Spin Label Investigation of the Crown Ether. Complex Formation between the Veratrole Analogue of Phenoxyl-labeled Benzo-15-crown-5 and Alkali and Alkaline Earth Metal Salts in Frozen Solution

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A stable "phenoxyl-veratrole" (**2**), a veratrole analogue of "phenoxyl-benzo-15-crown-5" (**1**), was prepared and the complex formation between **2** and the alkali and alkaline earth metal salts has been studied by the ESR technique. Existence of the 2:1 complex of **2** with K^+, Rb^+, and Cs^+ salts was confirmed by the observation of the triplet ESR spectra in ethanol rigid matrix at 77 K. Essentially the same *g*- and *D*-tensor values were observed for all the 2:1 complexes, indicating similar conformation of the ligand molecule **2**. By comparing the observed *D* and *E* parameters with those of the 2:1 complexes reported for the alkali and alkaline earth metal complexes of **1** in a previous paper (Ref. 10), the structure of the 2:1 complex in ethanol rigid matrix was discussed. On the other hand, the results of the ESR measurements of the Li^+, Na^+, and alkaline earth metal complexes suggested a 1:1 complex formation between **2** and the metal salts.

Many investigations have been performed for the complex formation between crown ether and alkali and alkaline earth metal salts.[1-3] The stoichiometry of the crystalline complexes depends on the relative size of the "hole" in the crown ether and of the cation.[2-6] 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 (B15C5) can cause a significant change in the complex formation constant.[7] They reported that the effect may be as large as that caused by a change in the structure of the polyether ring.

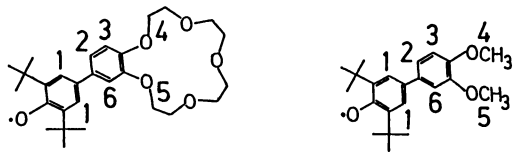
The spin label investigation of the crown ether has given useful and important information about the formation and structure of the crown-metal complexes, as described in previous papers:[8,9] For instance, both the nitroxide- and galvinoxyl-labeled B15C5 compounds form 1:1 complexes with NaSCN and 2:1 complexes with KSCN, as reported for the native benzo-15-crown-5. However, the structure of the above 2:1 complexes in frozen solution is different from that of B15C5 obtained by X-ray analysis.[6]

Recently, we have prepared a stable phenoxyl derivative of benzo-15-crown-5 (hereafter called "phenoxyl-B15C5" (**1**)) (see Fig. 1) and studied the complex formation between the spin-labeled crown ether **1** and the alkali (Li^+, Na^+, K^+, and Rb^+) and alkaline earth (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) metal salts by the ESR technique.[10] The result of ESR observation has established the new fact that two kinds of 2:1 complexes (hereafter called the dimer I_c and II_c complexes) having different structures (see Fig. 7 in Ref. 10) and a 1:1 complex coexist at equilibrium in all the ethanol solutions of **1** containing the above 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, and suggests that van der Waals interaction between the aryloxyl groups substituted to the cyclic polyether ring may play an important role in the complex formation and in fixing the conformation of the complex, in addition to the above ion-dipole interaction.

In the present paper, in order to obtain further information on such complex formations, we have prepared a veratrole analogue of **1** (hereafter called "phenoxyl-veratrole" (**2**)) (see Fig. 1), in which the cyclic polyether ring is substituted by two methoxyl groups, and observed ESR spectra of its alkali and alkaline earth metal complexes in ethanol at 77 K.

Experimental

Quinol Derivative of Veratrole (3). **3** was synthesized by the reaction of lithium derivative of 4-bromoveratrole with 2,6-di-*t*-butyl-*p*-benzoquinone, according to the procedure used by us to prepare the quinol precursor of **1**.[10] **3** was recrystallized twice from ligroin (bp 90—105 °C) to give white crystals: Mp 122—123 °C; UV (EtOH) λ_{max} 282 nm (log ε=3.89); NMR (CCl_4) δ=1.18 (18H, s, *t*-Bu), 2.18 (1H, s, OH), 3.70 (6H, s, OCH_3), 6.38 (2H, s, *m*-ring), 6.68 (2H, s, aromatic H), 6.78 (1H, s, aromatic H) with Me_4Si as internal



Phenoxyl-B15C5 (**1**) Phenoxyl-Veratrole (**2**)

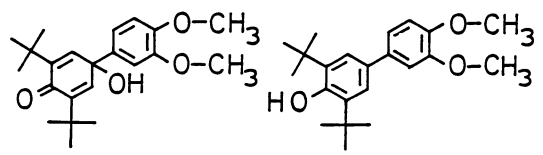
Fig. 1. Molecular structures of phenoxyl-Bl5C5 (**1**) and phenoxyl-veratrole (**2**), and atomic numbering system.

standard.

