

Metal-ion Complexation of Noncyclic Poly(oxyethylene) Derivatives. III.¹⁾ Complexation in Aprotic Solvent and Isolation of Their Solid Complexes[†]

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The interaction of homogeneous polyethylene glycol(PEG)(EO*n*, *n*=1—8) with the alkali and magnesium metal cations and the ammonium cation was investigated on the basis of ¹H NMR(PMR) downfield shifts in acetone-*d*₆ or in acetonitrile-*d*₃. The specific complexations of EO4 with Mg²⁺, EO6 with Na⁺ and Ca²⁺, and EO7 with K⁺ were demonstrated by PMR studies, and their solid complexes were isolated. No specific interaction was detected for Rb⁺ and Cs⁺ in PMR studies. The magnesium ion interacts strongly with 15-crown-5, 18-crown-6, and PEG in acetone, and the Mg(SCN)₂-EO4 and the Mg(SCN)₂-above crown ether complexes were isolated. The terminal hydroxyl groups of PEG play an important role in the complexation with Li⁺ and Mg²⁺ in acetone. The formation of the 1:1 complex with Ca(SCN)₂ was observed both for EO6 and for EO7. Strontium and barium thiocyanates formed solid complexes with PEG(EO*n*, *n*=2—8) and with glymes(tri- to octaglyme). Some novel complexes of 12-crown-4 and 15-crown-5 with NaSCN and Ca(SCN)₂ were also isolated. The mechanism of metal-ion complexation of poly(oxyethylene) derivatives is discussed in terms of the coordination geometry.

PMR spectroscopy has often been used to detect ligand-metal cation interactions¹⁻⁷⁾ The changes in the PMR spectra induced by the typical metal cations are intrinsically complex phenomena. The use of the coordinating species as the solvent tends to mask the shifts, probably due to the competitive complexation. When aromatic anion salts such as tetraphenylborate²⁾ or fluorenyl salts⁴⁾ are used, the close proximity of the aromatic ring of the anion above the participating proton nuclei induces the upfield shifts, in spite of the complexation with the counter metal cation, which by itself would cause a downfield shift of the proton signals due to the increased electronegativity of the coordinating donor atom. Our previous study¹⁾ revealed that the downfield shifts of PEG protons caused by the interaction with alkaline earth metal thiocyanates in methanol can be a qualitative measure of the extent of their complexation. On the basis of PMR downfield shifts, it was demonstrated that homogeneous PEG's with at least more than five oxyethylene units have strong complexing powers toward Ca²⁺, Sr²⁺, and Ba²⁺ in methanol; these are quite comparable with those of crown ethers, cyclic poly(oxyethylene). However, the downfield shifts induced by the alkali or magnesium metal cations or the ammonium ion were too small for either PEG or crown ethers to predict a complexing tendency. This phenomenon can be attributed to the competitive complexation of the methanol solvent. When a less polar nonaqueous solvent, *e.g.*, acetone or acetonitrile, is used, the downfield shifts are found to be large enough to evaluate the intrinsic complexing tendency.

On the basis of the previous and present PMR analyses, we have isolated solid complexes of PEG with alkali and alkaline earth metal salts. Further, we have attempted to point out some inconsistency in the ion-radius cavity concept regarding the metal complexation of the crown ethers.

Experimental

Materials. The following chemicals were obtained in the best available purity from the sources indicated; acetone-*d*₆ and acetonitrile-*d*₃ (CEA products through Nakarai Chemicals Ltd.), sodium tetraphenyl borate (Specially prepared reagent) (Nakarai Chemicals Ltd.), triethylene glycol monomethyl ether (Tokyo Kasei Kogyo Co., Ltd.).

Hexaethylene glycol monomethyl ether(MeEO6)(167—171 °C/0.15 mmHg) and octaethylene glycol monomethyl ether(MeEO8)(215 °C/0.16 mmHg) were prepared by the reaction of diethylene glycol 2-chloroethyl methyl ether with tetraethylene glycol and with pentaethylene glycol, respectively.

Other salts and poly(oxyethylene) derivatives were the same as in the previous paper.¹⁾

Measurement of Spectra. The PMR spectra were obtained using a JEOL LMN-PS-100 spectrometer(100 MHz) on an expanded scale (sweep width, 270 Hz), with 8% dioxane in benzene as the external reference, as previously described, except for weighing the thiocyanates:¹⁾ thiocyanate concentration, 0.05 mol/kg; POE derivatives concentration, 1 wt %. Weighing the salts was done as follows: the acetone or methanol solution was injected in NMR tubes using a microsyringe and the NMR tubes were placed in a vacuum to evaporate the solvent. The chemical shifts for the split signals of EO7 and EO8 in acetonitrile-*d*₃ were averaged for the calculation of the downfield shifts.

The ¹³C NMR spectra were obtained using a JEOL JNM-FX-60 spectrometer.

The IR spectra were recorded with a Japan Electroscopic IR-E spectrophotometer.

Isolation of Solid Complexes. Solid complexes of cyclic and noncyclic poly(oxyethylene) derivatives (POE) were isolated by the following methods. An anhydrous metal salt was powdered in a mortar and was heated with a slightly more than equimolecular quantity of POE without solvent until the pasty mixture became an entirely homogeneous solution. Generally, the complexes solidified on cooling. The resulting complexes were purified by recrystallization (Method 1), or were broken up to pieces, washed thoroughly to remove excess POE or the salt, filtered, and dried under reduced pressure(Method 2).

[†] This work was presented at the 26th IUPAC Congress, Tokyo, September 1977.

It was found that some complexes could also be easily isolated from solution. Acetone or methanol was saturated with a salt and the stoichiometric quantity of POE was added to the above solution. The precipitation of the complexes was immediate (Method 3). The complexes were worked up as in Method 1 or in Method 2. The results are summarized in Tables 1, 2, and 4. The melting points were determined on a Büchi SMP-20 apparatus.

Typical examples are as follows.

