Selectivities and thermodynamic parameters of alkali-metal and alkaline-earth-metal complexes of polyethylene glycol dimethyl ethers in methanol and acetonitrile

Ng. van Truong*, A. R. Norris, H. S. Shin, E. Buncel**

Department of Chemistry, Queen's University, Kingston, Ont., K7L 3N6 (Canada)

R. A. B. Bannard

Protective Sciences Division, Defence Research Establishment Ottawa, Shirley Bay, Ottawa, Ont., K1A 0Z4 (Canada)

and **J. G. Purdon**

CB Defence Section, Defence Sciences Division, Defence Research Establishment Suffield, Medicine Hat, Alta., T1A 8K6 (Canada)

Abstract

Thermodynamic parameters ($\log K_s$, ΔH_c, $T\Delta S_c$) of alkali-metal and alkaline-earth-metal ion complexes of polyethylene glycol dimethyl ethers (glymes) have been determined in methanol and acetonitrile as solvents at 25 °C by using a modified calorimetric technique. It has been shown that, for a given number of donor sites, the stabilities of M^+ and M^{2+} complexes by glymes are lower than those of the corresponding macrocyclic polyethers and open chain antibiotic anions of the Nigericin group by a factor of up to 10^5. The stability constants ($\log K_s$) of the cation–glyme complexes are higher in acetonitrile than in methanol. The selectivities towards alkali and alkaline-earth cations with similar ionic radii (e.g. $K_s(Ca^{2+})/K_s(Na^+)$ and $K_s(Ba^{2+})/K_s(K^+)$) of the glymes are also low. This may result from less effective shielding of the cation from cation–solvent interactions in the glymes as compared to crown ethers and open-chain antibiotic anions. In both solvents, the stability constant of a given metal complex increases monotonically with increase of the glyme chain length. The stability of K^+ and Ba^{2+} complexes by glymes is largely enthalpy dominated, accompanied by an unfavourable entropy change in both methanol and acetonitrile, in which the contribution of the enthalpy term to the stabilities of complexes has also been found to increase with increase of chain length.

Introduction

There has been considerable interest in the open chain polyethylene glycols (PEGs) and their dimethyl ether derivatives (glymes) since Smid and his co-workers [1, 2] reported their first results on complexation of alkali metal carbanion salts by these substances. Their ability to form complexes with different metal cations in various solvents in a manner similar to the synthetic and naturally occurring polyether ionophores [3–5], as well as their usefulness as catalysts in phase transfer processes [6] and their influence on ion-pairing [2, 7] and reactivities of nucleophiles [8], has made these materials highly attractive in diverse areas of chemistry.

The lower molecular weight PEGs and glymes are especially effective solvents for a variety of organic and inorganic compounds [9]. Studies have shown that the rates of nucleophilic substitution reactions of alkyl halides and organosulfur and organophosphorus derivatives [10–12] are enhanced significantly in these solvents. It was also reported that the rates and the orders of nucleophilic substitution reactions of *p*-halophenyl sulfones with alkali metal phenoxides in the glyme solvents increase with the chain length of the glyme molecules [11]. These results were explained as being due to an increase of the cation-binding property of the glyme with chain length. Similar results were also obtained for the nucleophilic displacement reactions of alkyl halides and substituted alkylphosphorus derivatives in the glyme solvents [10, 12]. Thus it would be of interest to determine the binding constants of the

---

short chain glymes with alkali and alkaline-earth cations.

The thermodynamic parameters for complexation and the selectivities toward monovalent and bivalent cations, as well as the effects of the cavity sizes of crown ethers [13, 14] and cryptands [15, 16] on the stabilities of the cation complexes in various solvents, have been extensively studied in recent years. Similarly, the stabilities of metal ion complexes with the open chain antibiotic ionophores in various solvents have also been evaluated [17]. However, much less is known about selectivities and the effect of molecular weight of the open chain PEGs and their ether derivatives, especially the short chain glymes. In this paper we present results on selectivities and the thermodynamic parameters ($\log K_s$, ΔH_c and $T\Delta S_c$) of the complexes of several low molecular weight glymes with alkali and alkaline-earth cations in methanol and acetonitrile, as part of our study on metal ion–glyme complexes [5a] and the effect of open chain and cyclic ethers on the rates of nucleophilic reactions of organosulfur and organophosphorus compounds [12].

