## Electron Spin Resonance Studies of Alkali and Alkaline-Earth Metal Complexes of Phenoxyl-Labeled Benzo-15-crown-5 in Frozen Solution

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A stable phenoxyl derivative (1) of benzo-15-crown-5 (B15C5) has been prepared and the complex formation between the spin-labeled crown ether 1 and the alkali (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, and Rb<sup>+</sup>) and alkaline-earth (Mg<sup>2+</sup>, Ca<sup>2+</sup>,  $Sr^{2+}$ , and  $Ba^{2+}$ ) metal salts has been studied by the ESR technique. The result of the ESR observations has established the new fact that two kinds of 2:1 complexes having different structures and a 1:1 complex coexist at equilibrium in all the ethanol solutions of 1 containing the above metal salts. Structural information for the two kinds of 2:1 complexes was deduced from detailed analysis of the observed triplet ESR spectra and the calculation of the zero-field splitting (zfs) parameters.

### Introduction

The preparation and properties of a number of cyclic polyethers have been previously reported by Pedersen.<sup>1,2</sup> It was shown that certain of these polyethers form stable complexes with alkali and alkaline-earth metal cations. Many investigations of the positive ion effect for the complex formation in solution and in the solid state have been reported.<sup>3</sup> The stoichiometry of the crystalline complexes depends on the relative size of the "hole" in the cyclic polyether and of the cation. For example, benzo-15-crown-5 (B15C5) with a hole 1.7-2.2 Å in diameter usually forms 1:1 complexes with Li<sup>+</sup> (diameter, 1.20 Å), Na<sup>+</sup> (1.90 Å), Mg<sup>2+</sup> (1.30 Å), and Ca<sup>2+</sup> (1.98 Å), but it forms 2:1 complexes with K<sup>+</sup> (2.66 Å) and Ba<sup>2+</sup> (2.70 Å), the ions larger than the hole (see Table II).<sup>2-7</sup>

In recent papers, we have prepared the nitroxide (2),<sup>8</sup> galvinoxyl (3),  $^{9,10}$  and verdazyl  $(4)^{11}$  derivatives of benzo-15-crown-5 and investigated the complex formation between the spin-labeled crown ethers and the alkali metal  $(Na^+, K^+, and Rb^+)$  salts, using ESR spectroscopy. The technique of spin-labeling has given useful and important information about the formation and structure of the crown-metal complexes, as described in previous papers: for instance, both the nitroxide- and galvinoxyl-labeled B15C5 (2) and (3) form 1:1 complexes with NaSCN and 2:1 complexes with KSCN, as reported for the native benzo-15-crown-5. However, the structure of the 2:1 complexes of both 2 and 3 in frozen solution is different from that of B15C5 obtained by X-ray analysis.<sup>6</sup> Further, in the verdazyl-labeled B15C5 (4), NaSCN complex showed a triplet ESR spectrum, indicating the formation of a 2:1 complex, and a polymeric structure,  $(1:1)_n$ , with alternating

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array of potassium cations and the cyclic ethers has been proposed for the KSCN complex of 4.

In the present paper, in order to obtain further information on such complex formations, we have prepared a phenoxyl-labeled B15C5 (1) and observed ESR spectra of



its alkali (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, and Rb<sup>+</sup>) and alkaline-earth (Mg<sup>2+</sup>,  $Ca^{2+}$ ,  $Sr^{2+}$ , and  $Ba^{2+}$ ) metal complexes in ethanol rigid matrix at 77 K. The result of the ESR measurements described in this paper will establish the new fact that two kinds of 2:1 complexes having different structures and a 1:1 complex coexist at equilibrium in all the ethanol solutions of 1 containing the above metal salts. The zerofield splitting (zfs) parameters (D and E) were calculated on the basis of the spin distribution of 1 and the assumed molecular structures for the 2:1 complexes. By comparing the observed D and E parameters with the calculated ones, we discussed the structure of the 2:1 complexes.