Preparation of Crystalline KSCN Complex of Heptaethylene Glycol (EO7). Method 1. A mixture of 1.00 g (3.0 mmol) of EO 7 and 0.238 g (2.5 mmol) of powdered KSCN was melted in a test tube. The mixture solidified on cooling. The complex was broken up to pieces, washed with a small quantity of acetone, dried, and recrystallized twice from acetone. A crystalline 1 : 1 complex was obtained (0.47 g, 45% yield).

Preparation of $Ba(SCN)_2$ Complex of Tetraglyme (MeEO-4Me). Method 2. A mixture of 0.232 g (0.9 mmol) of powdered $Ba(SCN)_2$ and 0.210 g (0.95 mmol) of MeEO4Me was heated up in a test tube until the mixture became entirely homogeneous. After cooling, a mixture of benzene and acetone (9 : 1) was added to the mixture, giving the complex (0.12 g). When benzene was added to the filtrate, additional complex (0.13 g) was precipitated (total yield 58%).

Preparation of $Mg(SCN)_2$ Complex of Tetraethylene Glycol (EO4). Method 2. A mixture of 0.228 g (1.0 mmol) of $Mg(SCN)_2 \cdot 4H_2O$ and 0.203 g (1.0 mmol) of EO4 was heated up in a test tube until the mixture became a clear solution. During the workup, the evolution of water and the complex formation were observed. The resulting complex was washed with acetone and dried in a vacuum. The complex (0.117 g) was obtained. Additional complex (0.076 g) was recovered from the filtrate (total yield 58%).

Preparation of $Mg(SCN)_2$ Complex of 15-Crown-5. Method 3. In acetone (1 g), 0.216 g (1.0 mmol) of $Mg(SCN)_2 \cdot 4H_2O$ was dissolved, and the solution was filtered. To the filtrate, 0.223 g (1.0 mmol) of 15-crown-5 was added. White crystals were immediately formed. After a while, some additional 15-crown-5 (0.235 g, 1.1 mmol) was added, but no further precipitation was observed. The crystals were filtered, washed with acetone, and dried. The complex (0.231 g) was obtained (53% yield). The filtrate was concentrated in a rotary evaporator, yielding some additional complex (Table 4).

Preparation of $Ca(SCN)_2$ Complex of 12-Crown-4. Method 3. 12-Crown-4 (0.128 g, 0.73 mmol) was dissolved in 0.364 g of methanol. The methanol solution of $Ca(SCN)_2$ prepared from 0.109 g of anhydrous $Ca(SCN)_2$ and 0.6 ml of methanol was added to the above solution. After a while, white crystals precipitated. After the workup, 0.155 g of the complex with water of crystallization were obtained (60% yield) (Table 4).

Results and Discussion

Complexation with Alkali Metal and Ammonium Cations in Aprotic Solvent. Recent studies on the structure of crown ether complexes have revealed their induced fit for metal cations, i.e., their oxyethylene (EO) chains are flexible enough to coordinate to various metal cations in spite of their ring structure.⁸⁻¹⁰ Thus, it seems appropriate to make use of the downfield shift for crown ethers as a probe to evaluate the complexation of acyclic POE derivatives.

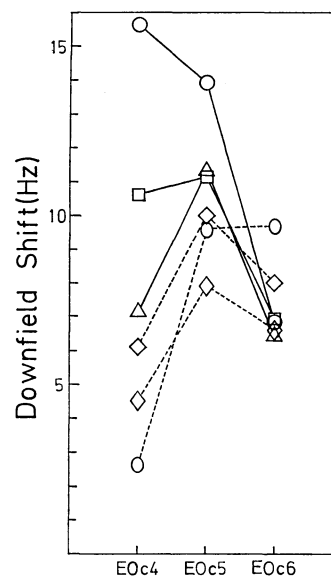


Fig. 1. Downfield shifts for crown ethers induced by alkali metal and ammonium cations in acetone- d_6 . Thiocyanate concentration, 0.05 mol/kg; crown ether concentration, 1 wt %. Δ : Li^+ , $\circ$: Na^+ , $\square$: K^+ , $\diamond$: Rb^+ , $\diamond$: Cs^+ , $\circ$: NH_4^+ .

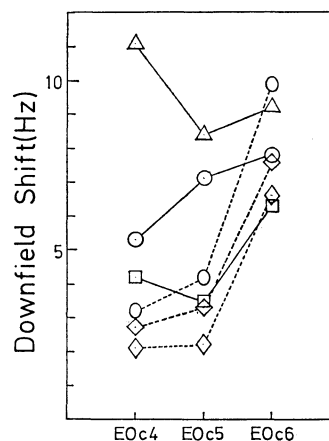


Fig. 2. Downfield shifts for crown ethers induced by alkali metal and ammonium cations in acetonitrile- d_3 . The conditions and symbols used are identical with those in Fig. 1 and all of the following figures.

The downfield shifts of the crown ethers' protons by the complexation of the alkali metal and ammonium cations were measured both in acetone- d_6 and in acetonitrile- d_3 . The results are shown in Figs. 1 and 2 as a function of the number of EO units. It is seen that the downfield shifts are generally larger in acetone- d_6 than in acetonitrile- d_3 . And it is also seen that in acetonitrile the signals of 18-crown-6 (EOc6) show the largest shifts for most of the cations, while in acetone the largest shifts are observed mostly for 15-crown-5 (EOc5). On careful examination, the chemical shift of 18-crown-6 in acetonitrile- d_3 was found to be ca. 5–7 Hz upfield, compared with those of the other crown ethers and PEG. The unusual upfield shift for 18-crown-6 is attributable to the magnetic anisotropy due to its specific interaction with the cyano group of acetonitrile.^{11,12} Thus, the observed largest

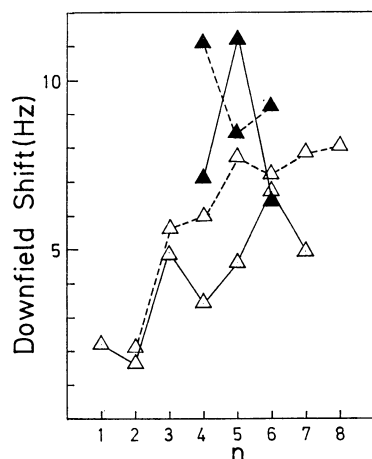


Fig. 3. Lithium-ion induced downfield shifts for the homogeneous PEG and crown ethers in acetone- d_6 and in acetonitrile- d_3 . $\triangle$ — $\triangle$: In acetone- d_6 , $\triangle$ -- $\triangle$: in acetonitrile- d_3 , $\blacktriangle$ — $\blacktriangle$: the shifts for the crown ethers in acetone- d_6 , $\blacktriangle$ -- $\blacktriangle$: the shifts for the crown ethers in acetonitrile- d_3 .