Experimental

Materials

Diethylene glycol dimethyl ether (diglyme, DG) and tetraethylene glycol dimethyl ether (tetraglyme, TG) were purchased from Aldrich and distilled at least twice from potassium metal under nitrogen atmosphere (DG) or from sodium metal *in vacuo* (TG), respectively. Hexaethylene glycol dimethyl ether (hexaglyme, HG) obtained from Parish was used without further purification.

Methanol was distilled from magnesium turnings and iodine. Acetonitrile was dried over molecular sieves overnight and then distilled from calcium hydride under nitrogen. All solvents except hexaglyme were stored under nitrogen atmosphere before use.

The following reagents of the highest purity were used: $NaClO_4$, KI, $KClO_4$, $Ca(NO_3)_2 \cdot 4H_2O$ and $Ba(ClO_4)_2$. Except for the hydrated calcium nitrate the salts were dried *in vacuo*. The solution of hydrated calcium nitrate salt in methanol or acetonitrile was dried over molecular sieves (type 5 Å) before use. Since the concentrations of the salts used are low, the amount of the water introduced in this way can be considered as negligible. However, the effect of added water on the stability constants of the metal complexes was also checked and the results will be described below.

Procedure and calculation

Stability constants of the glyme–metal complexes were determined by a modified batch calorimeter technique, in which successive increments of the glymes (100 or 400 μl) were repeatedly added via ampoules into the same batch of metal salt solution contained in the reaction vessel. The total heat released upon each addition was measured via a chart recorder. The heat of complexation could be determined from the total heat change and the heat of dilution and ampoule breakage. A BASIC program was employed to give the values of $\log K_s$ and ΔH_c of complexation by means of an iterative method. Details of the experimental procedure and calculation of stability constants of the glyme complexes have been described previously [5a, b].

The calorimetric measurements were performed on Tronac model 1250 or 450 calorimeters. For acetonitrile solvent, the solutions were prepared and transferred under nitrogen atmosphere. The ligand concentrations used were in the range of 6×10^{-3}–2.7×10^{-1} M and the salt concentrations in the range of 4×10^{-2}–2×10^{-1} M. No correction was made for activity coefficients since the salt concentrations used were rather low and the terms due to the ionic species appear in both the numerator and denominator in the expression for K_s.

The effect of a trace amount of water on the stability constant was tested by adding known amounts of water to the systems potassium ion–tetraglyme in methanol and acetonitrile. The results show that the effect of adding up to 0.1% vol./vol. water in methanol could be considered as negligible (reduction by 0.03 in $\log K_s$ value for the K^+–TG complex), but further addition of 1% vol./vol. water reduced the stability constant by 0.13 in $\log K_s$. Slightly different behaviour was observed for the K^+–TG system in acetonitrile, where addition of 0.1% vol./vol. water resulted in an increase of 0.08 in $\log K_s$. However, further addition of 1% H_2O led to a decrease in stability constant by 0.09 in $\log K_s$.

It has been shown that the water content in methanol and acetonitrile purified by procedures similar to those described above is less than 0.01% vol./vol. ($\approx 5.6 \times 10^{-3}$ M) [16a, b]. Hence the amounts of water contained in the solutions studied should be very small and any effect due to the presence of water on stability constants can be considered as negligible, i.e. within experimental error. Thus the stability constants obtained for the complexes can be taken to refer to the anhydrous solvents.

Results and discussion

Stability constants of alkali- and alkaline-earth-metal complexes of glymes in methanol and acetonitrile

In Table 1 are presented the results for the stability constants ($\log K_s$) of the glyme complexes with alkali

TABLE 1. Stability constants (log K_s) of alkali and alkaline-earth metal complexes with glymes in methanol and acetonitrile at 25 °C

Solvent	Cation	Log K_s[a]				
		DG	TG	PG	HG	HpG
Methanol	Na$^+$		1.11	1.50[b]	1.60[b]	1.67[b]
	K$^+$	0.34	1.68	2.20[b]	2.40	2.87[b]
	Ca^{2+}		≤0.1			
	Ba^{2+}		1.74	2.1[c]	2.65[c]	
Acetonitrile	K$^+$	0.71	2.06			

[a]Log $K_s \pm 0.05$. Abbreviations: DG, diglyme; TG, tetraglyme; PG, pentaglyme; HG, hexaglyme; HpG, heptaglyme.   [b]Ref. 3a.   [c]Ref. 13f.

and alkaline-earth cations in methanol and acetonitrile solvents. The values of log K_s were reproducible within ±0.05 log units except for the Ca^{2+} complex with tetraglyme where the total heat developed on addition of the tetraglyme solution to the salt solution contained in the reaction vessel was very close to the heat of dilution of the ligand solution. This would suggest that the Ca^{2+}–TG complex is very weak, i.e. log $K_s \leqslant 0.1$.

