiltonian,3) which may then be written as

$$\mathcal{H} = g\beta H\cdot S + D\left(S_z^2 - \frac{1}{3}S^2 \right). \qquad (1)$$

Thus the zero-field splitting parameter D will be given as

$$D = -\frac{3}{2} g^2\beta^2 \left\langle 1/\bar{r}^3{}_{1,2} \right\rangle .^{4)} \qquad (2)$$

The zero-field splitting parameters of these metal chelates are shown in Table I. The distances($\bar{r}_{1,2}$) between a pair of unpaired electrons of 2,9-dimethyl-1,10-phenanthroline metal chelates are longer than those of 1,10-phenanthroline metal chelates. This result will be understood if one will take account of the steric hindrance effect of the methyl groups attached to the molecule when forming a dimer.

We also investigated sodium and potassium chelates of both compounds, but the absorption spectra of their triplet states were almost hidden in those of the monomers. Hence we may conclude that the magnitude of D parameter of sodium or potassium chelate will be less than about 80 gauss.

Our data suggest that $\bar{r}_{1,2}$ is proportional to the ionic radius of each cation.

The dimer structures of these metal chelates will be illustrated by the similar model to that proposed by Weissman et al.[3)]

Half-resonance ($\Delta m = \pm 2$) spectra of these metal chelates have not clearly been observed yet.

A detailed report will be published elsewhere in due course.

ACKNOWLEDGEMENT The authors wish to thank Prof. K. Nakamura of Nagoya Institute of Technology for his kind discussions in this study.

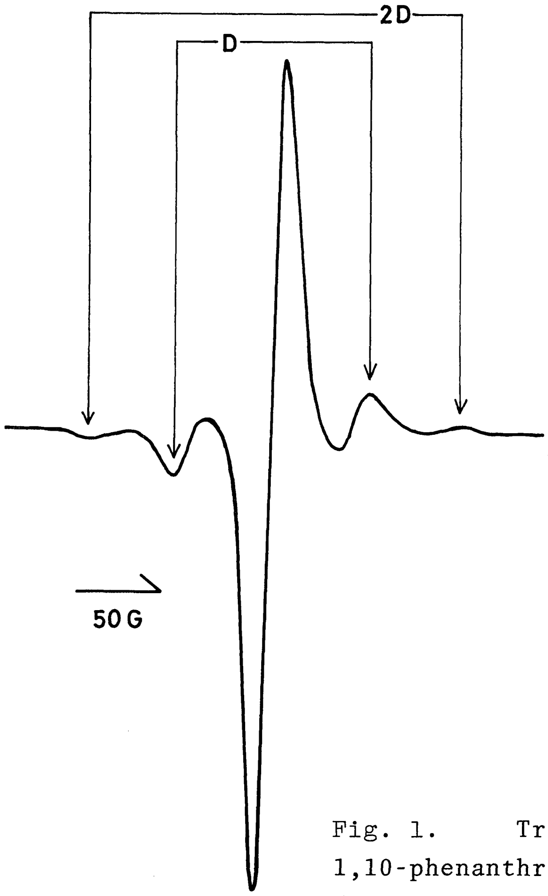

Fig. 1. Triplet state ESR spectrum of 1,10-phenanthroline lithium chelate (g=2.0037) at 77 K in MeTHF.

TABLE I. ZERO-FIELD SPLITTING PARAMETERS

Metal	D (gauss)	D/hc (cm^{-1})	$\bar{r}_{1,2}$ (Å)
1,10-phenanthroline			
Li^+	±110.2	±0.01029	6.3
Ca^{2+}	± 91.0	±0.00849	6.7
2,9-dimethyl-1,10-phenanthroline			
Li^+	± 87.0	±0.00813	6.8
Ca^{2+}	± 80.9	±0.00756	7.0

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(Received November 26, 1973)