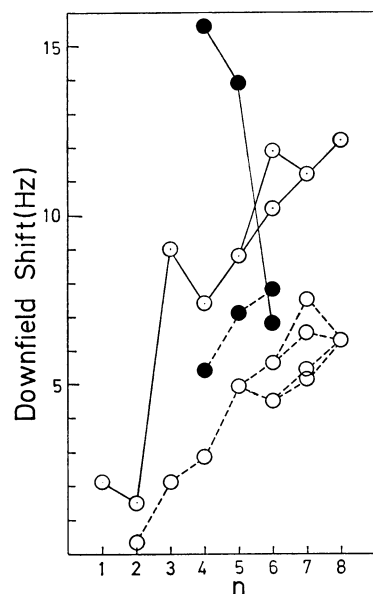


Fig. 4. Sodium-ion induced downfield shifts for the homogeneous PEG and crown ethers in acetone- d_6 and in acetonitrile- d_3 . $\circ$ — $\circ$: In acetone- d_6 , $\circ$ -- $\circ$: in acetonitrile- d_3 , $\bullet$ — $\bullet$: the shifts for the crown ethers in acetone- d_6 , $\bullet$ -- $\bullet$: the shifts for the crown ethers in acetonitrile- d_3 .

downfield shifts for 18-crown-6 in the presence of cations do not necessarily imply the strongest complexing power. It may be inferred that the specific interaction of 18-crown-6 with acetonitrile would easily disappear in the presence of cations.

On the basis of these large downfield shifts for the crown ethers in the presence of the cations, the corresponding shifts for a series of homogeneous PEG's were determined in acetone- d_6 and partly in acetonitrile- d_3 ; the results are plotted against the number of EO units in Figs. 3—4 and 7—10. The shifts for the crown ethers were also plotted in the respective figures for comparison. In general, the presence of

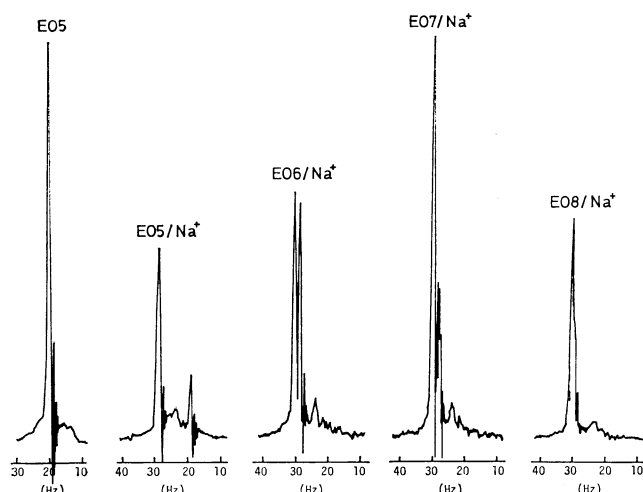


Fig. 5. PMR signals in acetone- d_6 of oxyethylene protons of the homogeneous PEG in the presence or the absence of sodium ion.

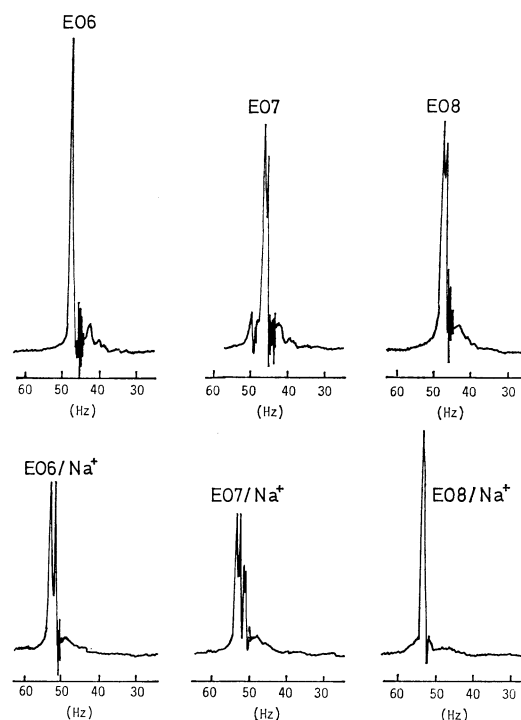


Fig. 6. PMR signals in acetonitrile- d_3 of oxyethylene protons of the homogeneous PEG in the absence and presence of sodium ion.

the cations made the signals of ethylene glycol(EO1) broaden and also those of the diethylene glycol(EO2) complex, but with small downfield shifts.