The glymes are formally open chain ligands but a number of studies have shown that they form 1:1 cation–ligand complexes in the solid state, in which the glyme chains are wrapped around the cations in quasi-cyclic structures [3b, 18]. Such conformational structures are also expected to exist in solution. The thermodynamic parameters obtained here for the alkali and alkaline-earth complexes of the glymes refer to 1:1 species.

The stability constants of alkali and alkaline-earth ion complexes of the glymes are generally lower than those with the corresponding cyclic crown ethers [13b–d] having the same number of oxygen binding sites, by a factor up to 10^4. For example, the values of $K_s(15\text{-}C\text{-}5)/K_s(TG)$ are c. 130, 50 and 250 for Na$^+$, K$^+$ and Ca^{2+} in methanol. Similarly, the values of $K_s(18\text{-}C\text{-}6)/K_s(PG)$ are 720, 9120 and 87 000 for Na$^+$, K$^+$ and Ba^{2+} in methanol. Similar high values are also observed for 21-C-7 and hexaglyme in methanol. The higher stability constants of crown ethers towards M$^+$ and M^{2+} cations over the corresponding glymes is probably due to the so-called macrocyclic effect, in which the cation is effectively accommodated in the cavity of the cyclic crown ether and partly shielded from interaction with the solvent with relatively little enthalpic and entropic cost [19].

In comparison with the open chain antibiotics of the Nigericin group, the stability constants of the alkali and alkaline-earth complexes with the glymes are also found to be lower than those of antibiotic

ionophores such as monensin and lasalocid (X-537A) anions [17a]. Lasalocid, the smallest naturally occurring ionophore anion in the Nigericin group, with only five binding oxygen atoms, forms stronger complexes with alkali and alkaline-earth cations than does tetraglyme (with the same number of binding sites) by a factor of 50 to 80 000. For example, the values of K_s (lasalocid)/K_s(TG) are 98 and 72 000 for K$^+$ and Ba^{2+} complexes in methanol, respectively. The stabilities of the metal complexes with monensin in methanol are also much higher than those for pentaglyme and hexaglyme, e.g. the ratio of binding constants (K_s) of monensin over pentaglyme and hexaglyme is found to be 500 and 290, respectively, for the K$^+$ complexes in methanol. Similarly, the stability of the Ba^{2+} complex with monensin in methanol is also higher than those for pentaglyme and hexaglyme by almost five orders of magnitude.

It is likely that the higher stabilities of M$^+$ and M^{2+} complexes with the open chain antibiotic anions of the Nigericin group over the corresponding neutral glymes derives from two main factors: the negative charge of these ionized antibiotic ligands and the macrocyclic effect. On the basis of purely electrostatic effects, the interaction of opposite charge on the metal cation and ligand anion should certainly be expected to increase the stability constants of the metal complexes with the antibiotic ionophores over the neutral glymes, especially for the divalent alkaline-earth cation complexes. In addition, studies have shown that in the metal ion complexes, the open chain antibiotic ionophores of the Nigericin group form cyclic structures stabilized by hydrogen bond formation between the carboxylic group (–COOH or –COO$^-$) and appropriate –OH groups within the molecules in which the cations are accommodated. The hydrogen-bonded cyclic structures adopted by these antibiotic ligands in the complexes are very similar to those of the crown ethers and this would

also be expected to contribute to the higher stabilities of their complexes as compared to those of the glymes [17, 21].

The results in Table 1 clearly show that the metal complexes of the glymes are more stable in acetonitrile than in methanol. This probably results from less effective solvation of the glymes and their cation complexes in acetonitrile. This finding is in accord with those reported in our previous work for the tetraglyme complexes with alkali metal cations in these solvents [5a].

