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ESR Investigation of Alkali Metal Complexes of Galvinoxyl-labeled Benzo-15-crown-5 in Frozen Solution

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A stable galvinoxyl derivative (**1**) of benzo-15-crown-5 was prepared and the complex formation between the spin labeled crown ether **1** and the alkali metal and ammonium salts was studied by the ESR technique. Existence of the (2:1) complex of **1** with potassium, rubidium, and ammonium salts was confirmed by the observation of the triplet ESR spectra in ethanol rigid matrix at 77 K. Essentially the same $\boldsymbol{g}$- and $\boldsymbol{D}$-tensor values are observed for all the (2:1) complexes, indicating similar conformation of the ligand molecule **1**. The zero-field splitting parameters (D and E) are calculated on the basis of the spin distribution of **1** and the assumed molecular structures for the (2:1) complex. By comparing the observed D and E parameters with the calculated ones, the structure of the (2:1) complex in ethanol rigid matrix is discussed. On the other hand, the sodium complexes of **1** show a slightly asymmetric single line, suggesting the (1:1) complex formation between **1** and the sodium salts. No anions (SCN^-, Br^-, and I^-) have any appreciable effect on the ESR spectra of both the (2:1) and (1:1) complexes.

It is well known that the cyclic polyethers synthesized by Pedersen form stable complexes with alkali and alkaline earth metal ions, both in solution and in the solid state.[1—3] The stoichiometry of the crystalline complexes depends on the relative size of the "hole" in the cyclic polyether and of the cation. For instance, benzo-15-crown-5 with a hole 1.7—2.2 Å in diameter usually forms a (1:1) complex with sodium (1.90 Å in diameter), and (2:1) complexes with the ions larger than the hole. Recently, we have prepared a galvinoxyl derivative (**1**) of benzo-15-crown-5 (*i.e.*, galvinoxyl-benzo-15-crown-5 (**1**)) (see Fig. 1) and studied the complex formation of the spin-labeled crown ether (**1**) with NaSCN or KSCN salt by using the ESR technique.[4] A triplet ESR spectrum has been observed for the KSCN complex of **1** in ethanol rigid matrix at 77 K, indicating the formation of a sandwiched dimer. On the other hand, the result of ESR measurement of the NaSCN complex suggested a (1:1) complex formation between **1** and NaSCN.

In the present paper, in order to obtain further information on such complex formations, we have measured ESR spectra of the complexes of **1** with eight kinds of salts in ethanol rigid matrix. Typical triplet ESR spectra have been observed for the K^+, Rb^+, and NH^+_4 complexes of **1**, clearly showing the (2:1) complex formation between **1** and the salts. The zero-field splitting (ZFS) parameters (D and E) were calculated for the assumed molecular structures by using McLachlan's spin densities of **1** which is a monoradical half of the sandwiched dimer. On the basis of these data, the structure of the (2:1) complex has been discussed. Solvent effect on the structure of the (2:1) complex has also been studied. On the other hand, the sodium complexes of **1** showed a slightly asymmetric single line, suggesting the (1:1) complex formation between **1** and the sodium salts. Three anions, SCN^-, Br^-, and I^-, used in this study have been found to have little effect on the spectral characteristics of either the (2:1) or the (1:1) complex.

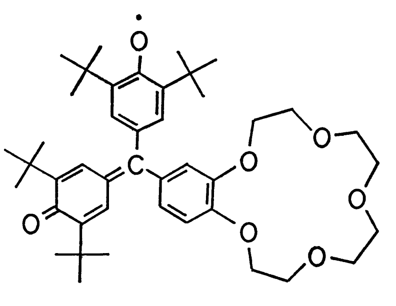

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Fig. 1. Molecular structure of galvinoxyl-benzo-15-crown-5 (**1**).