In the interaction of EO_n with Li^+ in acetone- d_6 (Fig. 3), the specific complexation of hexaethylene glycol (EO6) is to be noted. The shift for EO6 is far less than those of 12-crown-4 and 15-crown-5, but is quite comparable with that of 18-crown-6. Rather weak complexation of 12-crown-4 with Li^+ in acetone, implied by the small shift, can not be explained. In acetonitrile (Fig. 3), the larger shifts were observed for PEG with more than five EO units, but no specific complexation was observed. It should be noted

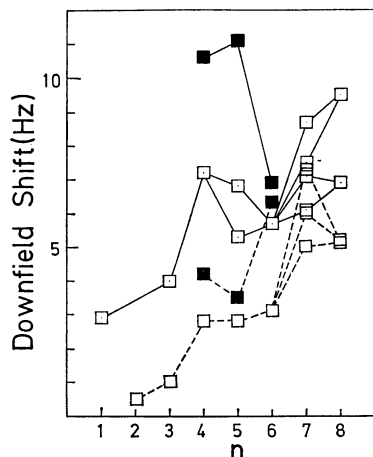


Fig. 7. Potassium-ion induced downfield shifts for the homogeneous PEG and crown ethers in acetone- d_6 and in acetonitrile- d_3 . $\square$ — $\square$: In acetone- d_6 , $\square$ -- $\square$: in acetonitrile- d_3 , $\blacksquare$ — $\blacksquare$: the shifts for the crown ethers in acetone- d_6 , $\blacksquare$ -- $\blacksquare$: the shifts for the crown ethers in acetonitrile- d_3 .

that the signals of heptaethylene glycol(EO7) and octaethylene glycol(EO8) were split into two peaks when measured in the absence of cations by an expanded scale (Fig. 6), and that the addition of LiSCN caused the coalescence of the signals with appreciable downfield shifts.

With regard to Na^+ in acetone- d_6 (Fig. 4), the large shifts were observed for EO n with more than four EO units and the signal of EO6 was clearly split into two peaks with a larger downfield shift than that of 18-crown-6(Fig. 5). The shifts in acetonitrile- d_3 (Fig. 4) were not so large as those in acetone- d_6 , but the clear splittings of the signals were observed not only for EO6 but also for EO7(Fig. 6). These splittings are in agreement with those observed in methanol- d_4 ,¹⁾ but the splittings accompanying the downfield shifts suggest that EO6 and EO7 should take more rigid conformation on complexation with Na^+ in the aprotic solvent.

The study of K^+ in acetone- d_6 (Fig. 7) found appreciable downfield shifts for EO n with more than four EO units. Pentaethylene glycol(EO5), EO7, and EO8 accompanied the splitting of the signals. EO7 gave the characteristic splitting which was observed in methanol- d_4 .¹⁾ The complexing power of EO n with more than four EO units, inferred from the large shifts, is far less than those of 12-crown-4 and 15-crown-5, but is quite comparable with that of 18-crown-6. This fact is quite consistent with the solid-liquid phase transfer catalysis of glymes with more than four EO units.¹³⁾ The shifts in acetonitrile- d_3 (Fig. 7) make the specific complexation of EO7 with K^+ more apparent.

For Rb^+ and Cs^+ in acetone- d_6 (Fig. 8), the large shifts comparable with those of the crown ethers were observed; splitting occurred for EO n with more than four EO units. These are almost proportional to the number of EO units, suggesting their rather non-specific interactions.

For the ammonium ion in acetone- d_6 (Fig. 9), no

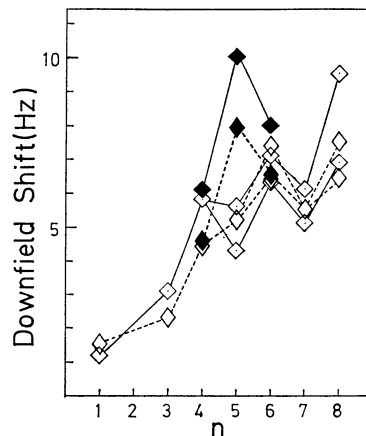


Fig. 8. Rubidium and caesium-ion induced downfield shifts for the homogeneous PEG and crown ethers in acetone- d_6 . $\diamond$: The shifts for the PEG in the presence of Rb^+ , $\diamond$: the shifts for the PEG in the presence of Cs^+ , $\blacklozenge$: the shifts for the crown ethers in the presence of Rb^+ , $\blacklozenge$: the shifts for the crown ethers in the presence of Cs^+ .

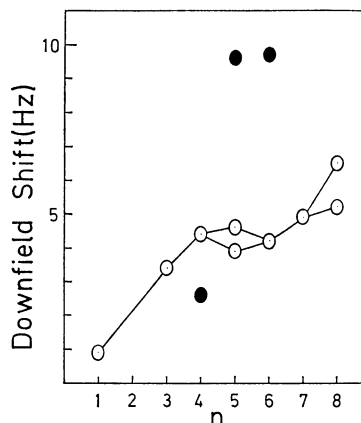


Fig. 9. Ammonium-ion induced downfield shifts for the homogeneous PEG and crown ethers in acetone- d_6 . $\bullet$: The shifts for the crown ethers.

remarkable complexation comparable with those of 15-crown-5 and 18-crown-6 was observed among the PEG investigated. However, increasing the number of EO units seems to increase the tendency of complexation.

Complexation with Magnesium Cation in Acetone.

The magnesium cation had been considered not to interact with any crown ethers, since the magnesium ion radii is apparently too small to fit the cavity of crown ethers larger than 12-crown-4. It has now been found that in acetone- d_6 , the proton signal of 15-crown-5 shifts *ca.* 31 Hz downfield by the presence of $\text{Mg}(\text{SCN})_2$ and the complex with the 1:1 composition precipitates under the conditions of the downfield shift measurement. Similarly, 18-crown-6 yielded the complex with the composition of 18-crown-6 $\cdot\text{Mg}(\text{SCN})_2\cdot 4\text{H}_2\text{O}$ (see Table 4). It is surprising to note, however, that 12-crown-4 neither formed any solid complex nor showed any appreciable shift in the presence of Mg^{2+} . In the light of the ion-radius cavity concept, 12-crown-4 should have shown the

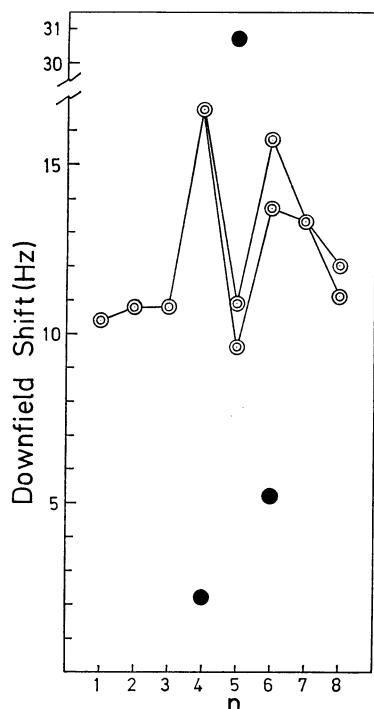


Fig. 10. Magnesium-ion induced downfield shifts for the homogeneous PEG and crown ethers in acetone- d_6 .
●: The shifts for the crown ethers.

maximum interaction with Mg^{2+} . The fact is quite contradictory to the concept.

