BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (11), 3375—3376 (1975)

ESR Studies of the Triplet-state Dimers of Michler's Ketone Metal Ketyls in Glassy Solutions

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(Received February 15, 1975)

Synopsis. The ESR spectra (the $\Delta M_s = \pm 1$ and $\Delta M_s = \pm 2$ transitions) of the triplet-states of Michler's ketone metal ketyl dimers are observed in glassy solutions at 77 K. For these metal ketyl dimers, the correlation of the mean separation between spins to the radius of the counter cation was experimentally examined.

Several ESR studies have shown that the ESR spectra due to the magnetic dipole-dipole interactions of spins in glassy solutions can offer important information on the electronic and geometrical structures of the biradical-like dimeric species.[1-5]

In a previous paper,[6] it has been shown that, in the 4,4'-tetramethyldiaminobenzophenone (Michler's ketone) anion radical, the unpaired electron is mainly localized in the vicinity of its carbonyl group.[7]

In the present paper the authors will report their observations of the ESR spectra of the triplet-state in the system of Micher's ketone metal ketyls as produced by several alkali metals in ethereal solvents.

Experimental

A commercially obtained Michler's ketone was purified by recrystallization from ethyl alcohol (mp 179 °C). Its metal ketyls were prepared by the standard alkali metal reduction method, while both ketyls with lithium and calcium were prepared by the use of amalgams of both metals. The solvents used in the present study were 2-methyltetrahydrofuran (MeTHF), tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), diethylene glycol dimethyl ether (diglyme), and triethylene glycol dimethyl ether (triglyme), each of which was treated by the standard purification method.

The ESR spectra were observed at 77 K by means of an X-band ESR spectrometer (JEOL ME-3) with 100 kHz field modulation. The zero-field splitting (ZFS) parameter, D, was determined by measuring the peak-to-peak separation of the $2F$ splitting, because no ZFS parameter, E, could be observed (see Fig. 1). The intensity of the weak signal for the half-field ($\Delta M_s = \pm 2$) transition was enhanced by the signal accumulation method of 32 or 64 scans by using a JEOL EC-6-type spectral computer. Thus, the ESR signals for the $\Delta M_s = \pm 2$ transitions could be observed in every case listed in Table 1. The magnetic field was calibrated by the hyperfine splittings of Mn^{2+} doped in MgO and of ^{14}N of the peroxylamine-disulfonate ion. The spectral simulations were carried out at the Computer Center of Kyoto University.

Results and Discussion

In Fig. 1 the observed and simulated ESR spectra of the triplet-state of Michler's ketone lithium ketyl dimer in MeTHF are shown as examples. In Fig. 1 (a), which depicts the spectrum for the full-field ($\Delta M_s =$

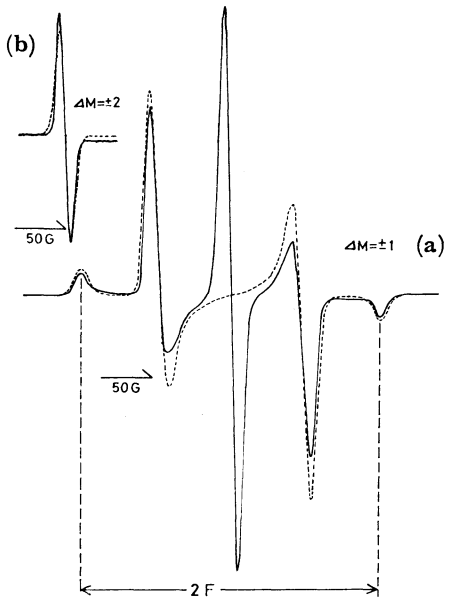

Fig. 1. The full line is the observed ESR spectrum of the triplet-state of Michler's ketone lithium metal ketyl dimer in MeTHF at 77 K, and the dotted line is its simulated one.

In the spectrum for the $\Delta M_s = \pm 1$ transition (a), the ZFS parameter D is 140.5 G. The spectrum for the $\Delta M_s = \pm 2$ transition (b) was enhanced by accumulation of 32 scans of the signal with the computer.