Experimental

The phenol precursor of **1** was synthesized by condensation of 2,6-di-*t*-butylphenol (2.06 g) with 4′-formylbenzo-15-crown-5 (2.96 g) in KOH (0.66 g)–ethanol (30 cm^3) solution under a nitrogen atmosphere at 30 °C, as described in a previous paper.[4] An orange crystal of the phenol precursor showed a melting point 209—211 °C (softens at 176 °C): Found: C, 74.13; 8.74%. Calcd for $C_{43}H_{60}O_7$: C, 74.97: H, 8.78%. UV and visible (C_2H_5OH) 276 (ε 18500) and 434 nm (ε 30200); NMR (CCl_4) $\delta=1.23$ (18H, s, *t*Bu, ring A), 1.43 (18H, s, *t*Bu, ring B), 3.5—4.2 (16H, m, $-CH_2-$), 5.37 (1H, s, OH, ring A), 6.70—6.82 (3H, m, ring C), 7.00 (2H, s, aromatic H, ring A), and 7.08 (2H, s, aromatic H, ring B).

Compound **1** was prepared by oxidation of the above phenol precursor with alkaline potassium hexacyanoferrate(III) in diethyl ether solvent under a nitrogen atmosphere, with the temperature kept between 0—5 °C. Compound **1** was isolated as a stable dark brown crystal from the etherial solution: UV and visible (C_2H_5OH) 280 (ε 17000), 388 (ε 18400), and 455 nm (ε 49500).

The magnetic susceptibility of **1** was measured in the temperature range 55—300 K. The data have been corrected for the diamagnetic contribution of $\chi_{\text{dia}}=-0.437\times 10^{-3}$ emu/mol calculated by Pascal's method. The susceptibility follows the Curie-Weiss law, with a paramagnetic Curie constant of 0.369 ± 0.010 K·emu/mol and a Weiss constant of -2 ± 3 K. The radical concentration of **1** calculated from the above Curie constant is 98%. All the ESR spectra were measured in a sealed, degassed system.

TABLE 1. $\boldsymbol{D}$- AND $\boldsymbol{g}$-TENSOR VALUES OF THE COMPLEXES OF **1** WITH SEVERAL SALTS IN ETHANOL AT 77 K

Salt	Complex	$\lvert D\rvert^{a)}$/G	$\lvert E\rvert^{a)}$/G	$g_{zz}{}^{b)}$	g_{yy}	g_{xx}	$g_{av}{}^{c)}$
KSCN	(2 : 1)	76.2	8.9	2.0032	2.0052	2.0072	2.0052
KBr	(2 : 1)	76.4	8.8	2.0030	2.0049	2.0069	2.0049
KI	(2 : 1)	75.9	8.7	2.0029	2.0049	2.0073	2.0051
RbI	(2 : 1)	76.4	8.8	2.0028	2.0048	2.0067	2.0048
NH_4SCN	(2 : 1)	76.2	8.6	2.0029	2.0050	2.0066	2.0048
NaSCN	(1 : 1)	a slightly asymmetric single line ($\Delta H_{msl} \simeq 6.6$ G)					
NaBr	(1 : 1)						
Na_2SO_4	(1 : 1)						

a) The experimental errors in the values of $|D|$ and $|E|$ are ± 0.3 G. 1 G$=10^{-4}$ T. b) The experimental errors in the values of g_{xx}, g_{yy}, g_{zz}, and g_{av} are ± 0.0002. c) $g_{av}=1/3(g_{xx}+g_{yy}+g_{zz})$.

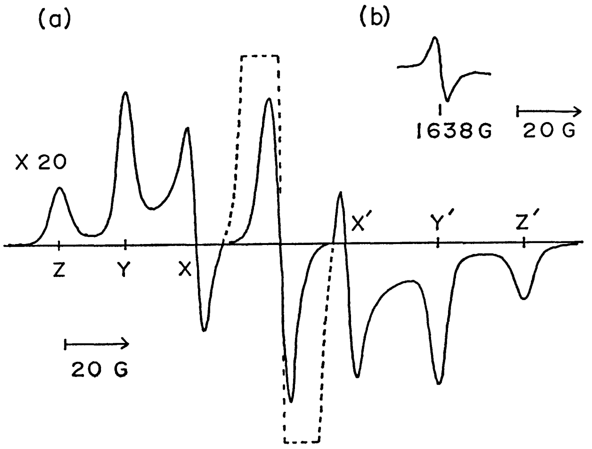

Fig. 2. ESR spectrum of the KI complex of **1** in ethanol at 77 K; (a) $\Delta m_s=\pm 1$ transition and (b) $\Delta m_s=\pm 2$ transition.