### **Experimental Section**

Quinol Derivative of Benzo-15-crown-5 (Quinol-B15C5). Quinol-B15C5 was synthesized by the reaction of the



## Quinol-BI5C5

lithium derivative<sup>12</sup> of 4'-bromo-benzo-15-crown-5<sup>13</sup> with

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### Complexes of Phenoxyl-Labeled Benzo-15-crown-5

2.6-di-*tert*-butyl-*p*-benzoquinone.<sup>14</sup> Under nitrogen, a solution of 5.0 g (14.4 mmol) of 4'-bromo-benzo-15-crown-5 in 25 mL of dry THF was cooled to -78 °C. A solution of 14.4 mmol of n-butyllithium in n-hexane was added dropwise, the mixture was stirred for 30 min, and a solution of 3.2 g (14.4 mmol) of 2,6-di-tert-butyl-p-benzoquinone in 20 mL of dry THF was added slowly. After an additional 3 h of stirring at -78 °C, the stirred solution was allowed to warm to -20 °C and stirring was continued for an additional 3 h. Then, the stirred solution was allowed to warm to 20 °C gradually. After the THF was evaporated, the reaction mixture remaining was hydrolyzed in saturated NH<sub>4</sub>Cl solution. The material was then taken up in CHCl<sub>3</sub>, washed with water, and dried over anhydrous sodium sulfate. After removal of the CHCl<sub>3</sub>, a viscous oil remained. The residue was chromatographed on 50 g of silica gel with  $CHCl_3$  as the eluting agent. The subsequent removal of the CHCl<sub>3</sub> from Quinol-B15C5 solution left an orange-yellow oil; this was recrystallized twice from ligroin (bp 90-105 °C) to give white crystals (1.5 g): mp 143-145 °C; UV (EtOH)  $\lambda_{max}$  282 nm (log  $\epsilon$  = 3.71); NMR (CCl<sub>4</sub>) δ 1.21 (18 H, s, t-Bu), 2.43 (1 H, s, OH), 3.40-4.05 (16 H, m,  $CH_2$ ), 6.35 (2 H, s, *m*-ring), 6.65 (2 H, s, aromatic H), 6.78 (1 H, s, aromatic H) with Me<sub>4</sub>Si as internal standard. Anal. Calcd for C<sub>28</sub>H<sub>40</sub>O<sub>7</sub>: C, 68.83; H, 8.25. Found: C, 68.25; H, 8.49.

Phenol Derivative of Benzo-15-crown-5 (Phenol-B15C5). Phenol-B15C5 was synthesized by the reduction of Qui-



### Phenol-BI5C5

nol-B15C5 (1.5 g, 3.1 mmol) with Zn powder (1.0 g, 15.3 mmol) and concentrated HCl (4.0 mL) in methyl alcohol (15 mL) at 20 °C for 20 min, by a process similar to that of Rieker and Scheffler.<sup>15</sup> The Zn powder was filtered off, and then the filtrate was taken up in ethyl ether and washed with water. After removal of the ethyl ether, a viscous oil remained. The residue was chromatographed on 50 g of silica gel with  $CHCl_3$  as the eluting agent. The subsequent removal of the CHCl<sub>3</sub> from Phenol-B15C5 solution left a yellow oil. This was recrystallized twice from ligroin (bp 90-105 °C) to give white crystals (1.3 g): mp 136–137 °C; UV (EtOH)  $\lambda_{max}$  268 nm (log  $\epsilon$  = 4.29); NMR (CCl<sub>4</sub>) δ 1.45 (18 H, s, t-Bu), 3.50-4.15 (16 H, m, CH<sub>2</sub>), 4.94 (1 H, s, OH), 6.74 (1 H, s, aromatic H), 6.78 (2 H, s, aromatic H), 7.08 (2 H, s, m-ring) with Me<sub>4</sub>Si as an internal standard).

Anal. Calcd for C<sub>28</sub>H<sub>40</sub>O<sub>6</sub>: C, 71.16; H, 8.53. Found: C, 70.91; H, 8.70.

Phenoxyl Derivative of Benzo-15-crown-5 (1). 1 was prepared by the oxidation of Phenol-B15C5 with alkaline potassium hexacyanoferrate(III) in diethyl ether solvent under a nitrogen atmosphere, with the temperature kept between 0 and 5 °C.<sup>16</sup> 1 was isolated as a stable dark



Figure 1. ESR spectrum of 1 in ethanol at 20 °C.

brown crystal from the etherial solution: UV-vis (cyclohexane)  $\lambda_{max}$  373 (log  $\epsilon$  = 4.02), 588 (log  $\epsilon$  = 3.31), 623 (log  $\epsilon = 3.33$ ) nm.