As is shown in Fig. 10, large downfield shifts were confirmed for a series of PEG's ranging from EO1 to EO8. Significant splitting or broadening of the signals were observed for PEG's with a longer chain than EO5. To our surprise, the 1:1 complex of EO4 with $Mg(SCN)_2$ was precipitated in acetone- d_6 just as those of 15-crown-5 and 18-crown-6. However, we could not succeed in isolating any other complexes of PEG. These facts indicate that Mg^{2+} interacts specifically with EO4.

The Role of Terminal Hydroxyl Groups in Complexation of PEG in Aprotic Solvents. Recently, a variety of noncyclic POE derivatives with chelating groups on the terminals have been reported to show remarkable complexing properties with metal cations.¹⁴⁻¹⁶ The significance of these findings is that they demonstrate the importance of the terminal groups which stabilize the metal-ion complexation. In preceding papers,^{1,17} however, we demonstrated that the TGT conformation of EO groups and the resulting helical conformation of the repeating EO units are the driving forces of the metal-ion complexation of noncyclic POE derivatives, and that the role of the terminal hydroxyl groups in the complexation of PEG varies with the properties of the metal cations and with the polarity of the solvent.

In this study, the effect of the terminal hydroxyl groups on complexation with Li^+ , Na^+ , K^+ , and Mg^{2+} in aprotic solvent was also examined by comparing the downfield shifts of PEG with those of the methylated PEG. As is shown in Fig. 11, the hydroxyl groups of PEG play an important role in the effective complex-

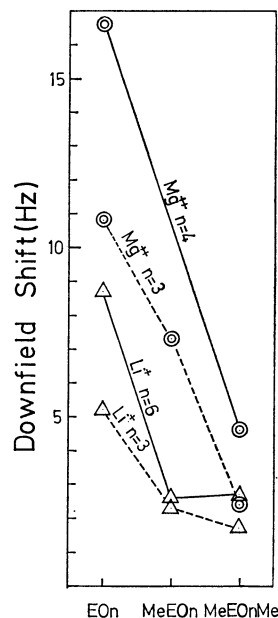


Fig. 11. Comparison of downfield shifts for PEG and methylated PEG induced by Lithium or magnesium ion. ○: Mg^{2+} in acetone- d_6 , △: Li^+ in acetone- d_6 .

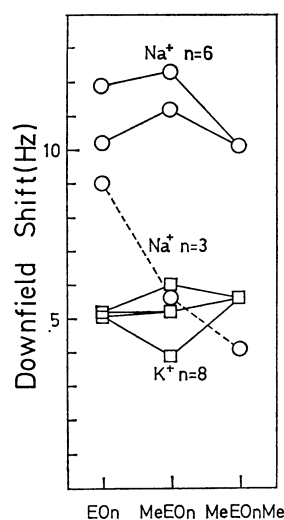


Fig. 12. Comparison of downfield shifts for PEG and methylated PEG induced by sodium or potassium ion. ○: Na^+ in acetone- d_6 , □: K^+ in acetonitrile- d_3 .

ation with Li^+ and Mg^{2+} in acetone. With regard to Na^+ in acetone (Fig. 12), the same is true for the tri(oxyethylene) derivatives. In case of the hexa(oxyethylene) derivatives, no drastic decrease in the shifts by methylation were observed, indicating that the terminal hydroxyl groups are not necessarily so important for complexation with Na^+ in acetone. This also holds true for potassium ion complexation of the octa(oxyethylene) derivatives in acetonitrile (Fig. 12).

Isolation of Solid Complexes. Some polar compounds have recently been found to form solid complexes with metal salts under appropriate conditions.¹⁸⁻²⁰ Our previous and present studies of PMR indicated that some homogeneous PEG should react