Results and Discussion

*Ethanol Rigid Matrix ESR Spectra of the Alkali Metal Complexes of **1**.* An ethanol solution of **1** (3.0×10^{-3} mol dm^{-3}) containing equimolar KI salt clearly shows three pairs of absorption lines with the same order of intensity at 77 K, as shown in Fig. 2(a). A slightly asymmetric central line with a width of about 6.0 G (1 G$=10^{-4}$ T) at $g\simeq 2.005$ shows a shape essentially the same as that of the metal-free **1** ($\Delta H_{msl}=6.5$ G and $g\simeq 2.005$), 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 metal-free **1** and/or the (1:1) complex between **1** and KI. The three pairs of absorption lines apparently represent zero-field splittings arising from the intermolecular spin-spin dipolar interaction of two electrons in a triplet state. In fact, the forbidden transition ($\Delta m_s=\pm 2$) was observed at about 1638 G, as shown in Fig. 2(b). These results clearly indicate the (2:1) complex formation between **1** and KI.

The spin Hamiltonian for the triplet radical pair may be expressed by

$$H=\beta\boldsymbol{H}\cdot\hat{\boldsymbol{g}}\cdot\boldsymbol{S}+\boldsymbol{S}\cdot\hat{\boldsymbol{D}}\cdot\boldsymbol{S} \quad (1)$$

$$=\beta\boldsymbol{H}\cdot\hat{\boldsymbol{g}}\cdot\boldsymbol{S}-XS_x^2-YS_y^2-ZS_z^2, \quad (2)$$

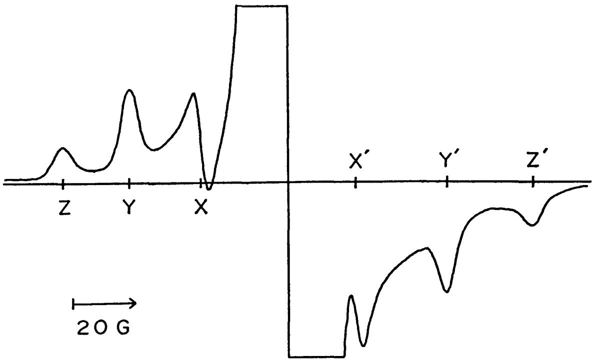

Fig. 3. ESR spectrum of the RbI complex of **1** in ethanol at 77 K.

where $\hat{\boldsymbol{g}}$ is $\boldsymbol{g}$ tensor, $\hat{\boldsymbol{D}}$ is the fine structure tensor with principal values of $-X$, $-Y$, and $-Z$, and the other symbols have the usual meanings. The separations (ZZ', YY', and XX') between the three pairs of absorption lines in the spectrum of the KI complex are 151.8 ±0.6, 102.0±0.6, and 49.8±0.6 G, respectively, so the ZFS parameters, $|D|$ and $|E|$, were evaluated as 75.9±0.3 and 8.7±0.3 G, respectively, by the method of Wasserman *et al.*[5] Assuming that the principal axes of the $\boldsymbol{D}$- and $\boldsymbol{g}$-tensors are coaxial, $\boldsymbol{g}$-tensor values have been estimated from the positions of three pairs of turning points (ZZ', YY', and XX').[5,6] They are $g_{zz}=2.0029\pm 0.0002$ (Z, Z'), $g_{yy}=2.0049\pm 0.0002$ (Y, Y'), and $g_{xx}=2.0073\pm 0.0002$ (X, X').