The radical concentration was obtained from the results of the paramagnetic susceptibility measurements at 20 °C, after correcting for the diamagnetic contribution ( $\chi_{dia}$  =  $-0.319 \times 10^{-3}$  emu mol<sup>-1</sup>) calculated by Pascal's method. The value of the radical concentration was 99%, assuming the Curie law. All the ESR spectra were measured in a sealed, degassed system.

### **Results and Discussion**

Ethanol-Solution ESR Spectrum of 1. The ethanolsolution ESR spectrum of 1 has been measured at 20 °C (see Figure 1). The spectrum can be reconstructed with three groups of one, three, and three equivalent protons, showing three different hyperfine couplings (2.35, 1.42, and 0.52 G, respectively). These couplings will be assigned to the ring protons at C-2  $(a_2^{\rm H} = 2.35 \text{ G})$ , C-1  $(a_1^{\rm H} = 1.42 \text{ G})$ , C-6  $(a_6^{\rm H} = 1.42 \text{ G})$ , and C-3  $(a_3^{\rm H} = 0.52 \text{ G})$  and two equivalently interacting methylene protons at O-4  $(a_4^{CH_2})$ = 0.52 G), the result of the McLachlan MO calculations being taken into account. No interaction was observed for the methylene protons at O-5 and the *tert*-butyl protons.

The experimental values of spin densities at C-1, C-2, C-3, and C-6 carbon atoms were estimated by using the relation  $a_1^{\rm H} = Q^{\rm H} \rho_i$ , where  $\rho_i$  is the spin density at the *i*th aromatic carbon atom.  $Q^{\rm H}$  was taken to be 27 G for ring protons.<sup>17</sup> It is well-known that the  $\beta$ -methylene proton couplings can be calculated by using the Heller-McConnell's equation<sup>18</sup>

$$a_i^{\rm CH_2} = (B_0 + B_2 \cos^2 \theta)\rho_i \tag{1}$$

where  $\theta$  is the usual dihedral angle, and where  $B_0$  and  $B_2$ were taken to be 0 and 54 G, respectively.<sup>17</sup> In the case of the present phenoxyl radical, one may expect that a rotation of the  $\beta$ -methylene residue would be largely restricted by its strong strain. As the results of the analysis of the ESR spectrum indicate, the two  $\beta$ -methylene protons of 1 have an equivalent hyperfine coupling within the present resolution. Thus, the dihedral angle must be equivalent for the two  $\beta$  protons, giving the value of  $\theta$  = 30°. Consequently, the experimental value of the spin density at the O-4 oxygen atom was estimated by using the relation  $a_4^{CH_2} = \frac{3}{4}(54)\rho_4$ . All the experimental spin densities  $\rho(\text{exptl})$  calculated from the ESR hyperfine couplings are listed in Table I.

Phenoxyl-benzo-15-crown-5 (1) is thought to be a derivative of 2,6-di-tert-butyl-4-phenylphenoxyl radical. The ESR spectrum of the latter radical has previously been reported.<sup>19</sup> On the basis of the proton hyperfine splittings,

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### 1340 The Journal of Physical Chemistry, Vol. 87, No. 8, 1983

TABLE I: Hyperfine Couplings  $(a_i^H)$  (in gauss) and Spin Densities  $(\rho_i)$  of 1 in Ethanol at 20 °C

	$a_1^H$	$a_{2}^{H}$	$a_3^{H}$	a <sub>4</sub> CH <sub>2</sub>	a <sub>6</sub> <sup>H</sup>
ESR	$1.42^{a}$	2.35	0.52	0.52	1.42
$\rho(\text{exptl})$	-0.0526	0.0870	~0.0193	$0.0128^{b}$	0.0526
$\rho(calcd)$	-0.0296	0.0827	-0.0269	0.0105	0.0341
<sup>a</sup> Expe	rimental er	rors, $\pm 0.0$	5G. 1G	$= 10^{-4} \mathrm{T}.$	<sup>b</sup> Spin

densities at O-4.



**Figure 2.** ESR spectrum of the KI complex of **1** in ethanol at 77 K: (a)  $\Delta m_s = \pm 1$  transition and (b)  $\Delta m_s = \pm 2$  transition.

the structure of the aryloxyl radical was investigated in terms of the McLachlan MO calculation; the result indicates that the aryloxyl radical has planar character. Therefore, in the case of 1, McLachlan spin densities ( $\rho_i$ ) were calculated, holding the twist angle  $\theta$  between the phenyl rings at 0° and varying the MO parameters. The final values of the MO parameters adopted are as follows:  $\alpha_0 = \alpha + 1.3\beta$ ,  $\beta_{C-0} = 1.5\beta$  for the oxygen atom of the carbonyl group, and  $\alpha_0 = \alpha + 2.0\beta$ ,  $\beta_{C-0} = 1.0\beta$  for the oxygen atom of the alkoxy group. The McLachlan MO parameter  $\lambda$  was given the standard value of 1.3. The McLachlan spin densities ( $\rho_i$ ) calculated with these parameters are given in Table I.