Selectivities of the glyme ligands

The results in Table 1 also show that the selectivities between alkali and alkaline-earth cations, i.e. $K_s(M^{2+})/K_s(M^+)$, with similar ionic radii (e.g. Ca^{2+}/Na^+ and Ba^{2+}/K^+) by the glymes are lower than selectivities displayed by the corresponding crown ethers [13] and the open-chain antibiotic ligands [17], and much lower than for cryptands [22]. For example, the values of $K_s(Ba^{2+})/K_s(K^+)$ are 1.1, 1.0 and 1.8 for tetraglyme, pentaglyme and hexaglyme complexes, respectively, compared to values of 850, 148, 10 and 17 for lasalocid, monensin, 18-C-6 and 21-C-7 in methanol [13, 17]. While the value of $K_s(Ca^{2+})/K_s(Na^+)$ is only c. 0.1 for tetraglyme in methanol, it is 0.17 and 78 for 15-C-5 and lasalocid, respectively (both ligands have the same numbers of binding sites as tetraglyme). The selectivities for cryptands are also much higher in this solvent [22].

It is known that there is competition between the solvent and the multidentate ligand for the cation in complexation, in which the energy gains from the cation–ligand coordination will favorably compensate the energy losses in disruption of cation–solvent interactions. Therefore, substitution of alkali-metal ion by alkaline-earth-metal ion will result in an increase in two opposite effects on complexation: increase of charge density on the cation favors cation–ligand interactions, thereby increasing the stability of the complexes, while it also increases solvation of the cation which could destabilize the complexes. Thus the selectivity of the ligand will be dependent on a gain (or loss) in the energy difference between these two interactions on going from M^+ to M^{2+}. However, the energy differential is also related to the conformational structures of the ligands and their complexes, which may reduce the cation–solvent interactions.

Although available data for the free energies of solvation of alkaline-earth cations is limited, especially in non-aqueous solvents, one would expect that solvation energies of M^{2+} cations should be substantially larger than those of alkali-metal cations of comparable radii. For example, hydration energies of Na^+ and K^+ are -411 and -337 kJ mol^{-1}, compared to -1593 and -1318 kJ mol^{-1} for Ca^{2+} and Ba^{2+}, respectively [23, 24]. The solvation of Ba^{2+} in methanol (-1300 kJ mol^{-1}) is also much higher than for K^+ (-327 kJ mol^{-1}) [24]. In our previous paper it was shown that there is still a significant interaction between the solvent and the complexed cation with the glyme complexes [5a]. Therefore, the smaller stability of the Ca^{2+} complex with tetraglyme probably derives from a larger solvation energy of this cation by methanol, while the interaction energy between Ba^{2+} and glymes favorably compensates for the energy loss resulting from partial desolvation of this cation. However, the results for the stability constants of the K^+ and Ba^{2+} complexes with the glymes in methanol ($K_s(K^+) \simeq K_s(Ba^{2+})$) suggest that the energy gain on complexation by the glymes in methanol would be very similar to the increase in energy required for desolvation of the cation on going from K^+ to Ba^+. On the other hand, the macrocyclic ionophores are capable of shielding effectively the complexed cation from solvent interactions, thereby increasing the cation–ligand interactions. This may certainly lead to higher selectivities of the alkaline-earth cations over alkali cations with similar radii by macrocyclic ligands as compared to the glymes. This would hold especially for the monensin and lasalocid antibiotics in which the high selectivity should mainly result from a significant increase of the interaction between the antibiotic anion and the complexed cation on going from M^+ to M^{2+}.

Effect of chain length of glymes

The results in Table 1 show that for a given cation (e.g. K^+), stability (log K_s) increases monotonically with increase of glyme chain length. This contrasts with the characteristics of the crown ether complexes [14a], in which the relative size of the cation and ligand cavity is generally one of the important factors in determining the stability of the metal complex, other factors being solvation, number of donor atoms, ligand flexibility, etc. As a result, the stability constants of a given metal complex have a maximum value for a particular crown ether. Figure 1 also shows the variation of the stability constants with the number of oxygen binding sites of the glymes and crown ethers for the potassium complexes.