First, the effect of the negative ions on the structure of the KI complex of **1** was examined. The ESR spectra of both the KBr and KSCN complexes of **1** in ethanol at 77 K are similar to that of the KI complex of **1**, and the observed $\boldsymbol{D}$- and $\boldsymbol{g}$-tensor values of these (2:1) complexes are summarized in Table 1. Live and Chan[7] have measured the proton NMR spectra of some crown ethers and their alkali metal complexes in organic solvents, and studied the solution structure of the "crown" cyclic polyether rings in detail. They observed the variation in chemical shifts of ether protons with anions (I^-, SCN^-, and $ClO^-{}_4$), and concluded that the difference in the shifts is due to the ion-pair formation. However, as it is clear from the results shown in Table 1, 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.

Second, the effects of the positive ions on the complex formation and on the molecular structure of the complex were studied. The ESR spectrum of the RbI complex of **1** in ethanol rigid-matrix at 77 K shows a shape essentially the same as that of the KI complex (see Fig. 3), except for the difference in the central signal intensity, indicating the (2:1) complex formation. The ZFS parameters (D and E) and $\boldsymbol{g}$-tensor values have been estimated from the positions of the three pairs of turning points (ZZ', YY', and XX'), as performed for the KI complex of **1**. These values are $|D|=76.4\pm0.3$ G, $|E|=8.8\pm0.3$ G, $g_{zz}=2.0028\pm0.0002$, $g_{yy}=2.0048\pm0.0002$, and $g_{xx}=2.0067\pm0.0002$. The ethanol rigid-matrix ESR spectrum of the NH_4SCN complex of **1** is also quite similar to that of the KI complex of **1**, giving the ZFS parameters of $|D|=76.2\pm0.3$ G and $|E|=8.6\pm0.3$ G. The ZFS constants are the same for all the (2:1) complexes of **1** examined in the present work. We can then conclude that the same molecular conformation persists in all the (2:1) complexes studied. On the other hand, the solution of **1** (3.0×10^{-3} mol dm^{-3}) containing the equimolar NaSCN salt shows a slightly asymmetric single line with a width of 6.6 G located at $g\simeq2.005$ at 77 K, unequivocally suggesting (1:1) complex formation between **1** and NaSCN. Further, by changing the anion of Na salt from SCN^- to Br^- and SO_4^{2-} in the ethanol solution, no detectable changes were observed in the ESR spectra (see Table 1).

*The Structure of the (2:1) Complexes of **1** with K, Rb, and NH_4 Salts.* The crystal structure of a (2:1) complex of benzo-15-crown-5 with potassium iodide has been investigated by Mallinson and Truter.[8] The crystal system of the complex is tetragonal with a space group of P4/n and with lattice constants of $a=b=17.84$, $c=9.75$ Å, and $z=4$. The complex cation has crystallographic symmetry $\bar{1}$, the potassium being 'sandwiched' between the two centro-symmetrically 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 ten oxygen neighbors form a pentagonal antiprism. The benzo-group is nearly coplanar with the oxygens, the greatest deviation being 0.11 Å. If the KI complex of **1** takes a conformation (hereafter referred to as the "*trans*" conformation) similar to that of the benzo-15-crown-5 complex, the interatomic distance between the central triphenylmethyl carbon atoms in the pair of **1** will become about 13 Å. A zero-field splitting of $|D|=75.9$ G has been observed for the KI complex of **1**, as described above. Consequently, the calculated average interelectronic distance, using a model of two-point dipoles ($|D|=(3/2)g\beta r^{-3}$), is about 7.2 Å. From comparison of these distances, the "*trans*" conformation is not acceptable for the KI complex of **1**. Therefore, in order to clarify the structure of the (2:1) complex of **1** with KI in ethanol rigid matrix, the calculations of the $\boldsymbol{D}$-tensor values were performed for the assumed structure of the complex, using McLachlan's spin densities of **1** which is considered to be a monoradical half of the (2:1) complex.[9,10]