Anal. Calcd for $C_{22}H_{30}O_4$: C, 73.71; H, 8.44%. Found: C, 73.42; H, 8.57%.

Phenol Derivative of Veratrole (4). **4** was synthesized by the reduction of **3** with Zn powder and concentrated HCl in methanol at 20 °C for 20 min.[11] **4** was recrystallized twice from ligroin (bp 95—105 °C) to give white crystals: Mp 135—136 °C; UV (EtOH) λ_{max} 268 nm (log ε=4.25); NMR (CCl_4) δ=1.45 (18H, s, *t*-Bu), 3.79 (3H, s, CH_3O), 3.81 (3H, s, CH_3O), 4.96 (1H, s, OH), 6.78 (1H, s, aromatic H), 6.83 (2H, s, aromatic H), 7.13 (2H, s, *m*-ring) with Me_4Si as an internal standard.

Anal. Calcd for $C_{22}H_{30}O_3$: C, 77.16; H, 8.83%. Found: C, 77.41; H, 9.00%.



Quinol-Veratrole (**3**) Phenol-Veratrole (**4**)

Phenoxyl Derivative of Veratrole (Phenoxyl-veratrole) (2). Phenoxyl-veratrole (**2**) was prepared by the oxidation of corresponding phenol (**4**) with alkaline potassium hexacyanoferrate(III) in diethyl ether solvent under a nitrogen atmosphere, with the temperature kept between 0 and 5 °C.[12] **2** was isolated as stable dark brown crystals from the etherial solution: UV-vis (cyclohexane) λ_{max} 373 (log ε=3.71), 576 (log ε=2.93), 625 nm (log ε=3.05).

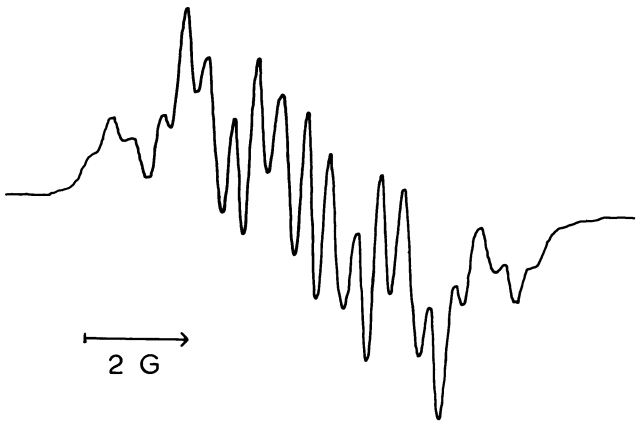


Fig. 2. ESR spectrum of **2** in ethanol at 20 °C.

The radical concentration was obtained from the results of the paramagnetic susceptibility measurements at 20 °C, after correcting for the diamagnetic contribution (χ_{dia}=−0.237×10^{-3} emu mol^{-1}) calculated by Pascal's method. The value of the radical concentration was 95%, assuming the Curie law. All the ESR spectra were measured in a sealed, degassed system.

Results and Discussion

Ethanol Solution ESR Spectrum of 2. The ethanol solution ESR spectrum of **2** has been measured at 20 °C (see Fig. 2). The observed hyperfine couplings are listed in Table 1. The value of each hyperfine splitting of phenoxyl-veratrole (**2**) is very close to the corresponding value of phenoxyl-B15C5 (**1**) radical,[10] except for the β-methyl and -methylene proton hyperfine splitting at O-4 (see Table 1). The g_{iso}-value (2.00416±0.00005) of **2** in an ethanol solution also show a good agreement with that (g_{iso}=2.00421± 0.00005) of **1** within the limits of experimental error. These results indicate that the effects of the substitution of the cyclic polyether ring by two methoxyl groups are very small to induce a change in the unpaired spin distribution of aryloxyl group.

