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A SPIN LABELED CROWN ETHER (I). ESR STUDIES ON THE ALKALI METAL COMPLEXES OF TANOL DERIVATIVE OF BENZO-15-CROWN-5

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A TANOL derivative of benzo-15-crown-5 shown in the Fig. 1, was synthesized, and the complex formation between the spin labeled crown ether and the alkali metal isocyanate was studied by ESR technique. The potassium complex revealed a strong spin-spin interaction due to formation of the sandwiched dimer and the structure was investigated on the basis of the ESR parameters of the triplet cluster.

Since the cyclic polyethers and their metal complexes were primarily reported by C. J. Pedersen,$^{1)}$ complex formations between the alkali metals and the crown ethers, which have the various ring diameters, have been studied spectrophotometrically,$^{2)}$ calorimetrically$^{3)}$ and electrometrically.$^{4)}$

In the present investigations, a TANOL derivative of benzo-15-crown-5 shown in the Fig. 1 was synthesized, and the complexation of the alkali metal isocyanate with cyclic ether was investigated by ESR spectroscopy. A spin-spin interaction was detected for potassium complexes.

The spin hamiltonian parameters of the triplet cluster were determined and the structure of the cluster was assumed.

A spin labeled crown ether was synthesized according to the following processes. 4-(4'-carboxybenzo-15-crown-5) [I] was obtained in the same method as described

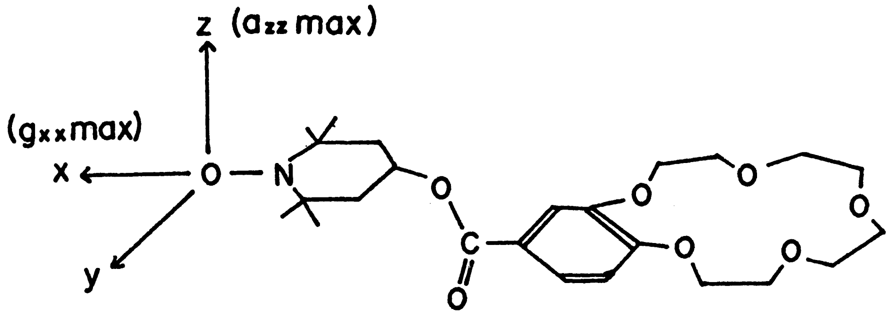

Fig. 1. Structure of spin labeled benzo-15-crown-5 and principal axes of the (g) and (a) tensors for a planar NO radical.

in the previous work[2,5) : mp 191°C. 4-Hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl [II] was prepared from 4-hydroxy-2,2,6,6-tetramethylpiperidine according to the typical method; (mp 73°C).[6)] 1.5 g of [I] was acylated by utilizing $SOCl_2$ in chloroform for 3 hours. After removal of solvent and excess $SOCl_2$ in vacuum, 0.5 ml of dry pyridine was added to and followed by 0.8 g of [II] dissolved in 4.5 ml of dry pyridine. A reaction mixture was kept in dark for about 2 days. The reaction mixture was poured into 25 ml of cold water, and the material was extracted by ethyl ether. The ether layer was washed by cold water and dried with anhydrous sodium sulfate. After evaporation of the solvent, the crude radical (1.4 g) was purified by recrystallization using hexane-ether mixture (1:1). A reddish yellow needle of the pure radical showed the constant melting at 113-114°C (uncorrected). Elementary analysis, Calcd. C, 61.76; H, 7.78; N, 3.00 %. Found. C, 61.78; H, 8.08; N, 2.67 %, for $C_{24}H_{36}O_8N$=466. Mass spectrum, m/e 466 (M^+).

The ESR spectra were recorded changing the molar ratio of isocyanate and the crown ether dissolved in ethyl alcohol. The g-values and the magnetic fields were calibrated by taking the value of peroxylamine disulfonate (g=2.0054, a_N=13.05 ± 0.03 gauss) and Li-salt of TCNQ (g=2.00252) as the standard.

The ESR parameters of the crown ether (a_N=15.86 gauss, g_0=2.0058) were nearly identical with those of TANOL (a_N=15.99 gauss, g_0=2.0058).