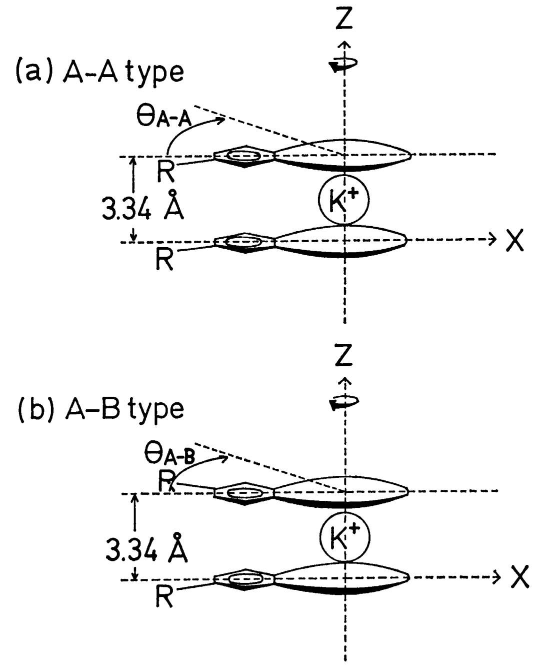

Fig. 4. Molecular structures and the coordinate systems chosen for "*cis*" conformation of the K complex of **1**.
(a) A-A type, (b) A-B type.

For the KI complex of **1**, we can expect two possible structures, (i) and (ii), in which each monoradical half is considered to have a planar structure, as a whole molecule. These two structures, (i) and (ii), are shown in Fig. 4 and named as "A-A type" and "A-B type" structures, respectively. Thus, as a most plausible case, the $\boldsymbol{D}$-tensor values were calculated, assuming that the interplanar spacing between the two monoradical halves is 3.34 Å and varying the rotation angles θ_{A-A} and θ_{A-B}. The coordinate systems (x, y, and z) chosen for both the structures are shown in Fig. 4, where $\theta=0°$ corresponds to a planar "*cis*" conformation and $\theta=180°$ is a planar "*trans*" conformer in each structure.

The orbital containing the unpaired electron of phenylgalvinoxyl radical has, at least in the Hückel approximation, a node in the central phenyl ring; in fact, the results of McLachlan MO calculation of phenylgalvinoxyl[11] showed the exsistence of a very small unpaired electron density (1.0—1.5%) in the phenyl ring, and, further, an ENDOR study found a small hyperfine splitting ($a^{\mathrm{H}}=0.207$ G) for the phenyl-ring protons.[11] In such a case, the unpaired electron distribution of **1** must be similar to that of phenylgalvinoxyl. In fact, the values of the hyperfine splittings ($a^{\mathrm{H}}_{\mathrm{m}}=1.31\pm0.02$ G) of the *meta* ring protons and the isotropic g_{iso} value ($=2.0044\pm0.0001$) of **1** show an excellent agreement with the corresponding values ($a^{\mathrm{H}}_{\mathrm{m}}=1.32\pm0.02$ G, $g_{\mathrm{iso}}=2.0044\pm0.0001$) of phenylgalvinoxyl.