Ethanol Rigid-Matrix ESR Spectra of the Alkali and Alkaline-Earth Metal Complexes of 1. An ethanol solution of 1 ( $3.0 \times 10^{-3}$  mol dm<sup>-3</sup>) containing equimolar KI salt gives an ESR spectrum consisting of (i) a central strong singlet and (ii) two pairs of absorption lines (X<sub>I</sub>, X<sub>I</sub>'; and Y<sub>I</sub>, Y<sub>I</sub>') on both sides of the central singlet at 77 K, as shown in Figure 2a. A slightly asymmetric central line with a width of about 6.5 G (1 G =  $10^{-4}$  T) at  $g \simeq 2.0043$ shows a shape essentially the same as that of the metal-free 1 ( $\Delta H_{msl} = 6.6$  G and  $g \simeq 2.0042$ ), and the relative intensity of this central line changes depending on the ratio of the potassium salt to 1. Therefore, this line is attributable to the 1:1 complex (hereafter called the monomer complex) between 1 and KI.

The two pairs of absorption lines (X<sub>I</sub>, X<sub>I</sub>'; and Y<sub>I</sub>, Y<sub>I</sub>') apparently represent zero-field splittings arising from the intermolecular spin-spin dipolar interaction of two electrons in a triplet state. In fact, the ESR absorption lines which are constructed by excluding the central single strong absorption line are similar in line shape to the spectra observed for various phenoxyl biradicals with spin-spin dipolar interaction. Further, the forbidden transition ( $\Delta m_s = \pm 2$ ) was observed as a weak signal at about 1640 G, as shown in Figure 2b. These results clearly indicate the formation of the 2:1 complex (hereafter called



Figure 3. ESR spectrum of the KI complex of 1 in ethanol at 77 K.

the dimer-I complex) between 1 and KI.

The zero-field splitting parameters  $(D_{\rm I} \text{ and } E_{\rm I})$  and **g**-tensor values have been tentatively estimated from the positions of the two pairs of turning points  $(X_{\rm I}, X_{\rm I}'; Y_{\rm I}, Y_{\rm I}')$ , by the method of Wasserman et al.<sup>20</sup> These values are  $|D_{\rm I}| = 24.1 \pm 0.6$  G and  $|E_{\rm I}| = 0.9 \pm 0.6$  G and  $g_{xx}^{\rm I} = 2.0047 \pm 0.0003$  and  $g_{yy}^{\rm I} = 2.0040 \pm 0.0003$  for dimer I, respectively.

In addition to the above monomer and dimer-I absorption signals, three weak pairs of absorption lines (X<sub>II</sub>, X<sub>II</sub>'; Y<sub>II</sub>, Y<sub>II</sub>'; and Z<sub>II</sub>, Z<sub>II</sub>') (see Figure 3) were observed on both sides of the above signals, when the spectra were recorded under higher amplitude. These absorption lines also indicate the formation of another 2:1 complex between 1 and the KI (hereafter called the dimer-II complex). The separations between the three pairs of turning points (Z<sub>II</sub>, Z<sub>II</sub>'; Y<sub>II</sub>, Y<sub>II</sub>'; and X<sub>II</sub>, X<sub>II</sub>') in the spectrum of the KI complex are 195.2 ± 1.2, 117.0 ± 1.2, and 78.2 ± 1.0 G, respectively. Similarly, the zero-field splitting parameters and **g**-tensor values were evaluated as  $|D_{II}| = 97.6 \pm 0.6$  G,  $|E_{II}| = 6.5 \pm 0.6$  G,  $g_{zz}^{II} = 2.0026 \pm 0.0003$ ,  $g_{yy}^{II} = 2.0036 \pm 0.0003$ , and  $g_{xx}^{II} = 2.0061 \pm 0.0003$ . The average,  $g_{av}^{II} = 1/_3(g_{xx}^{II} + g_{yy}^{II} + g_{zz}^{II}) = 2.0041 \pm 0.0005$  value measured at room temperature, indicating that the **g**-tensor values obtained by the above analysis are consistent.