TABLE 1. PREPARATION AND ANALYTICAL DATA OF COMPLEXES OF PEG

Salt	PEG	Stoichiometry Salt : POE : H ₂ O	Method ^{a)} (solvent)	Mp (°C)	Infrared spectra (KBr disk) ^{b)}			Found (Calcd)%		
					ν_{OH}	ν_{SCN}	ν_{C-O-C}	C	H	N
NaBPh ₄	EO6	1 : 1 : 1/2	1(THF)	93.5—95.0	3550 3350		1120 sh, 1100, 1060 sh, 1030	69.09 (69.23)	7.68 (7.42)	
KSCN	EO7	1 : 1	2(Ac) 1(Be)	84.8—85.4	3360 3260 sh, 3340	2065	1115, 1090 sh	42.38 (42.54)	7.32 (7.14)	3.30 (3.31)
KI	EO7	1 : 1	2(Ac)	101.0—101.5			1115, 1100 sh, 1070 sh	34.00 (34.15)	6.29 (6.14)	
RbSCN	EO7	1 : 1	2(Ac/Be=1/1)	67.2—68.0	3380 3260 sh	2060	1115, 1090	37.90 (38.34)	6.98 (6.44)	2.25 (2.98)
NH ₄ SCN	EO7	1 : 1	2(EtAc)	50.2—51.2	3320 sh 3200	2050	1115, 1090 sh, 1075 sh	44.43 (44.76)	7.67 (8.51)	8.02 (6.96)
Mg(SCN) ₂	EO4	1 : 1	2(Ac)	289.0—290.5	3280	2100	1115, 1085, 1050, 1035	35.70 (35.89)	5.33 (5.41)	8.30 (8.36)
Ca(SCN) ₂	EO6	1 : 1	2(Ac/Be=1/1)	108.0—112.0	3360 3200 sh	2050	1110, 1090	39.44 (38.34)	6.05 (5.98)	6.07 (6.39)
Ca(SCN) ₂	EO7	1 : 1	1(Ac)	123.3—123.7	3300	2040	1110 sh, 1085	39.75 (39.82)	6.35 (6.27)	5.90 (5.80)
Ca(SCN) ₂	EO8	3 : 2	2(Ac)	212.2—213.0	3400 sh	2050	1105 sh, 1090 sh, 1075	38.05 (37.73)	5.68 (5.67)	6.72 (6.95)
Sr(SCN) ₂	EO2	1 : 2	2(E)	140.0—159.0	3380	2060 2040 sh	1110, 1080, 1045	29.18 (28.87)	4.91 (4.85)	6.62 (6.73)
Sr(SCN) ₂	EO3	1 : 2	2(E)	151.0—154.5	3300	2080 2050	1120 sh, 1100, 1080 sh, 1065, 1050 sh, 1030 sh	33.10 (33.36)	5.38 (5.60)	5.57 (5.56)
Sr(SCN) ₂	EO4	3 : 4	2(Ac)	142.5—144.0	3360	2060	1110, 1080, 1050 sh, 1030 sh	32.73 (32.89)	5.25 (5.23)	5.95 (6.05)
Sr(SCN) ₂	EO5	1 : 1	1(Ac)	215.0—218.0 (dec)	3400	2040	1110, 1080, 1040	32.46 (32.61)	5.05 (5.02)	6.42 (6.34)
Sr(SCN) ₂	EO6	1 : 1	1(Ac)	169.0—170.0	3420 3280	2080	1110, 1085, 1050 sh, 1030 sh	34.49 (34.59)	5.39 (5.39)	5.58 (5.76)
Sr(SCN) ₂	EO7	1 : 1	1(Ac)	187.0—187.5	3260 3060	2045	1085, 1052 sh, 1020 sh	36.20 (36.25)	5.63 (5.70)	5.24 (5.28)
Sr(SCN) ₂	EO8	1 : 1	2(Ac/Be=1/1)	137.5—138.5	3400 3160	2045	1090	35.30 (34.91)	5.13 (5.34)	5.57 (5.81)
Ba(SCN) ₂	EO2	1 : 2	2(E)	88.0—89.0 (dec)	3380	2060 2040 sh	1113, 1080, 1050	25.50 (25.79)	4.33 (4.33)	5.73 (6.02)
Ba(SCN) ₂	EO3	1 : 1	2(Be)	210.5—213.5 (dec)	3380	2040	1130, 1100, 1075 sh, 1050 sh	23.96 (23.80)	3.54 (3.50)	6.73 (6.94)
Ba(SCN) ₂	EO4	1 : 2	2(Ac)	158.0—159.0	3280 3160 sh	2060	1120, 1095, 1075 sh, 1055	33.61 (33.68)	5.52 (5.65)	4.57 (4.36)
Ba(SCN) ₂	EO5	1 : 1	2(Ac)	156.2—157.3	3340	2040	1100 sh, 1080, 1045	29.30 (29.31)	4.68 (4.51)	5.70 (5.70)

TABLE 1. (Continued)

Salt	PEG	Stoichiometry Salt : POE : H ₂ O	Method ^{a)} (solvent)	Mp (°C)	Infrared spectra (KBr disk) ^{b)}			Found (Calcd)%		
					ν OH	ν SCN	ν C-O-C	C	H	N
Ba(SCN) ₂	EO6	1 : 1	1(Ac)	148.2—149.0	3310	2060	1105, 1080, 1050 sh, 1020	31.30 (31.38)	4.99 (4.89)	5.25 (5.23)
Ba(SCN) ₂	EO7	1 : 1	1(Ac)	176.0—177.5	3340	2050	1120 sh, 1080, 1045 sh	32.79 (33.14)	5.28 (5.22)	4.88 (4.83)
Ba(SCN) ₂	EO8	1 : 1	1(Ac)	151.5—152.0	3300 3120	2040	1090, 1060 sh	34.34 (34.65)	5.42 (5.49)	4.45 (4.49)
BaI ₂	EO7	1 : 1	2(Ac)	247.0—251.0	3300		1090, 1075 sh, 1045 sh, 1025 sh	23.46 (23.44)	3.97 (4.21)	

a) See experimental section. THF = tetrahydrofuran, Ac = acetone, Be = benzene, EtAc = ethyl acetate, E = ether. b) sh = shoulder peak.