The $\boldsymbol{D}$-tensor components of the dipolar splittings

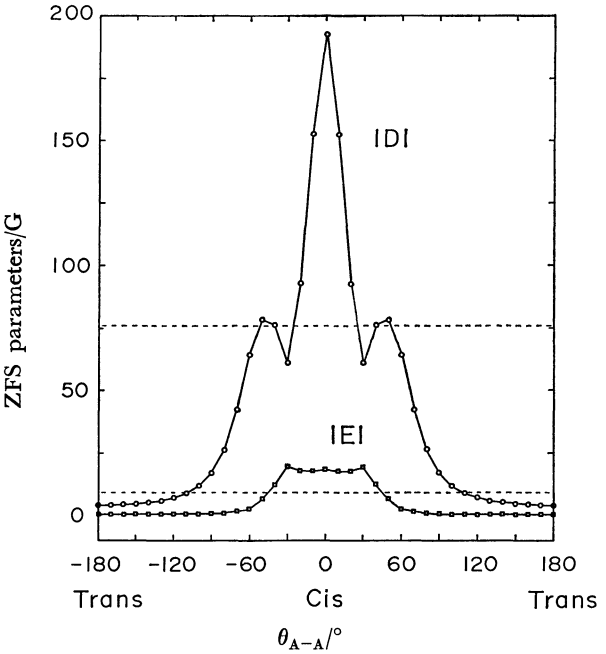

Fig. 5. The variation of the ZFS parameters $|D|$ and $|E|$ as a function of the rotation angle θ_{A-A}. Broken lines represent the observed $|D|$ (75.9 G) and $|E|$ (8.7 G) values for the KI complex of **1.**

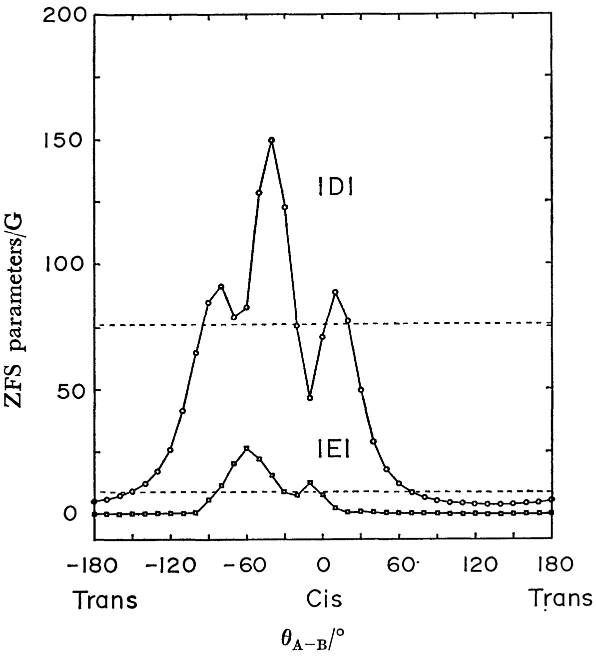

Fig. 6. The variation of the ZFS parameters $|D|$ and $|E|$ as a function of the rotation angle θ_{A-B}. Broken lines represent the observed $|D|$ (75.9 G) and $|E|$ (8.7 G) values for the KI complex of **1.**

can be calculated with the aid of the following equations:

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

$(m=\mathrm{x},\ \mathrm{y},\ \mathrm{z})$

$$D_{mn} = (1/2)g^2\beta^2 \sum_{i,j} \rho_i\rho_j(-3m_{ij}n_{ij})/r_{ij}^5, \qquad (4)$$