TABLE 1. THE ZERO-FIELD SPLITTING PARAMETERS FOR MICHLER'S KETONE METAL KETYL AT 77 K

Solvent and cation		$\lvert D \rvert$ (G)	$\lvert D \rvert / hc$ (cm^{-1})	$\bar{r}_{1,2}$ (Å)
MeTHF	Li^+	140.5	0.01312	5.83
	Na^+	113.8	0.01063	6.26
	K^+	97.6	0.00911	6.59
	Rb^+	84.4	0.00788	6.92
	Cs^+	75.2	0.00702	7.19
	Ca^{2+}	118.2	0.01104	6.19
THF	Li^+	119.4	0.01115	6.16
	Na^+	112.3	0.01049	6.29
	K^+	94.6	0.00883	6.66
	Rb^+	93.5	0.00873	6.68
	Cs^+	86.4	0.00807	6.86
	Ca^{2+}	102.9	0.00961	6.47
Diglyme	Li^+	121.8	0.01137	6.12
	Na^+	105.3	0.00983	6.42
	K^+	96.9	0.00905	6.61
	Rb^+	89.3	0.00834	6.79
	Cs^+	69.9	0.00653	7.37
	Ca^{2+}	101.9	0.00952	6.49

± 1) transitions, the sharp central absorption can be assigned to the paramagnetic monomer, its integrated intensity being about 10 per cent of the total absorption. Then, the residual part of the absorption (about 90 per cent) is attributable to the paramagnetic dimer.

In Fig. 1(a) the measured value of the ZFS parameter, D, is 140.5 G ($2F=281.0$ G), where the microwave frequency used is 9198.0 MHz and the g-value is 2.0036. The values of the ZFS parameter, D, as measured in different combinations of cations and solvents are summarized in Table 1.

The spectral simulations carried out under the assumption of the ZFS parameter, E, being zero are exhibited as dotted lines in Figs. 1(a) and (b). These simulated spectra fit well with those observed. From these results, we may safely conclude that $E=0$ in the ground-triplet-state spin Hamiltonian. Then, using the theoretical ZFS parameter, D ($D=-2/3g^2\beta^2<1/r_{1-2}^3$),[1,2] the average distances ($\bar{r}_{1,2}$) between two unpaired electrons in every dimer for these metal ketyls are calculated and tabulated in Table 1, where the values of $\bar{r}_{1,2}$ measured in DME and triglyme are omitted since they are nearly equal to the corresponding values of diglyme.

In Fig. 2 the values of $\bar{r}_{1,2}$ for the system of MeTHF in Table 1 are plotted against the radius (R) of the counter cations, for each of which the values of Goldschmidt's ionic radii (Li^+, 0.78; Na^+, 0.98; K^+, 1.33; Rb^+, 1.49; Cs^+, 1.65; and Ca^{2+}, 1.06 Å) were adopted.[8] The fact that $\bar{r}_{1,2}$ increases linearly with an increase in R may be understood if one considers each model as having either a triple-ion structure $(Me_2N\phi)_2CO^-M^+{}^-OC(\phi NMe_2)_2$ or an ion-quadruplet structure $(Me_2N\phi)_2CO^-{}_{M^+}^{M^+}{}^-OC(\phi NMe_2)_2$ with respect to two ketyls.[3,5,9] However, theoretical or quantitative explanation for this result is not yet available.

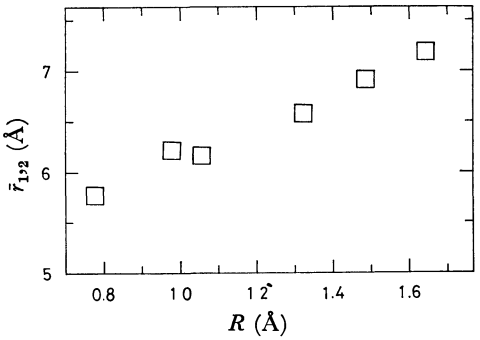

Fig. 2. The values of $\bar{r}_{1,2}$ in MeTHF are plotted against the values of R.

The authors are sincerely grateful to Professor Kohichi Itoh of Osaka University for offering the simulation program of the triplet-state ESR spectrum and also for his useful suggestions during the course of this work. They are also indebted to Dr. Jun Yamauchi and his collaborators for their helpful discussions.

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