ESR STUDIES OF THE ALKALI METAL COMPLEXES OF VERDAZYL-LABELED
BENZO-15-CROWN-5

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A verdazyl derivative of benzo-15-crown-5 (1) has been prepared,
and the complex formation between the spin labeled crown ether (1)
and the alkali metal salts has been studied by ESR spectroscopy.

It is well known that the cyclic polyethers synthesized by Pedersen form
stable complexes with alkali metal cations, and the stoichiometry depends on
the relative sizes of the "hole" in the cyclic polyether and of the cation.[1-3]
For instance, benzo-15-crown-5, one of the polyethers, with a hole 1.7-2.2 Å in
diameter forms usually a (1:1) complex with sodium (diameter, 1.90 Å), but it
forms only (2·1) complex with potassium (2.66 Å), an ion larger than the hole.

In the present work, in order to obtain further information on such
complex formation, we have prepared a verdazyl derivative of benzo-15-crown-5
(1) and observed ESR spectra of its alkali metal complexes in ethanol rigid
matrix at 77 K.   The rigid matrix ESR spectrum of the KSCN complex of 1 showed
an exchange-narrowed, Lorentz-type absorption with a width of 4.9 G, differing
from that expected for the (2:1) complex.   On the other hand, the NaSCN
complex of 1 showed a typical triplet ESR spectrum in ethanol rigid matrix at
77 K, clearly indicating the (2:1) complex formation between 1 and the NaSCN
salt.

The verdazyl-benzo-15-crown-5 (1) was prepared
by the standard procedure, as reported for the
syntheses of the verdazyl radicals by Kuhn
and Trischmann.[4]   Mp 119-122°C.   (Found:
C, 66.01; H, 6.10; N, 10.85 %.   Calcd for
$C_{28}H_{31}N_4O_5$: C, 66.78; H, 6.20; N, 11.13 %).
UV spectrum (λ_{max}=414 nm, log ε=3.91, λ_{max}=
740 nm, log ε=3.68 in THF).   Radical
concentration was obtained from the results of
the paramagnetic susceptibility measurements at
20°C, after correcting for the diamagnetic
contribution (χ_{dia}=-0.306×10^{-3} emu/mol) calculated
by the Pascal's method.   The value of the radical
concentration was 91 %, assuming the Curie law.
All the ESR spectra have been measured in a sealed, degassed system.

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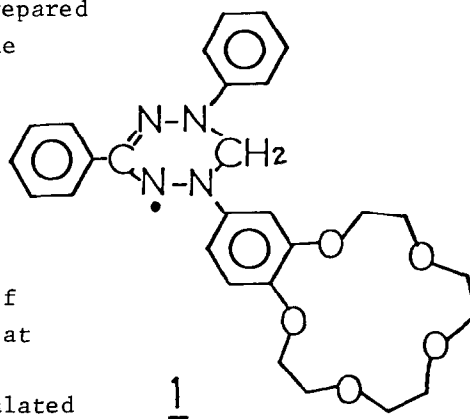
Complex formations were carried out by dissolving 1 and salts separately in acetone followed by mixing and evaporating the solvent under vacuum until solids separate.   Toluene is a good solvent for 1 but it does not dissolve the uncomplexed salts, and ethanol is a good solvent for the salts but a poor one for 1.   The crystalline complexes produced are easily soluble in ethanol but do not dissolve in toluene, indicating the complex formation between 1 and the salts.