$(m,\ n=\mathrm{x},\ \mathrm{y},\ \mathrm{z};\ \text{but}\ m\neq n)$

where r_{ij} is the distance between the i and j atoms, and ρ_i and ρ_j are the McLachlan π-spin densities[11] on the i-th atom in one phenylgalvinoxyl group and the j-th atom in the other phenylgalvinoxyl group, respectively, in a (2:1) complex. Here we have used the following bond lengths for the galvinoxyl group: the C–O bond length is 1.27 Å and the C–C bond length is 1.40 Å on the average, as obtained by an X-ray analysis of the galvinoxyl radical.[12] Atomic coordinates of benzo-15-crown-5 are taken from its KI complex reported by Mallinson and Truter.[8] Then, 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 just how the ZFS parameters D and E vary as a function of θ_{A-A} and θ_{A-B}, respectively. In the case of A–A structure, the D parameter varies with θ_{A-A} from 192.3 G for $\theta_{A-A}=0°$ to 3.9 G for $\theta_{A-A}=180°$ and the E parameter from 19.3 G for $\theta_{A-A}=30°$ to 0.1 G for $\theta_{A-A}=180°$, but the dependence on the changes in θ_{A-A} is not simple. Similarly, in the case of A–B structure, the D and E parameters vary with θ_{A-B} from 149.3 G ($\theta_{A-B}=-40°$) to 3.9 G ($\theta_{A-B}=140°$) and from 26.2 G ($\theta_{A-B}=-60°$) to 0.1 G ($\theta_{A-B}=170°$), respectively. By comparing the observed D and E parameters ($|D|=75.9$ G, $|E|=8.7$ G) with the calculated ones, agreements were found for two cases of about $\theta_{A-A}=\pm45°$ ($|D|=77.5$ G, $|E|=9.1$ G) in A–A structure, and in A–B structure, for two cases of about $\theta_{A-B}=0°$ ($|D|=71.3$ G, $|E|=7.6$ G) and $\theta_{A-B}=-20°$ ($|D|=75.9$ G, $|E|=7.5$ G).

Unfortunately, it is not possible to decide whether the KI complex takes 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. Although the calculation presented here is of a very approximate nature for the (2:1) complex of **1**, the result has shown that the "*trans*" conformation observed for the KI complex of benzo-15-crown-5 by the X-ray analysis is improbable for the present KI complex of **1** in ethanol rigid matrix. This is consistent with our previous expectation. The results of the calculation of the ZFS parameters suggest that the complex has a structure near to "*cis*" conformation rather than "*trans*" one, showing the overlap between two galvinoxyl groups in the complex. It is probable that the van der Waals interaction between two galvinoxyl groups induces such a conformation.

As described in a previous section, **1** makes the (2:1) complex with Rb and NH_4 salts as well. If the Rb and NH_4 complexes of **1** also have a "sandwiched" structure with an alkali metal ion between the two benzo-15-crown-5 rings, we can expect the increase in the interplanar spacing between the two crown ether rings, as the ion diameter increases from K^+ (2.66 Å) to Rb^+ (2.96 Å) or NH^+_4 (2.84 Å). This will induce the decrease in the ZFS parameter $|D|$. However, the $|D|$ and $|E|$ values observed for the K, Rb, and NH_4 complexes remain constant, within the limit of experimental error (see Table 1). As

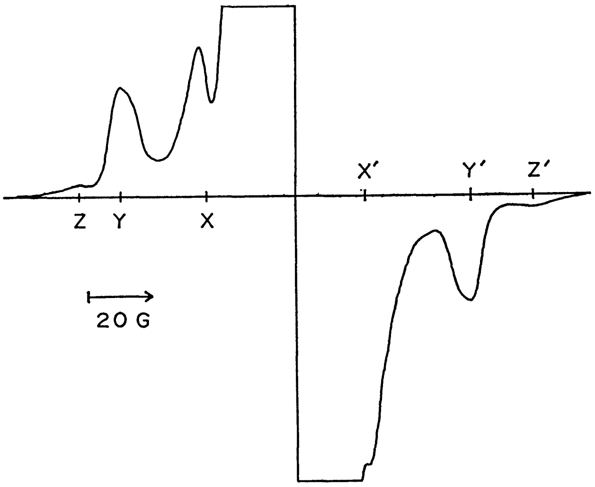

Fig. 7. ESR spectrum of the KSCN complex of **1** in 1,2-dichloroethane at 77 K.