As discussed above, several studies have shown that the glymes are able to wrap around the metal ion on complexation [18]. In our previous paper it was shown that the enclosed cations in the quasi-cyclic structures of the metal ion–glyme complexes are still exposed to solvent interactions [5a]. This interaction is much stronger for tetraglyme complexes than for corresponding crown ether and cryptand complexes. Therefore, when the chain length of the
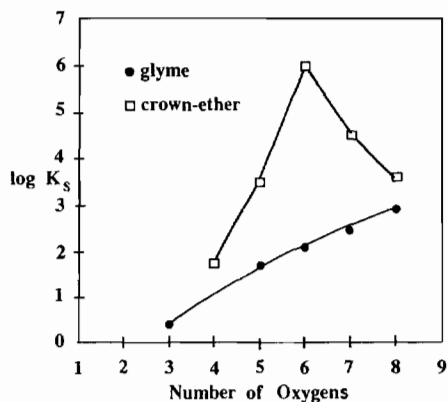
Fig. 1. Variation of stability constant ($\log K_s$) for K^+ complexes with number of oxygens in glymes and crown ethers, in methanol at 25 °C.

TABLE 2. Thermodynamic data for alkali- and alkaline-earth-metal complexes with glymes[a] in methanol and acetonitrile at 25 °C (in kJ mol^{-1})

Solvent	Cation		DG	TG	HG
Methanol	K^+	ΔG_c	−1.95	−9.30	−13.7
		ΔH_c	−24.5	−26.9	−42.2
		$T\Delta S_c$	−25.0	−17.6	−28.5
	Ba^{2+}	ΔG_c	–	−9.7	−15.1[b]
		ΔH_c	–	−23.8	−28.3[b]
		$T\Delta S_c$	–	−14.1	−13.1[b]
Acetonitrile	K^+	ΔG_c	−4.0	−11.7	
		ΔH_c	−17.3	−21.8	
		$T\Delta S_c$	−13.1	−10.1	

[a]Abbreviations as in Table 1. [b]Ref. 4c.

glyme (or the number of binding sites) increases, the glyme would more readily wrap around the cation, and the binding sites might stepwise displace the solvent molecules from the cation–solvent interaction, thereby increasing the stability constant of the complex. Thus more binding sites (and high flexibility of the glymes) will lead to more effective binding and the glyme may form a complex with the cation in a spiral structure.

In contrast, crown ethers having fairly rigid cyclic structures will generally form the strongest complex with the cation which is optimally fitted into a cavity. For a given cation the stability constant of the complex will decrease with a larger, or smaller, cavity size relative to the cation size. For the smaller crown ether the cation will be situated outside the ligand cavity and therefore exposed appreciably to solvent interactions, while for the larger crown ether the cation does not interact effectively with all the binding sites of the crown ether. Thus, the ligand cavity size-selection may play an important role in determining the stability maximum at 18-C-6 for the K^+–crown ether complex in methanol (Fig. 1).

Thermodynamics of complex formation

In Table 2 are presented the thermodynamic parameters (ΔG_c, ΔH_c and $T\Delta S_c$) for alkali and alkaline-earth complexation by the glymes in methanol and acetonitrile at 25 °C. The results show that the stabilities of the K^+ and Ba^{2+} complexes by the glymes are largely enthalpy dominated, though accompanied by unfavourable entropy change ($\Delta S_c < 0$) in both methanol and acetonitrile.

It is seen that the $T\Delta S_c$ value for a given complex is more negative in methanol than in acetonitrile. This suggests that the metal ion and the glymes are not completely desolvated in methanol on complexation. There may still exist hydrogen bonding

between methanol molecules and the cation–glyme complexes. These findings are also in agreement with those reported earlier for alkali-metal–tetraglyme complexes in different solvents [5].

The results indicate that the enthalpy of complexation for a given cation becomes more negative with increasing chain length of the glymes in both solvents. Since the glymes are open chain ligands which should be capable of wrapping around the metal ion in the complexation, an increase in the glyme chain length will increase the cation–ligand interactions as the binding sites of the ligand increase. This would lead to more negative ΔH_c values, although this is an oversimplification as solvation of the cation and interactions between solvent and the glymes should also be taken into consideration. However, the former should be constant for a given metal ion in the given solvent, while the latter would be expected not to differ greatly with variation of chain length of the glymes as compared to the cation–ligand interaction.