Ethanol Rigid-matrix ESR Spectra of the Alkali and Alkaline Earth Metal Complexes of 2. An ethanol solution of **2** (3.0×10^{-3} mol dm^{-3}) containing equimolar KI salt gives an ESR spectrum consisting of (i) a central strong singlet and (ii) three pairs of absorption lines (X, X′; Y, Y′; and Z, Z′) on both sides of the central singlet at 77 K, as shown in Fig. 3 (a). A slightly asymmetric central line with a width of about 7.6 G at $g\cong2.0043$ shows a shape essentially the same as that of the metal-free **2** (ΔH_{msl}=6.9 G and $g\cong2.0042$), and the relative intensity of this central line changes depending on the ratio of the potassium salt to **2**. Therefore, this line is attributable to the 1:1 complex (hereafter called the monomer complex) between **2** and KI. The three pairs of absorption lines apparently represent zero-field splittings (zfs) arising from the intermolecular spin-spin dipolar interaction of two electrons in a triplet state. The result clearly indicates the formation of the 2:1 complex (hereafter called the dimer II_v complex) between **2** and KI. The zfs parameters (*D* and *E*) and *g*-tensor values observed for the dimer II_v complex are listed in Table 2.

First, the effects of positive ions on the complex for-

Table 1. Hyperfine couplings (a_i^H) and spin densities (ρ_i) of **1** and **2** in ethanol at 20 °C

		a_1^H	a_2^H	a_3^H	$a_4^{CH_3}$	a_6^H
2	ESR	1.41 G[a]	2.38	0.55	0.37	1.41
	ρ(exptl)	−0.0522	0.0881	−0.0204	0.0137[b]	0.0522
1	ESR	1.42 G	2.35	0.52	0.52[c]	1.42
	ρ(exptl)	−0.0526	0.0870	−0.0193	0.0128[b]	0.0526
	ρ(calcd)	−0.0296	0.0827	−0.0269	0.0105[b]	0.0341

a) Experimental errors, ±0.05 G. 1 G=10^{-4} T. b) Spin densities at O—4. c) Methylene proton hyperfine couplings.

TABLE 2. *D*- AND *g*-TENSOR VALUES OF THE COMPLEXES OF PHENOXYL-VERATROLE (**2**) WITH ALKALI METAL SALTS IN ETHANOL AT 77 K

Salts	$\frac{\lvert D\rvert}{G}$ [a]	$\frac{\lvert E\rvert}{G}$ [a]	g_{xx} [b]	g_{yy}	g_{zz}	g_{av}	Complex
LiI	a slightly asymmetric single line ($\Delta H_{msl} \cong 7.5$ G)						(1 : 1)
NaI	a slightly asymmetric single line ($\Delta H_{msl} \cong 7.8$ G)						(1 : 1)
KI	96.1	5.8	2.0062	2.0041	2.0031	2.0045	(2 : 1)
RbI	96.0	6.0	2.0057	2.0039	2.0032	2.0043	(2 : 1)
CsI	96.4	5.7	2.0063	2.0039	2.0028	2.0043	(2 : 1)
KBr	96.0	5.7	2.0062	2.0040	2.0032	2.0044	(2 : 1)
KSCN	96.0	5.8	2.0062	2.0040	2.0031	2.0042	(2 : 1)
KIO_4	a slightly asymmetric single line ($\Delta H_{msl} \cong 7.7$ G)						(1 : 1)
K_2SO_4	a slightly asymmetric single line ($\Delta H_{msl} \cong 7.3$ G)						(1 : 1)

a) The experimental errors in the values of $|D|$ and $|E|$ are ± 0.4 G. 1 G $= 10^{-4}$ T. b) The experimental errors in the values of g_{xx}, g_{yy}, and g_{zz} are ± 0.0002.

