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

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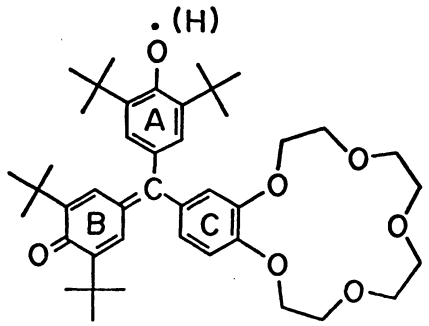
A galvinoxyl derivative of benzo-15-crown-5 (1) has been synthesized, and the complex formation between the spin labeled crown ether (1) and the alkali metal thiocyanate has been studied by ESR measurement. A typical triplet ESR spectrum was observed for the potassium complex in ethanol rigid matrix at 77 K, clearly indicating the (1:2) complex formation between the KNCS salt and the 1. On the other hand, the sodium complex showed a symmetrical single line, suggesting the (1:1) complex formation between the NaNCS salt and the 1.

The cyclic polyethers synthesized by Pedersen have attracted considerable interest because of their unusual properties of forming relatively stable complexes with alkali and alkaline earth metal ions in solution and in the solid state.[1-3] The schemes of the complex formation have been extensively studied using several physical methods, such as UV, IR spectroscopies, and X-ray analysis.[4] In a previous paper, a nitroxide derivative of benzo-15-crown-5 has been prepared, and the complex formation between the nitroxide-labeled crown ether and the alkali metal thiocyanate has been investigated with ESR techniques.[5] The potassium complex showed a triplet ESR spectrum, suggesting the formation of a sandwiched dimer. However, because of (i) the flexibility of the bond angles between the benzene ring of the crown ether and the nitroxide group and (ii) the complexity of the triplet ESR spectrum observed, the detailed structure of



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the nitroxide-labeled crown ether was not thoroughly visualized.

In this communication, we report the synthesis of a galvinoxyl derivative of benzo-15-crown-5 (1) and its complex formation with alkali metal thiocyanate. A typical triplet ESR spectrum was observed for the potassium complex in an ethanol rigid matrix at 77 K. Consequently, the structure of the complex is discussed on the basis of the g- and D-tensor values obtained from the triplet spectrum.

4'-Formylbenzo-15-crown-5 was prepared according to the method of Ungaro et al.[6] 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 ml) solution under a nitrogen atmosphere at 30°C.[7] The reaction was continued for five days under stirring. The subsequent removal of the ethanol from the reaction mixture left a blue-colored viscous oil. Then this was taken up in chloroform, washed with water, and dried over anhydrous magnesium sulfate. After removal of the chloroform, a viscous oil remained. By adding hexane to the viscous oil, orange solids were isolated. The solids obtained were washed twice with hot hexane, recrystallized from hexane-benzene, and finally heated at 170°C for 6 h under vacuum (5×10^{-3} Torr) to completely remove the solvents included in the crystal. Mp. 209-211°C (softens at 176°C), $C_{43}H_{60}O_7$; λ_{max} (EtOH), 434 nm (ε 30200); ^{1}H-NMR (CCl_4) δ 1.23 (s, 18H, tBu, ring A), 1.43 (s, 18H, tBu, ring B), 3.5-4.2 (m, 16H, $-CH_2-$), 5.37 (s, 1H, OH), 6.70-6.82 (m, 3H, ring C), 7.00 (s, 2H, aromatic H, ring A), 7.08 (s, 2H, aromatic H, ring B).

The galvinoxyl derivative of benzo-15-crown-5 (1) was prepared by the oxidation of the above phenol precursor with alkaline potassium ferricyanide in diethyl ether under a nitrogen atmosphere, with the temperature kept at 0-5°C.[8] The concentration of radical was obtained from the results of the paramagnetic susceptibility measurements at 20°C, which were corrected for the diamagnetic contribution (χ_{dia} = -0.437×10^{-3} emu/mol) calculated by the Pascal's method. The value of the radical concentration is 98%, assuming the Curie law. All the ESR spectra have been measured in a sealed, degassed system.

The ESR spectrum of the metal-free 1 in ethanol shows a five-line hyperfine splitting (a_m^H = 1.27 ± 0.04 G, g_{iso} = 2.00431 ± 0.00003) due to the equivalent four meta-ring protons in the galvinoxyl ring at 20°C. When the ethanol solution of 1 (3.0×10^{-3} mol/l) containing equimolar KNCS was frozen into a rigid glass at 77 K, three pairs of absorption lines were clearly observed with the same order of

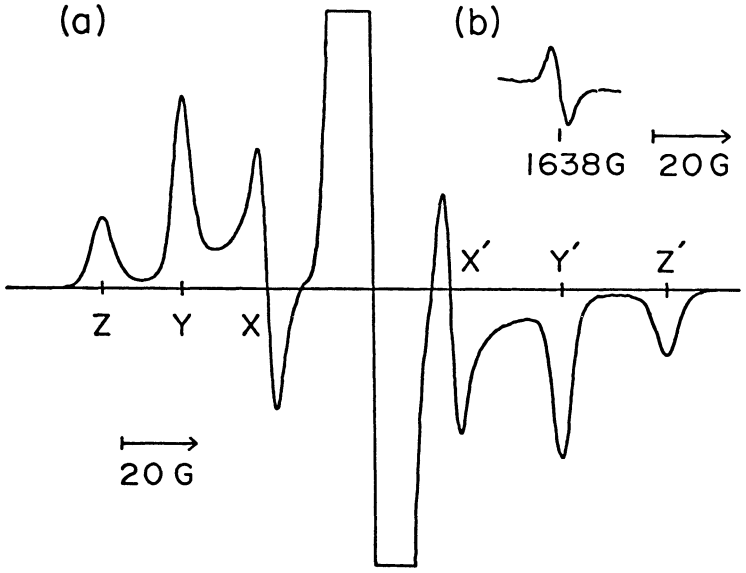

Figure 1. ESR spectrum of 1 in ethanol at 77 K; (a) $\Delta m_s = \pm 1$ transition and (b) $\Delta m_s = \pm 2$ transition.