A solution of the crown ether (5.4×10^{-3} mol/l) containing the equimolar NaSCN also showed the similar ESR spectrum, and no important changes were detected except a slight decrease of the hyperfine line width; a_N=15.81 gauss, g_0=2.0058.

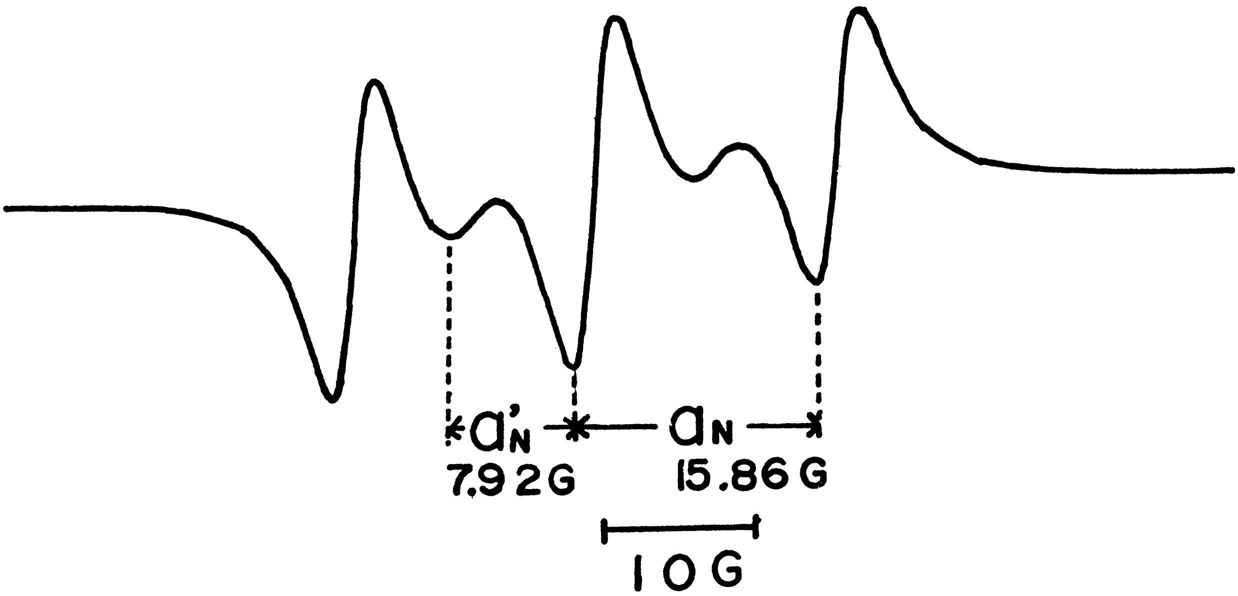

Fig. 2. ESR spectrum of KSCN triplet cluster at room temperature.

In the case of potassium, however, a drastic change of the ESR spectrum was noted upon addition of the isocyanate with the molar ratio (KSCN : crown ether =1:2). The hyperfine splitting (1/2 $a_N=a_{N'}=7.92$ gauss) shown in Fig. 2, was attributed to a spin-spin interaction between each of nitroxyl group in the sand-wiched ligand.[7)]

Of interest was the fact that the line intensity arising from the spin-spin interaction was gradually diminished with successive increase of isocyanate concentration and the ESR spectrum altered to that of the monoradical species with the equal line intensity ratio 1:1:1. This means that the stability of the 1:2 complex of the KSCN with crown ether is much larger than that of 1:1 complex.

The ESR spectrum of 1:2 complex recorded in a frozen matrix of ethyl alcohol at 77°K is shown in Fig. 3. The fine structure revealed the zero-field splitting of the triplet species without axial symmetry. The $\Delta M_s=2$ transition was also observed at 1632 gauss. The largest splitting (2D=136.1 gauss) is assumed to be dipolar splitting for Z-axis, since the principal value for Z axis of the cluster G-tensor, G_{zz} (2.0032), is fairly closed to that of the monomer determined in the frozen matrix; $g_{zz}=2.0023$, $a_{zz}=36.27$ gauss.