TABLE 2. PREPARATIONS AND ANALYTICAL DATA OF COMPLEXES OF GLYMES

Salt	Glyme	Stoichiometry Salt : POE : H ₂ O	Method ^{a)} (solvent)	Mp (°C)	Infrared spectra (KBr disk) ^{b)}			Found (Calcd)%		
					δ H ₂ O ^{c)}	ν SCN	ν C-O-C	C	H	N
Sr(SCN) ₂	MeEO3Me	1 : 1 : 1/2	2(E)	179.0—181.0 (dec)	1620 (3400)	2050	1110, 1080, 1055, 1020, 1010	29.85 (30.71)	3.84 (4.90)	8.07 (7.16)
Sr(SCN) ₂	MeEO4Me	1 : 1 : 1	2(E)	167.0—168.0	1620 (3320)	2050	1110, 1080, 1050, 1020	32.56 (32.45)	5.10 (5.45)	6.43 (6.31)
Sr(SCN) ₂	MeEO5Me	1 : 1 : 1/2	2(E)	247.0—250.5 (dec)	1625 (3360)	2045	1095, 1085, 1060 sh, 1020	35.35 (35.09)	5.65 (5.68)	5.88 (5.85)
Sr(SCN) ₂	MeEO6Me	1 : 1	2(E)	156.5—158.0		2040	1095, 1075 sh	37.07 (37.38)	5.80 (5.88)	5.51 (5.45)
Sr(SCN) ₂	MeEO7Me	3 : 2	2(E)	138.5—142.0		2040	1080, 1055 sh	33.69 (34.57)	4.84 (5.19)	6.29 (6.37)
Sr(SCN) ₂	MeEO8Me	2 : 1	2(E)	225.0 (dec)		2040	1080	33.21 (32.53)	4.97 (4.75)	6.24 (6.95)
Ba(SCN) ₂	MeEO2Me	1 : 1	2(E)	144.5—154.0		2040	1110, 1090, 1065 sh	23.44 (24.79)	2.80 (3.64)	7.31 (7.23)
Ba(SCN) ₂	MeEO3Me	1 : 1 : 1/2	2(E)	83.5—85.0	1620 (3380)	2030	1085, 1060, 1020	27.49 (24.79)	3.84 (3.64)	6.34 (6.36)
Ba(SCN) ₂	MeEO4Me	1 : 1	2(E or Ac/Be)	144.0—145.0		2050	1105, 1085, 1060, 1020	30.21 (30.29)	4.36 (4.66)	5.86 (5.89)
Ba(SCN) ₂	MeEO5Me	1 : 1 : 1	2(Ac)	162.0—164.4	1630 (3380)	2050	1090, 1055, 1020	31.39 (31.26)	5.28 (5.25)	5.19 (5.21)
Ba(SCN) ₂	MeEO6Me	1 : 1	1(Ac)	171.5—172.5		2060 2040	1110, 1090, 1060 sh, 1020	33.90 (34.08)	5.44 (5.36)	4.80 (4.97)
Ba(SCN) ₂	MeEO7Me	1 : 1	1(Ac/Be = 3/25)	148.5—149.2		2040	1080, 1055 sh, 1030, 1020	35.43 (35.56)	5.71 (5.64)	4.57 (4.61)
Ba(SCN) ₂	MeEO8Me	1 : 1	2(Ac)	89.8—90.7		2040	1090, 1020	36.53 (36.84)	5.98 (5.88)	4.33 (4.30)

a), b) See Table 1. The values in parentheses of δ H₂O are those of ν H₂O. c) The values in parentheses are ν H₂O.

TABLE 3. ^{13}C NMR AND PROTON NMR OF SOME SOLID COMPLEXES

Complex	Solvent (concn %)	^{13}C NMR Chemical shift (ppm from TMS)		
		$\text{CH}_2\text{CH}_2\text{OH}$	Other carbons	$\text{CH}_2\text{CH}_2\text{OH}$
EO7	acetone- d_6 (20%)	61.9	71.0, 71.1	73.5
EO7-KSCN	acetone- d_6 (15%)	61.1	70.0, 70.2, 70.5	73.1
EO7-Sr(SCN) $_2$	methanol- d_4 (9%)	61.5	70.9, 71.3, 71.6, 71.8	73.5
EO7-Ba(SCN) $_2$	methanol- d_4 (12%)	62.4	71.3, 71.6, 71.9, 72.2	74.2
EO6-Ca(SCN) $_2$	methanol- d_4 (10%)	62.3	70.5, 70.9, 71.2, 71.8	73.3
EOc6-Ba(SCN) $_2$	methanol- d_4 (6%)	—	72.2	—

Complex	Solvent (concn %)	Proton NMR	
		Standard	Chemical shift
EO7-KSCN	methanol- d_4 (0.8%)	8% dioxane in benzene(external)	45.7, 47.2(Hz) ^a
EO7-KSCN	acetone- d_6 (15%)	TMS(internal)	3.64, 3.66, 3.67(ppm)
EO7-KSCN	acetonitrile- d_3 (17%)	TMS(internal)	3.57, 3.58, 3.59(ppm)
EO7-Ba(SCN) $_2$	methanol- d_4 (0.8%)	8% dioxane in benzene(external)	60.7(Hz) ^a

a) The chemical shift is expressed in Hz downfield. No correction of the bulk magnetic susceptibility was made. In the absence of metal cations, the chemical shift of EO7(ca. 1%) was in the range of 45—47 Hz.

TABLE 4. PREPARATIONS AND ANALYTICAL DATA OF NOVEL COMPLEXES OF CROWN ETHERS

Salt	Crown ^a ether	Stoichiometry salt : POE : H $_2$ O	Method ^b (solvent)	Mp (°C)	Infrared spectra(KBr disk) ^a			Found(Calcd)%		
					$\delta\text{H}_2\text{O}$	νSCN	$\nu\text{C-O-C}$	C	H	N
LiSCN	EOc4	1 : 1	3(Ac)	260.0—261.0		2050	1134, 1087	44.64 (44.81)	6.77 (6.69)	5.71 (5.81)
NaSCN	EOc4	1 : 2 : 1/2	1(Ac)	138.0(dec)	1630 (3450)	2040 2060	1140, 1095	46.18 (46.13)	7.51 (7.51)	3.13 (3.17)
Mg(SCN) $_2$	EOc5	1 : 1	3(Ac)	360		2060	1090, 1060, 1040	39.80 (39.95)	5.56 (5.58)	7.71 (7.76)
Mg(SCN) $_2$	EOc6	1 : 1 : 4	1(AN)	360	1650 (3450)	2080	1140, 1110, 1090	34.89 (35.26)	6.64 (6.77)	5.84 (5.87)
Ca(SCN) $_2$	EOc4	1 : 1 : 2	3(M)	320	1620 (3380)	2080	1135, 1110, 1090	32.71 (32.60)	5.57 (5.47)	7.55 (7.60)
Ca(SCN) $_2$	EOc5	1 : 1 : 1	3(Ac)	310	1615 (3320) (3400 sh)	2090 2050	1120, 1095	36.57 (36.58)	5.74 (5.62)	7.08 (7.10)
Ca(SCN) $_2$	EOc6	1 : 1	3(Ac)	320		2045	1135, 1090	39.80 (39.98)	5.78 (5.75)	6.57 (6.66)
Ba(SCN) $_2$	EOc6	1 : 1	3(Ac)	270—300(dec)		2040	1085	31.95 (32.47)	4.32 (4.67)	5.39 (5.41)

a) EOC4=12-crown-4, EOC5=15-crown-5, EOC6=18-crown-6. b) See experimental section. Ac=acetone, AN=acetonitrile, M=methanol. c) The values in parentheses of $\delta\text{H}_2\text{O}$ are those of $\nu\text{H}_2\text{O}$.