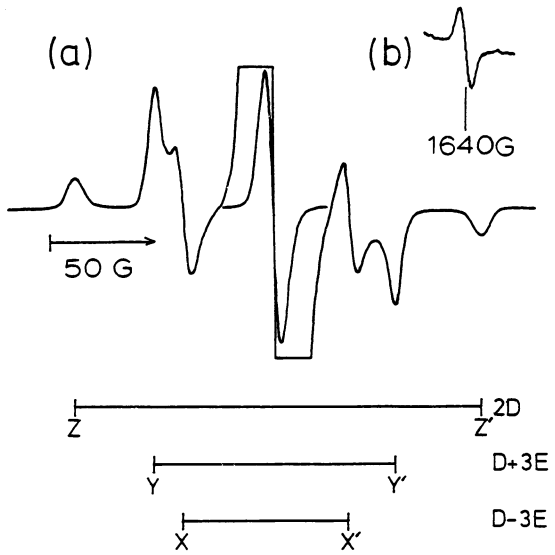


Fig. 3. ESR spectrum of the KI complex of **2** in ethanol at 77 K: (a) $\Delta m_s = \pm 1$ transition and (b) $\Delta m_s = \pm 2$ transition.

mation and on the molecular structure of the complex were studied. The ESR spectra of both the RbI and CsI complexes of **2** in ethanol at 77 K show shapes essentially the same as that of the KI complex, indicating the coexisting of a dimer and a monomer. As it is clear from the results shown in Table 2, the variation in zfs parameters with cations (K^+, Rb^+, and Cs^+) is almost negligible in the present dimer II_v complexes. On the other hand, ethanol solutions of **2** (3.0×10^{-3} mol dm^{-3}) containing equimolar alkali (LiI and NaI) and alkaline earth ($MgCl_2$, $SrCl_2$, and BaI_2) metal salts show a slightly asymmetric single line with a width of about 7 G located at $g \cong 2.004$ at 77 K, respectively, unequivocally suggesting 1 : 1 complex formation between **2** and the above salts.

Second, the effects of the negative ions (Br^-, I^-, SCN^-, IO_4^-, and SO_4^{2-}) on the complex formation and on the molecular structure of the complex have been studied. The anions were varied in the K^+ and Na^+ salts. ESR spectra of the KBr and KSCN complexes of **2** in ethanol rigid-matrix at 77 K are very similar to that of the KI complex, except for the difference in the central signal intensity, indicating the coexisting of a dimer II_v and a monomer. The observed *D*- and *g*-tensor values are summarized in Table 2. The result indicates that the effect of the change in anions is too small to induce the change in the molecular structure of the 2:1 complex. However, triplet ESR spectrum was not observed for the KIO_4 and K_2SO_4 complexes of **2**, suggesting the effect of anions on complex formation. On the other hand, similar single line ESR spectra were observed in all the Na complexes of **2** studied, indicating the 1:1 complex formation.

Here, an attempt to establish the molar ratio of the monomer and dimer II_v was achieved by observing the ethanol rigid-matrix ESR spectrum of **2** containing equimolar KI salt. The approximate ratio can be determined from the integrated spectral intensity of a first-derivative ESR absorption line.[13] The ratio obtained is monomer:dimer II_v=4:1.

The Structure of the 2:1 Complexes of 2 with K^+, Rb^+, and Cs^+ Metal Salts. As reported in a previous paper,[10] the results of the ESR observations have established the new fact that two kinds of 2:1 complexes (the dimer I_c and II_c complexes) having different structures and a 1:1 complex coexist at equilibrium in all the ethanol solutions of phenoxyl-B15C5 (**1**) containing the eight kinds of the alkali and alkaline earth metal salts. In addition, both in dimer I_c and II_c, the *D* and *E* values and *g*-tensor values observed for all the alkali and alkaline earth metal complexes remain constant, respectively, within the limit of experimental error, except for the small change in dimer II_c complexes of **1** with $SrCl_2$ and BaI_2. For instance, the *D* and *E* values and *g*-tensor values observed for the KI complex of **1** are $|D_I|$= 24.1 G, $|E_I|$=0.9 G, g^I_{xx}=2.0047, g^I_{yy}=2.0040 for dimer I_c, and $|D_{II}|$=97.6 G, $|E_{II}|$=6.5 G, g^{II}_{xx}=2.0061, g^{II}_{yy}=

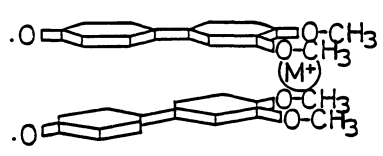


Fig. 4. Conformation of dimer II_v.