intensity, as shown in Fig. 1(a). The three pairs of absorption lines apparently represent the zero-field splittings arising from the intermolecular dipolar interaction of two electrons in a triplet state.[9] In fact, the forbidden transition ($\Delta m_s = \pm 2$) was observed at about 1638 G, as shown in Fig. 1(b). These results clearly indicate the (1:2) complex formation between the KNCS salt and the galvinoxyl-labeled crown ether (1). On the other hand, the solution of 1 containing the equimolar NaNCS salt shows a symmetrical single line with a width of 7.2 G located at $g \simeq 2.00$ at 77 K, which unequivocally suggests the (1:1) complex formation between the 1 and the NaNCS salt. By changing the molar ratio of 1 with NaNCS or KNCS from (1:1) to (2:1) in the ethanol solution, no detectable changes were observed in the ESR spectra. The separations between the three pairs of turning points (Z, Z'; Y, Y'; and X, X') in the spectrum of the KNCS complex are 152.4 ± 0.6, 102.8 ± 0.6, and 49.7 ± 0.6 G, respectively. Thus, the values |D| and |E| were estimated to be 76.2 ± 0.3 G and 8.9 ± 0.3 G, respectively.[9] Under the assumption that the principal axes of the D- and g-tensors are coaxial, the values of the g-tensor have been estimated from the positions of three pairs of turning points. These values are $g_{zz} = 2.0032 \pm 0.0002$ (Z, Z'), $g_{yy} = 2.0052 \pm 0.0002$ (Y, Y') and $g_{xx} = 2.0072 \pm 0.0002$ (X, X').

Mallinson and Truter[10] have reported the crystal structure of a 1:2 complex of potassium iodide with the benzo-15-crown-5. The crystals are tetragonal with a=b=

17.84, c=9.75 Å, z=4, space group P4/n. The complex cation has the crystallographic symmetry $\bar{1}$, the potassium being 'sandwiched' between two centro-symmetrically related ligand molecules. If the KNCS complex of 1 takes a conformation (hereafter referred to as the 'trans' conformation) similar to that of the benzo-15-crown-5, the interatomic distance between the central triphenylmethyl carbon atoms of 1 will become at least 13 Å. A zero-field splitting of $|D| = 76.2$ G has been observed for the KNCS complex of 1, as described above. Consequently, the average interelectronic distance calculated with a model of two point dipoles ($|D| = (3/2)g\beta r^{-3}$) is 7.2 Å. The comparison of these distances suggests that the 'trans' conformation is not acceptable for the KNCS complex of 1. As the molecular model indicates, the 1 is considered to have an approximately planar structure, as a whole molecule. Therefore, if the KNCS complex of 1 has a 'cis' conformation,[11] the principal Z axis of the D-tensor, corresponding to the maximum value of 2D, would be perpendicular (or nearly so) to the molecular plane of 1.[12] In fact, the observed value of g_{zz} (2.0032), calculated from the frequency center of the Z and Z' lines in Fig. 1(a), is close to the free-spin value, while g_{xx}(2.0072) and g_{yy}(2.0052) are larger than g_e. This conformation is considered to be similar to that of the KNCS complex of the nitroxide-labeled-benzo-15-crown-5 ether, which also exhibits the ESR zero-field splittings at low temperature, as reported in a previous paper.[5]

References

1) C. J. Pedersen, J. Am. Chem. Soc., 89, 7017 (1967).
2) C. J. Pedersen, J. Am. Chem. Soc., 92, 386 (1970).
3) D. E. Fenton, M. Mercer, N. S. Poonia, and M. R. Truter, Chem. Commum., 66 (1972).
4) J. J. Christensen, D. J. Eatough, and R. M. Izatt, Chem. Rev., 74, 351 (1974), and references cited therein.
5) K. Ishizu, H. Kohama, and K. Mukai, Chem. Lett., 1978, 227 .
6) R. Ungaro, B. El Haj, and J. Smid, J. Am. Chem. Soc., 98, 5198 (1976).
7) T. H. Coffield, A. H. Filbey, G. G. Ecke, and A. J. Kolka, J. Am. Chem. Soc., 79, 5019 (1957).
8) E. Müller and K. Ley, Chem. Ber., 87, 922 (1954).
9) E. Wasserman, L. C. Snyder, and W. A. Yager, J. Chem. Phys., 41, 1763 (1964).
10) P. R. Mallinson and M. R. Truter, J. Chem. Soc., (Perkin II) 1818 (1972).
11) As the 'cis' conformation, we considered the structure that the two galvinoxyl groups in the (1:2) complex stack face-to-face each other.
12) K. Mukai and J. Sakamoto, J. Chem. Phys., 68, 1432 (1978).

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