Table 2. D- and g-tensor values of the KSCN complex of **1** in several solvents at 77 K

Solvent	$\frac{\lvert D\rvert}{G}$	$\frac{\lvert E\rvert}{G}$	g_{zz}	g_{yy}	g_{xx}	g_{av}
Ethanol	76.2	8.9	2.0032	2.0052	2.0072	2.0052
2-Propanol	76.1	8.8	2.0029	2.0048	2.0069	2.0049
1-Butanol	76.9	8.8	2.0032	2.0052	2.0073	2.0052
1,2-Dichloroethane	73.5	13.3	2.0029	2.0050	2.0072	2.0050

the results of the calculation of the ZFS parameters indicate, the KI complex of **1** is thought to have a structure close to "*cis*" conformation, in which the galvinoxyl skeletons stack over one another. In such a case, because of the overlapping of the bulky tertiary butyl group, the real interplanar spacing between the two crown ether rings will become larger than that (3.34 Å) reported for the KI complex of benzo-15-crown-5.[8] Therefore, the cavity which exists between the two polyether rings can accommodate the K^+, Rb^+, and NH^+_4 ions without varying the intermolecular distance between the two galvinoxyl group. Thus, we can understand the experimental fact that the ZFS constants are the same for all the (2:1) complexes of **1**.

*Solvent Effect on the Structure of the Potassium Complex of **1**.* In addition to the above van der Waals interaction, the asymmetric environment due to frozen solvent molecules may contribute to the change in molecular structure found for the K complex of **1** in the low-temperature rigid matrix. Therefore, solvent effect on the structure of the (2:1) complex of **1** with KSCN has been studied. The solubilities of **1** and KSCN place some restriction on the choice of solvents. For this reason, ethanol, 2-propanol, 1-butanol, and 1,2-dichloroethane solvents could only be used in the present study. In the KSCN complex of **1**, identical triplet spectra were obtained in frozen ethanol, 2-propanol, and 1-butanol solutions, while a different triplet spectrum was obtained in frozen 1,2-dichloroethane solution, as shown in Fig. 7. The observed $|D|$ and $|E|$ values are summarized in Table 2. The result indicates that the change in conformation for the (2:1) complex is almost negligible for the above alcoholic solvents. On the other hand, the $|D|$ (73.5 G) and $|E|$ (13.3 G) values in 1,2-dichloroethane are 2.7 G smaller and 4.4 G larger than the corresponding ones in ethanol, respectively. These results may be explained by assuming that the rotation angle θ_{A-A} or θ_{A-B} varies several degrees in 1,2-dichloroethane solvent, as it can be seen from the results shown in Figs. 5 and 6. It has been reported that solvent molecules may play an important role in fixing the conformation of the triplet molecules in frozen solution.[13–15] However, the present experimental results suggest that such a role of solvent molecules is not notable in the (2:1) complex of **1**.

We wish to thank Miss Yoshiko Kumamoto for her kind help in the synthesis of **1**.

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) K. Mukai, N. Iida, Y. Kumamoto, H. Kohama, and K. Ishizu, *Chem. Lett.*, **1980**, 613.
5) E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.* **41**, 1763 (1964).
6) K. Mukai, T. Mishina, and K. Ishizu, *J. Chem. Phys.*, **66**, 1680 (1977).
7) D. Live and S. I. Chan, *J. Am. Chem. Soc.*, **98**, 3769 (1976).
8) P. R. Mallinson and M. R. Truter, *J. Chem. Soc., Perkin Trans. 2*, **1972**, 1818.
9) N. Azuma, H. Ohya-Nishiguchi, J. Yamauchi, K. Mukai, and Y. Deguchi, *Bull. Chem. Soc. Jpn.*, **47**, 2369 (1974).
10) K. Mukai and A. Sogabe, *J. Chem. Phys.*, **72**, 598 (1980).
11) K. Mukai, T. Kamata, T. Tamaki, and K. Ishizu, *Bull. Chem. Soc. Jpn.*, **49**, 3376 (1976).
12) D. E. Williams, *Mol. Phys.*, **16**, 145 (1969).
13) A. Calder, A. R. Forrester, P. G. James, and G. R. Luckhurst, *J. Am. Chem. Soc.*, **91**, 3724 (1969).
14) T. Ito and J. Higuchi, *Chem. Lett.*, 1519 (1974).
15) B. J. Scheve and P. J. Wagner, *Chem. Phys. Lett.*, **25**, 324 (1974).