An attempt to establish the molar ratio of the three kinds of KI complexes—monomer, dimer I, and dimer II—was achieved by observing the ethanol rigid-matrix ESR spectrum of 1 containing equimolar KI salt. The approximate ratio can be determined from the integrated spectral intensity of a first-derivative ESR absorption line, although the integration of the ESR absorption line is troublesome and the determination of the ratio is responsible for large error.<sup>21</sup> The ratio obtained is monomer:dimer I:dimer II = 10:20:1. The relative intensity of the central singlet due to the monomer increases with increasing the ratio of the KI salt to 1. On the other hand, by changing the molar ratio of 1 with KI in the ethanol solution, we observed no detectable changes in the relative

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TABLE II: D- and g-Tensor Values of the Complexes of 1 with Alkali and Alkaline-Earth Metal Salts in Ethanol at 77 K

 salt	ionic radius, A	$ D_{\mathrm{I}} ,^{a}_{\mathrm{G}}$	${}^{ E_{\mathrm{I}} ,a}_{\mathrm{G}}$	g <sub>xx</sub> <sup>Ib</sup>	$g_{yy}^{I}$	$ D_{II} , G$	$[E_{II}], G$	$g_{xx}^{II}$	$g_{yy}^{II}$	$g_{zz}^{II}$	B15C5 complex
LiI	0.60	23.4	0.6	2.0049	2.0040	97.4	6.8	2.0054	2.0041	2.0029	1:1
NaI	0.95	24.2	1.0	2.0048	2.0040	97.9	6.5	2.0054	2.0038	2.0023	1:1
KI	1.33	24.1	0.9	2.0047	2.0 <b>0</b> 40	97.6	6.5	2.0061	2.0036	2.0026	2:1
RbI	1.48	24.3	0.8	2.0047	2.0040	97.4	6.5	2.0053	2.0037	2.0024	
MgCl,	0.65	23.7	1.1	2.0048	2.0037	97.6	6.7	2.0058	2.0038	2.0026	1:1
CaCl,	0.99	23.7	1.0	2.0048	2.0041	96.4	6.8	2.0055	2.0038	2.0027	1:1
SrCl,	1.13	23.9		2.0044		103.6	6,2	2.0061	2.0038	2.0026	
Bal <sup>2</sup>	1.35	23.7		2.0045		103.6	6.4	2.0061	2.0039	2.0028	2:1

<sup>a</sup> The experimental errors in the values of |D| and |E| are  $\pm 0.6$  G.  $1 \text{ G} = 10^{-4}$  T. <sup>b</sup> The experimental errors in the values of  $g_{xx}$ ,  $g_{yy}$ , and  $g_{zz}$  are  $\pm 0.0003$ .

TABLE III: D- and g-Tensor Values of the Complexes of 1 with KI, KBr, KSCN, KIO<sub>4</sub>, and K<sub>2</sub>SO<sub>4</sub> Salts in Ethanol at 77 K

rolt =  D    A C =  F    A C = a   Ib = a   I =  D    C =  F    C = a   I =	
sait $D_{I}$ , $G$ $E_{I}$ , $G$ $g_{xx}$ $g_{yy}$ $D_{II}$ , $G$ $E_{II}$ , $G$ $g_{xx}$ $g_{yy}$ $g_{zz}$	salt
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	KI KBr KSCN KIO <sub>4</sub> K <sub>2</sub> SO <sub>4</sub>

<sup>a</sup> The experimental errors in the values of |D| and |E| are  $\pm 0.6$  G. 1 G = 10<sup>-4</sup> T. <sup>b</sup> The experimental errors in the values of  $g_{xx}$ ,  $g_{yy}$ , and  $g_{zz}$  are  $\pm 0.0003$ .

intensity of the ESR spectra due to dimers I and II.

The ESR spectra of the alkali and alkaline-earth metal complexes of 1 have been measured in ethanol rigid matrix, in order to elucidate the effects of the positive ions on the complex formation and on the molecular structure of the complex. The ESR spectra of all the complexes of 1 show shapes essentially the same as that of the KI complex, except for the difference in the relative intensity of the ESR absorptions due to the monomer, dimer I, and dimer II, indicating the coexisting of two kinds of dimers and a monomer. The zfs parameters (D and E) and g-tensor values have been estimated from the positions of the two pairs of turning points (X\_I, X\_I'; and Y\_I, Y\_I') for dimer I and of the three pairs of turning points  $(X_{II}, X_{II}'; Y_{II}, Y_{II}'; and$  $Z_{II}, Z_{II}'$ ) for dimer II, respectively, as performed for the KI complex of 1. The observed D and E values are summarized in Table II.