The ESR spectrum of green ethanol solution of 1 at 20°C (see Fig. 1(a)) shows only nine line splittings (a^N=5.8±0.1 G, g_{iso}=2.0032±0.0001) due to four nitrogens in the heterocyclic ring; the hyperfine splittings from the protons in the three phenyl rings were unresolved.[5]   The ESR spectrum of this solution at 77 K shows an asymmetric broad absorption with a width of about 20 G located at g≃2.003, as shown in Fig. 1(b).   When the ethanol solution of 1 ($5.0×10^{-3}$ mol/l) containing equimolar NaSCN was frozen into a rigid glass at 77 K, two pairs of absorption lines (Z, Z' and Y, Y') were clearly observed with the separations of ZZ'=236±2 and YY'=138±2 G, as shown in Fig. 2(a).   A central line at g≃2.003 shows a shape essentially the same as that of the metal-free 1 (see Fig. 1(b)), and, in addition, the relative intensity of this central line changes depending on the ratio of the sodium salt to 1. Therefore, this line is attributable to the metal free 1 and/or the (1:1) complex between 1 and the NaSCN.   The two pairs of absorption lines apparently represent zero-field splitting arising from the intermolecular dipolar interaction of two electrons in a triplet state.[6]   In fact, the forbidden transition (Δm_s =±2) was observed at about 1634 G, as shown in Fig. 2(b).   These results clearly indicate the (2:1) complex formation between 1 and the NaSCN.   The zero-field splitting parameters, |D| and |E|, were evaluated as 118±1 G
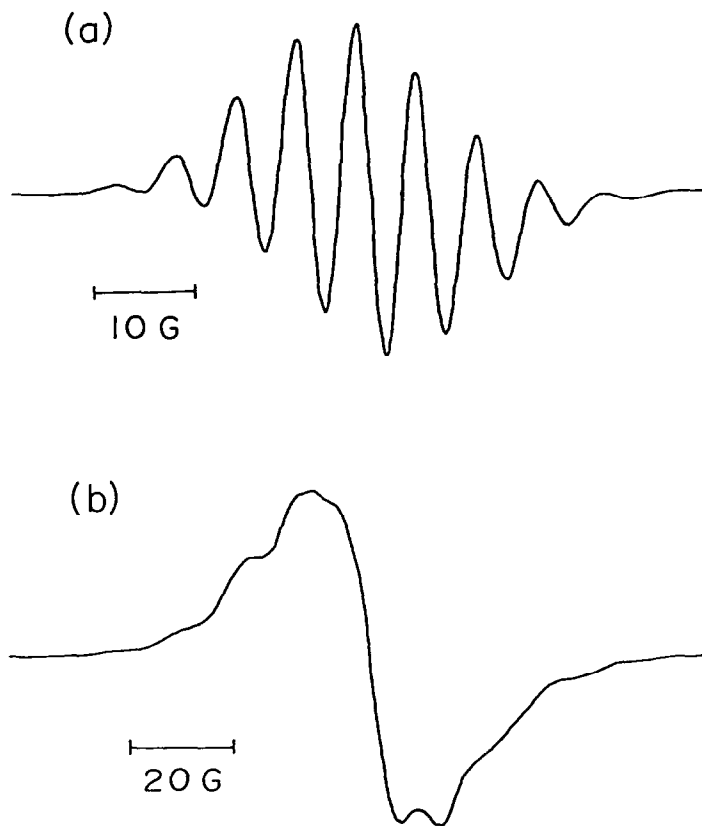

(a)

10 G

(b)

20 G

Figure 1.   ESR spectra of 1 in ethanol
(a) at 20°C and (b) at 77 K.

and 7±1 G, respectively, by the method of Wasserman et al.[6]   Assuming that the principal axes of the D- and g-tensors are coaxial, g-tensor values have been estimated from the positions of two pairs of absorption lines.   These values are g_{zz}=2.0025±0.0005 (Z, Z') and g_{yy}=2.0033±0.0005 (Y, Y').   On the other hand, in ethanol rigid matrix at 77 K, the ESR spectrum of the KSCN complex of 1 shows an exchange-narrowed, Lorentz-type absorption, with a linewidth of 4.9 G and g=2.0034±0.0002, as shown in Fig. 3.   The spectrum differs from that expected for the (2:1) complex.

In the previous papers,[7,8] we have prepared the nitroxide and phenoxyl derivatives of benzo-15-crown-5, and investigated the complex formation between the spin-labeled crown ethers and the alkali metal thiocyanate, using ESR technique.   In these spin-labeled crown ethers, each KSCN complex showed a triplet ESR spectrum, indicating the formation of a (2:1) complex.   As a structure of the (2:1) complex, we considered a sandwich-type structure that the two radical groups in the (2:1) complex stack face-to-face each other.   On the other hand, the results of the ESR measurements of the NaSCN complexes suggested a (1:1) complex formation between the spin-labeled crown ethers and the NaSCN.