with alkali and alkaline earth metal thiocyanates to give stable solid complexes. However, our preliminary attempts of isolation using methanol as a solvent were unsuccessful. When a roughly 1 : 1 mixture of PEG and metal thiocyanates, which showed appreciable PMR downfield shifts, was heated up without solvent, some solid complexes were formed almost quantitatively, with a few exceptions(Table 1).

Among alkali metal thiocyanates, NaSCN gave a solid complex with EO6, while KSCN and RbSCN formed solid complexes with EO7. The complex with NaSCN was not isolated because of the difficulty in purification. The complex with NaBPh $_4$ was isolated and analyzed instead. Their compositions were all 1 : 1. Hexaethylene glycol(EO7) also produced a

solid 1 : 1 complex with KI. Our attempts to isolate complexes with LiSCN and CsSCN, however, were all unsuccessful.

Ammonium thiocyanate gave a 1 : 1 complex with EO7, although two examples of the ammonium complexes with the diphenoxylated EO4 and EO6 have recently been reported.¹⁹⁾

The magnesium complex with EO4 was confirmed to form on heating without solvent even when the thiocyanate has water of crystallization, and evolution of its water was observed during the complexation. Surprisingly, the resulting complex is no longer hygroscopic.

Calcium thiocyanate yielded the 1 : 1 complexes not only with EO6 but also with EO7. The solid complex

with EO8 was also isolated and its elemental analysis agreed with the 3:2 composition.

With $\text{Sr}(\text{SCN})_2$ and $\text{Ba}(\text{SCN})_2$, not only PEG with more than two EO units, but also glymes with more than two or three EO units gave the solid complexes with various compositions (Tables 1 and 2). As expected, the complex of EO7 with BaI_2 was also isolated.

Some of the above complexes could be recrystallized from aprotic solvent, suggesting that they are stable even in solution. This fact is also supported by ^{13}C NMR and PMR spectra of the complexes, in which, compared with the spectra of PEG, the splitting of signals or the shifts were observed especially in the PMR spectra (Table 3).

Remarkable differences between the IR spectra of PEG or glymes and those of their complexes may be noticed. The greatest changes are observed in the region $1000\text{--}1200\text{ cm}^{-1}$ which is assigned to the CH_2 rocking band and the C-C and C-O stretching bands.²¹⁾ It was reported²¹⁾ that the crystalline PEG's ($n \geq 3$) exhibit strong bands at about 1150, 1100–1115, and 1060–1065 cm^{-1} . Upon complexation, the bands are shifted to lower energy, giving one strong band which has a few shoulder peaks ranging from 1020–1080 cm^{-1} . The shifts are very similar to those of the crown ether complexes (see Table 4).²²⁾ From these observations, it may be inferred that the structures of the complexes with PEG would be very similar to those of the crown ethers.²³⁾

Mechanism of Metal-ion Complexation of Poly(oxyethylene) Derivatives.

From the ion-radius concept, it is widely recognized that the selective and strong metal-ion complexation of crown ethers is related to the relative sizes of the metal cations and the hole sizes of the crown ethers.^{24–27)} As is shown in Table 4, we have also succeeded in isolating some novel complexes of the crown ethers with thiocyanates of comparatively small ion-radius alkali and alkaline earth metals. The significance of these findings is that 12-crown-4, of which the cavity diameter is less than 1.2 Å, coordinate to both Li^+ (ion diameter 0.78 Å) and Ca^{2+} (1.06 Å) with the 1:1 stoichiometry, but never to Mg^{2+} (0.78 Å). Further the 2:1 complex of 12-crown-4 with NaSCN including water of crystallization was found to form only in the presence of water, and could be recrystallized in acetone. The latter fact, implies along with the largest downfield shift on its complexation with Na^+ in acetone, that the complex is stable even in acetone. As was noted, $\text{Mg}(\text{SCN})_2$ very easily gave the stable complexes with 15-crown-5 and 18-crown-6. Recently some magnesium complexes with benzo-15-crown-5 were reported.²⁸⁾ From these various observations, it may be concluded that the cavity size of crown ethers is not the substantial factor governing their strong complexing properties. The poor complexing abilities of some rigid cyclic polyethers also support this conclusion.^{29–32)}

On the other hand, studies of the coordination geometry of the alkali metal cations based on PMR or metal element magnetic resonance experiments have attracted special interest recently. For the sodium ion, the existence of the four coordinated species were

confirmed in THF,^{3,33)} DMSO,^{34,35)} or 1-methyl-2-pyrrolidone³⁵⁾ by the PMR studies. Detellier and Laszlo³⁶⁾ reported on the basis of the ^{23}Na NMR study that the tetracoordination and tetrahedral configuration of the sodium cation is of lowest energy. On the basis of the largest PMR downfield shifts, we have observed the strongest complexing ability of 15-crown-5 with the alkali and alkaline earth metal cations in acetone or methanol, with a few exceptions. Furthermore, it has been confirmed that there exists the specific interaction of PEG with the smaller metal cations, that is, Mg^{2+} with EO4, Na^+ and Ca^{2+} with EO6, and K^+ with EO7. These facts suggest that the fulfillment of the energetically favorable coordination geometry of the alkali and alkaline earth metal cations and the compatibility of the POE ligands should be the important factors governing the specific or the selective complexation. This mechanistic concept well explains an inclination of the induced fit of the crown ethers in complexation.^{7,8)}

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