If both dimers I and II have a "sandwiched" structure with a metal ion between the two benzo-15-crown-5 rings, we can expect the change in the interplanar spacing between the two crown ether rings, as the ion diameter of the cation varies. This will induce the change in the zfs parameters. However, in dimer I, the  $|D_{I}|$  and  $|E_{I}|$  values observed for all the alkali and alkaline-earth metal complexes remain constant, within the limit of experimental error (see Table II). This indicates that the effect of the change in ion diameter of the cation is too small to induce the change in the molecular structure of the complex. On the other hand, in dimer II, the  $|D_{II}|$  and  $|E_{II}|$  values of the Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup> complexes are the same within the experimental error, but those of the Sr<sup>2+</sup> and Ba<sup>2+</sup> complexes are slightly different from the above ones.

Many investigations of the positive ion effect for the complex formation, including B15C5, in solution and in the solid state have been reported.<sup>1-3</sup> For instance, B15C5 with a hole 1.7-2.2 Å in diameter usually forms a 1:1 complex with Na<sup>+</sup> (diameters, 1.90 Å), because the Na<sup>+</sup> cation fits tightly in the crown cavity.<sup>2,4</sup> But, it forms a 2:1 complex with K<sup>+</sup> (2.66 Å), the ion larger than the hole.<sup>2,5</sup> Such complex formations will be induced by the ion-dipole interaction between the positive ion and the cyclic polyether ring. On the other hand, Ungaro et al. have shown that a change in the 4'-substituent for benzo-15-crown-5 can cause a significant change in the complex formation constant. They reported that the effect

may be as large as that caused by a change in the structure of the polyether ring. As described above, the result of the present ESR observations provides a new experimental fact that two kinds of 2:1 complexes having different conformations and a 1:1 complex coexist at equilibrium in all the ethanol solutions of 1 containing the eight kinds of alkali and alkaline-earth metal salts. The result is contrary to the well-known fact that the stoichiometry of the crystalline complexes depends on the relative size of the hole in the crown ether and of the cation. Therefore, the present result suggests that the van der Waals interaction between the aryloxyl groups substituted to the cyclic polyether ring may play an important role in the complex, in addition to the above ion-dipole interaction.

Similarly, the effects of the negative ions on the complex formation and on the molecular structure of the complex have also been studied. The anions were varied only in the K<sup>+</sup> salts. Each ESR spectrum of the KBr, KSCN,  $KIO_4$ , and  $K_2SO_4$  complexes of 1 in ethanol rigid matrix at 77 K shows a shape essentially the same as that of the KI complex, except for the difference in the central signal intensity, indicating the coexisting of two kinds of dimers and a monomer. The observed D- and g-tensor values of the dimers are summarized in Table III. Moore et al. have studied the effects of changes in guest anions on association constants.<sup>12</sup> Live and Chan have measured the proton NMR spectra of some crown ethers and their alkali metal complexes in organic solvents and observed the variation in chemical shifts of ether protons with anions (I<sup>-</sup>, SCN<sup>-</sup>, and  $ClO_4^{-}$ ).<sup>22</sup> They concluded that the difference in the shifts is due to ion-pair formation. However, as is clear from the results shown in Table III, the variation in zfs parameters with anions is almost negligible in the present 2:1 complexes. The result indicates that the ion pairing is unimportant in determining the structure of the 2:1 complex.

Structure of Dimers I and II. In order to clarify the structure of the dimer-I and -II complexes of 1 with the alkali and alkaline-earth metal salts in ethanol rigid matrix, we performed the calculations of the **D**-tensor values for the assumed structure of the complex, using McLachlan's spin densities of 1, which is considered to be a monoradical

<sup>(22)</sup> D. Live and S. I. Chan, J. Am. Chem. Soc., 98, 3769 (1976).