The nuclear hyperfine splitting A_{zz} (14.2 gauss) due to the two equivalent ^{14}N nuclei can be observed in the G_{zz} splitting with an intensity ratio 1:2:3:2:1. This suggests that a large exchange interaciton ($J \gg A_{zz} \approx 1/2\ a_{zz}$) can be expected along the z-axis of each nitroxyl group (coordinate system of the NO group is shown in Fig. 1). The dipolar splittings for X and Y axes, (D - 3E=55.1 gauss)

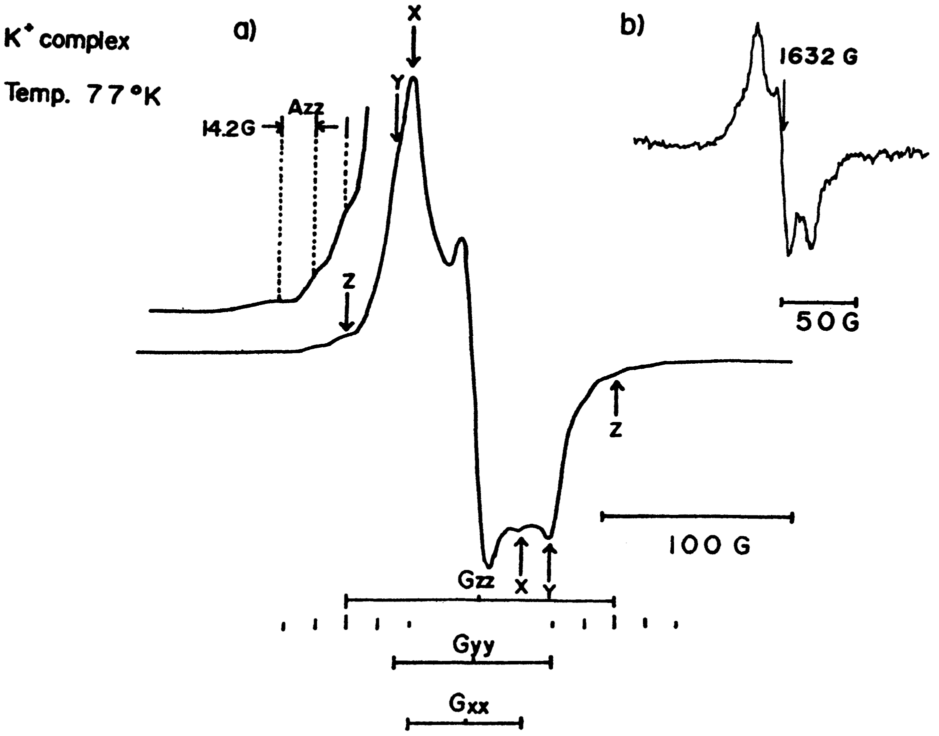

Fig. 3. ESR spectra of KSCN triplet cluster at 77°K.
a) $\Delta M_s=1$ transition.
b) $\Delta M_s=2$ transition.

and (D + 3E=81.0 gauss) are assigned from the turning point in the spectrum and the spin hamiltonian parameters of triplet cluster D, E were thus obtained; that is D=68.0 and E=4.3 gauss respectively. The X and Y principal values of the cluster G-tensor were determined from the midpoint of the splitting; G_{xx}=2.0085 and G_{yy}=2.0057. The G_{xx} and G_{yy} values are much close to those of di-t-butyl nitric oxide (g_{xx}=2.0089, g_{yy}=2.0061), whose electronic structure is much alike to the TANOL radical.[8] The average $G_{av}=(G_{xx}+G_{yy}+G_{zz})/3$ =2.0058 is nearly identical with the g_0-value of the monomer measured at the room temperature. Based on the D-parameter, the average distance R between the unpaired electrons is calculated in the piont dipole approximation; $D_{obsd}=12.74 + 2.009\times10^4/R^3$, R=7.1 Å.[9]

The R value assumed here cannot be taken seriously, because accurate estimation is difficult because of the local movement of the functional groups. Nevertheless, it is rather surprising that the two nitroxyl groups can be closely accessible in the cluster. At the equilibrium position, the C_2NO plane of the two nitroxyl group may be arrayed by taking a stacking structure as to align the direction of g_{zz} tensor of monoradical nearly to the direction of the G_{zz} component of the cluster. Further investigation of the other metal complexes are now underway.

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