If the KSCN complex of 1 takes a structure similar to those of the nitroxide- and phenoxyl-labeled benzo-15-crown-5, we can expect a triplet ESR spectrum.   However, the KSCN complex of 1 shows a symmetric sharp absorption
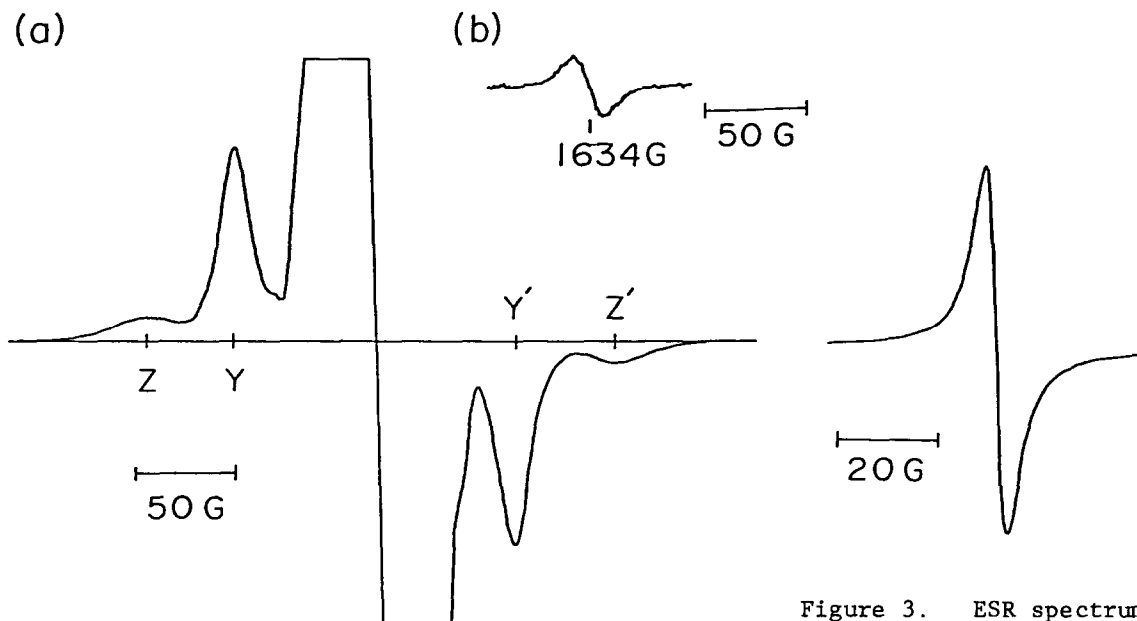

Figure 2.   ESR spectrum of the NaSCN complex of 1 in ethanol rigid matrix at 77 K; (a) Δm_s=±1 transition and (b) Δm_s=±2 transition.

Figure 3.   ESR spectrum of the KSCN complex of 1 in ethanol rigid matrix at 77 K.

line with a linewidth of 4.9 G, as described above.   The dimer structure
cannot explain the above ESR absorption.   On the other hand, if the 1 forms
a (1·1) complex with KSCN, an asymmetric broad absorption similar to that of
the metal-free 1 in ethanol rigid matrix (see Fig. 1(b)) will be observed.
The exchange-narrowed, Lorentz-type absorption may be due to a polymeric
structure with alternating array of potassium cations and the cyclic ethers.
In fact, such a polymeric structure has been proposed for the cobaltous complex
of dicyclohexyl-18-crown-6 by Su and Weiher.[9]   However, no more, detailed
discussions of the structure can be done from the present ESR spectrum.   As
the NaSCN complex of 1 shows a typical triplet ESR spectrum with the zero-field
splitting parameters $|D|=118$ G and $|E|=7$ G and the average interelectronic
distance calculated with a model of two point dipoles ($|D|=(3/2)g\beta r^{-3}$) is 6.2
Å, the structure of the complex is considered to be the sandwich-type one in
which the two verdazyl groups stack face-to-face each other.   It is well
known that benzo-15-crown-5 forms usually a (1:1) complex with sodium salt.
The result of single crystal X-ray structural analysis accomplished by Bush
and Truter[10] also supports a (1:1) complex formation.   On the other hand,
Pedersen[2] and Parsons and Wingfield[11] have reported that benzo-15-crown-5 may
yield both (1:1) and (2:1) complexes with sodium salts, depending on the
reaction conditions of the complex formation.   Our result provides a direct
experimental evidence for the (2:1) complex formation between a derivative
of benzo-15-crown-5 and a sodium salt.

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