Figure 4. Molecular structures and the coordinate systems chosen for cis conformation of the  $K^+$  complex of 1: (a) A-A type and (b) A-B type.

half of the 2:1 complex. Mallinson and Truter have investigated the crystal structure of a 2:1 complex of benzo-15-crown-5 with KI.<sup>6</sup> The complex cation has crystallographic symmetry  $\bar{I}$ , the K<sup>+</sup> being sandwiched between the two centrosymmetrically related ligand molecules. In each of these, the five ether-oxygen atoms are approximately coplanar, the cation lying 1.67 Å away from this plane, so that the 10 oxygen neighbors form a pentagonal antiprism. The benzo group is nearly coplanar with the oxygens, the greatest deviation being 0.11 Å. Thus, as a most plausible case, the **D**-tensor values have been calculated, assuming that 1 has a planar structure, as a whole molecule.

For the KI complex of 1, we can expect two possible structures, A and B. These two structures, A and B, are shown in Figure 4 and named as A-A type and A-B type structures, respectively. Consequently, the D-tensor values were calculated, assuming that the interplanar spacing between the two monoradical halves is 3.34 Å and varying the rotation angles  $\theta_{A-A}$  and  $\theta_{A-B}$ . The coordinate systems (x, y, and z) chosen for both structures are shown in Figure 4, where  $\theta = 0^{\circ}$  corresponds to a planar cis conformation and  $\theta = 180^{\circ}$  is a planar trans conformer in each structure.

In such a case, the **D**-tensor components of the dipolar splitting can be calculated with the aid of the following equations:

$$D_{mm} = (1/2)g^2\beta^2 \sum_{i,j} \rho_i \rho_j (r_{ij}^2 - 3m_{ij}^2) / r_{ij}^5$$
(2)

$$D_{mn} = (1/2)g^2\beta^2 \sum_{i,j} \rho_i \rho_j (-3m_{ij}n_{ij}) / r_{ij}^5$$
(3)

$$m, n = x, y, z$$
; but  $m \neq n$ 

where  $r_{ij}$  is the distance between the *i* and *j* atoms and where  $\rho_i$  and  $\rho_j$  are the  $\pi$ -spin densities on the *i* atom in one aryloxyl group and on the *j* atom in the other aryloxyl group, respectively, in a 2:1 complex. Atomic coordinates of benzo-15-crown-5 are taken from its KI complex reported by Mallinson and Truter.<sup>6</sup> Thus, the resulting tensor was diagonalized, giving the principal values (X, Y, and Z) and, thus, the zero-field splitting parameters, D and E.

Figures 5 and 6 show how the D and E parameters vary as a function of  $\theta_{A-A}$  and  $\theta_{A-B}$ , respectively. In the case of dimer I having smaller zfs parameters, by comparison of



**Figure 5.** Variation of the zfs parameters |D| and |E| as a function of the rotation angle  $\theta_{A-A}$ . Broken lines (---) represent the observed  $|D_I|$  (24.1 G) and  $|D_{II}|$  (97.6 G) values for the KI complex of 1.



**Figure 6.** Variation of the zfs parameters |D| and |E| as a function of the rotation angle  $\theta_{A-B}$ . Broken lines (---) represent the observed  $|D_1|$  (24.1 G) and  $|D_{11}|$  (97.6 G) values for the KI complex of 1.

the observed D and E parameters  $(|D_{I}| = 24.1 \text{ G}, |E_{I}| = 0.9$ G) with the calculated ones, agreements were found for the two cases of about  $\theta_{A-A} = \pm 75^{\circ}$  (|D| = 23.0 G, |E| = 1.1 G) in the A-A structure, and, in the A-B structure, for the two cases of about  $\theta_{A-B} = 50^{\circ}$  (|D| = 23.9 G, |E| = 0.0 G) and  $\theta_{A-B} = -100^{\circ}$  (|D| = 22.0 G, |E| = 1.0 G). The results of the calculation show that dimer I has a structure showing no overlap between two aryloxyl groups in the complex. On the other hand, in the case of dimer II having larger zfs parameters ( $|D_{II}| = 97.6 \text{ G}, |E_{II}| = 6.5 \text{ G}$ ), agreements were found for the two cases of about  $\theta_{A-A} =$  $\pm 30^{\circ}$  (|D| = 102.1 G, |E| = 8.9 G) in the A-A structure, and, in the A-B structure, for the two cases of about  $\theta_{A-B} = 0^{\circ}$  $(|D| = 89.6 \text{ G}, |E| = 5.3 \text{ G}) \text{ and } \theta_{A-B} = -60^{\circ} (|D| = 107.3 \text{ G})$ G, |E| = 7.3 G). In this case, the results of the calculation suggest that dimer II takes a conformation having some overlap between two aryloxyl groups in the complex.