2.0036, g_{zz}^{II}=2.0026 for dimer II_c.

The result of the present ESR observations showed that a kind of 2:1 complex and a 1:1 complex coexist at equilibrium in the ethanol solutions of **2** containing the K^+, Rb^+, and Cs^+ metal salts. For instance, the *D*, *E*, and *g*-tensor values observed for the KI complex of **2** in ethanol rigid-matrix are $|D|$=96.1 G, $|E|$=5.8 G, g_{xx}=2.0062, g_{yy}=2.0041, and g_{zz}=2.0031, as listed in Table 2. It is very interesting that the phenoxyl-veratrole (**2**) having no crown ether ring forms 2:1 complex with alkali metal salts. And, further, these values are very similar to those observed for the dimer II_c complex of KI salt of **1**. As has been descrived in a previous section, **1** and the veratrole analogue (**2**) have similar spin distribution in a fluid solution. Therefore, the similarity of the *D*, *E*, and *g*-values observed for **1** and **2** suggests that the dimer II_v structure of the KI complex of **2** is similar to that of the dimer II_c structure of the KI complex of **1** (see Fig. 7 in Ref. 10). That is, the dimer II_v has a structure in which the aryloxyl radical parts of the complex overlap each other. From the results of the observed zfs parameters, a preferable conformation of the dimer II_v complex of **2** was assumed as illustrated in Fig. 4.

Many investigations have been performed for the complex formation between crown ether and alkali and alkaline earth metal salts, including B15C5, in solution and in the solid state.[1-7] The stoichiometry of the crystalline complexes depends on the relative size of the hole in the crown ether and of the cation. For instance, B15C5 with a hole 1.7—2.2 Å in diameter usually forms a 1:1 complex with Na^+ (diameter, 1.90 Å), because the Na^+ cation fits tightly in the crown cavity. But, it forms a 2:1 complex with K^+ (2.66 Å), the ion larger than the hole. Such complex formations will be induced by the ion-dipole interaction between the positive ion and the cyclic polyether ring. Therefore, by substituting the two methoxyl groups for the cyclic polyether ring, the above ion-dipole interaction will decrease considerably, and thus the complex formation will not be observed.

However, the result of the present investigation showed that the phenoxyl-veratrole (**2**), having no polyether ring, forms 2:1 complexes with alkali metal salts (K^+, Rb^+, and Cs^+). Further, the 2:1 complexes of **2** have a structure, in which the aryloxyl skeletons stack over one another, as shown in Fig. 4. It is probable that the van der Waals interaction between the two substituted aryloxyl groups induces such a complex formation and a conformation. On the other hand, the fact that the phenoxyl-veratrole (**2**) does not form 2:1 complex with LiI, NaI, and alkaline earth salts suggests that the ion-dipole interaction also play an important role in the above complex formation.

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References

1) C. J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017 (1967).
2) C. J. Pedersen, *J. Am. Chem. Soc.*, **92**, 386 (1970).
3) J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, **74**, 351 (1974), and references cited therein.
4) M. A. Bush and M. R. Truter, *J. Chem. Soc. Perkin Trans, 2*, **1972**, 341.
5) N. S. Poonia and M. R. Truter, *J. Chem. Soc. Dalton*, **1973**, 2062.
6) P. R. Mallinson and M. R. Truter, *J. Chem. Soc. Perkin Trans 2*, **1972**, 1818.
7) R. Ungaro, B. El Haj, and J. Smid, *J. Am. Chem. Soc.*, **98**, 5198 (1976).
8) K. Ishizu, H. Kohama, and K. Mukai, *Chem. Lett.*, **1978**, 227.
9) K. Mukai, N. Iida, and K. Ishizu, *Bull. Chem. Soc. Jpn.*, **55**, 1362 (1982).
10) K. Mukai, M. Yamashita, K. Ueda, K. Tajima, and K. Ishizu, *J. Phys. Chem.*, **87**, 1338 (1983).
11) A. Rieker and K. Scheffler, *Ann. Chem.*, **689**, 78 (1965).
12) E. Müller and K. Ley, *Chem. Ber.*, **87**, 22 (1954).
13) H. Yokoi and T. Isobe, *Bull. Chem. Soc. Jpn.*, **46**, 447 (1973).