Figure 7. Conformations of (a) dimer I and (b) dimer II in A-A type structure.

Figures 7, a and b, shows the conformations of dimer I ( $\theta_{A-A} = \pm 75^{\circ}$ ) and dimer II ( $\theta_{A-A} = \pm 30^{\circ}$ ) obtained for the A–A type structure.

Unfortunately, it is not possible to decide whether dimers I and II take an A-A or A-B structure because both the |D| and |E| values experimentally obtained can be well explained by those calculated for the above structures. However, the results of the calculation of the zfs parameters indicate that the trans conformation observed for the KI complex of native benzo-15-crown-5 by X-ray analysis<sup>6</sup> is improbable for the present KI complex of 1 in ethanol rigid matrix. In a recent paper, we reported that the KI complex of the galvinoxyl-labeled B15C5 has a structure close to the cis conformation, in which the galvinoxyl skeletons stack over one another, based on the results of a calculation of the zfs parameters.<sup>10</sup> It is probable that the van der Waals interaction between the two substituted galvinoxyl groups induces such a conformation. However, it is not clear at present why the two kinds of 2:1 complexes coexist in ethanol rigid matrix and take different conformations as described above.

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Registry No. 1, 84812-26-0; 1.LiI (1:1 complex), 84824-33-9; 1.LiI (2:1 complex), 84824-46-4; 1.NaI (1:1 complex), 84824-34-0; 1-NaI (2:1 complex), 84824-47-5; 1-KI (1:1 complex), 84824-36-2; 1-KI (2:1 complex), 84824-48-6; 1-RbI (1:1 complex), 84824-35-1; 1.RbI (2:1 complex), 84824-49-7; 1.MgCl<sub>2</sub> (1:1 complex), 84824-37-3; 1.MgCl<sub>2</sub> (2:1 complex), 84824-50-0; 1.CaCl<sub>2</sub> (1:1 complex), 84824-38-4; 1.CaCl<sub>2</sub> (2:1 complex), 84824-51-1; 1.SrCl<sub>2</sub> (1:1 complex), 84824-39-5; 1.SrCl<sub>2</sub> (2:1 complex), 84824-52-2; 1.BaI<sub>2</sub> (1:1 complex), 84824-40-8; 1-BaI<sub>2</sub> (2:1 complex), 84824-53-3; 1-KBr (1:1 complex), 84824-41-9; 1·KBr (2:1 complex), 84824-54-4; 1·KSCN (1:1 complex), 84824-43-1; 1.KSCN (2:1 complex), 84824-56-6; 1.KIO<sub>4</sub> (1:1 complex), 84824-44-2; 1.KIO<sub>4</sub> (2:1 complex), 84824-57-7; 1·K<sub>2</sub>SO<sub>4</sub> (1:1 complex), 84824-45-3; 1·K<sub>2</sub>SO<sub>4</sub> (2:1 complex), 84824-58-8; quinol-B15C5, 84812-24-8; phenol-B15C5, 84812-25-9; 4'-bromobenzo-15-crown-5, 60835-72-5; 2,6-di-tert-butyl-pbenzoguinone, 719-22-2.

# Spin Trapping in Electrochemistry. Nonaqueous Electrochemical Behavior of Nitroso Spin Traps

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The oxidative and reductive behavior of 11 nitroso compounds has been characterized in *N*,*N*-dimethylformamide (DMF) and acetonitrile, in order to evaluate their utility as spin traps in electrochemical processes. The "potential windows" of these spin traps are reported as well as preliminary applications to the study of direct or indirect electrochemical reduction of alkyl halides.

Spin trapping is now recognized as a standard method to investigate reaction mechanisms.<sup>2</sup> This technique has recently been used to characterize radical intermediates arising from electrooxidations,<sup>3</sup> photoassisted oxidations,<sup>4</sup> and electroreductions of substrates<sup>5</sup> in solution.

The characteristics of both nitrones and nitroso compounds, the most widely used spin traps, have been investigated and compared extensively.<sup>2</sup> The main advantage of nitroso spin traps over nitrones lies in their ability of forming nitroxides which give more direct information on the structure of the trapped radical. The electrochemical behavior of a large series of nitrones has recently been reported.<sup>6</sup> The present paper is intended to describe

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