In contrast, the ΔH_c variation of the crown ether complexes with ligand size is quite different from that for the glyme complexes, as ΔH_c for the crown ether complexes passes through a minimum value on increasing the ligand size from 12-C-4 to 21-C-7. For example, ΔH_c values of the potassium complexes with 12-C-4, 15-C-5, 18-C-6 and 21-C-7 in methanol are −21.3, −32.2, −56.1 and −35.9 kJ mol^{-1}, respectively [13b].

Since in crown ethers the binding sites are situated on the ligand ring, the cation–ligand interactions should be strongly dependent on the relative sizes of the cation and the ligand cavity. It can be expected that ΔH_c for a given cation will have a minimum value (i.e. the most negative value) for the complex where the cation fits most snugly into the cavity of the ligand. This may explain simply the variation of ΔH_c for the potassium ion complex with crown ethers in methanol on going from 12-C-4 to 21-C-7, where

the most negative value of ΔH_c was found for 18-C-6 ($\Delta H_c = -56.1$ kJ mol^{-1} for 18-C-6).

It is noteworthy that the $T\Delta S_c$ values for the K$^+$-glyme complexes in methanol do not vary linearly with chain length of the ligand. The effect of chain length upon ΔS_c is not clear from the results, though the more negative $T\Delta S_c$ values for HG and DG as compared to TG may suggest that the more flexible hexaglyme may lose more degrees of freedom on complexation, while a smaller glyme such as diglyme should form a more rigid structure of the complex compared to tetraglyme.

The thermodynamic data of the K$^+$ and Ba^{2+} complexes with the glymes in methanol (both cations have similar ionic radii) show that the complexation enthalpy of the K$^+$ complex is larger than for the Ba^{2+} complex. However the reverse is observed for the complexation entropy of these complexes, i.e. ΔS_c (K$^+$-glyme) $< \Delta S_c$ (Ba^{2+}-glyme). This could be a reflection of the interactions of solvent molecules with the uncomplexed and complexed cations. These interactions should be higher for the alkaline-earth cation, thereby reducing the complexation enthalpy of the complex. On the other hand, the solvent release from desolvation of the cation on complexation should be greater for M^{2+} cations than for M$^+$ cations. This would lead to higher complexation entropies of alkaline-earth complexes as compared to alkali-metal complexes with the same glyme. These results are in agreement with those observed for the crown ether complexes with alkali and alkaline-earth cations of similar ionic radii (i.e. Na$^+$ versus Ca^{2+}; K$^+$ versus Ba^{2+}) in various solvents [13b–d].

References

1 (a) L. L. Chan and J. Smid, *J. Am. Chem. Soc., 89* (1967) 4547; (b), *90* (1968) 4654.

2 (a) L. L. Chan, K. H. Wong and J. Smid, *J. Am. Chem. Soc., 92* (1970) 1955; (b) U. Takaki and J. Smid, *J. Am. Chem. Soc., 96* (1974) 2588.

3 (a) G. Chaput, G. Jeminet and J. Juillard, *Can. J. Chem., 53* (1975) 2240; (b) B. Tümmler, G. Maass, F. Vögtle, H. Sieger, U. Heimann and E. Weber, *J. Am. Chem. Soc., 101* (1979) 2588; (c) L. Töke, G. T. Szabo and K. Aranyosi, *Acta Chim. Acad. Sci. Hung., 100* (1979) 257; (d) K. Ono, K. Konami and K. Murakami, *J. Phys. Chem., 83* (1979) 2665; (e)Y. Hirashima, K.

Kanetsuki, I. Yonezu, N. Isobe and J. Shiokawa, *Bull. Chem. Soc. Jpn., 59* (1986) 25.

4 (a) H.-J. Buschmann, *Inorg. Chim. Acta, 98* (1985) 43; (b) *102* (1985) 95; (c) *105* (1985) 59.

5 (a) E. Buncel, H. S. Shin, Ng. van Truong, R. A. B. Bannard and J. G. Purdon, *J. Phys. Chem., 92* (1988) 4176; (b) M. H. Abraham, in M. A. V. Ribeiro da Silva (ed.), *Thermochemistry and its Applications to Chemical and Biochemical Systems,* Reidel, Dordrecht, The Netherlands, 1984, p. 275.

6 (a) G. W. Gokel, D. M. Goli and R. A. Schultz, *J. Org. Chem., 48* (1983) 2837; (b) R. Neumann and Y. Sasson, *J. Org. Chem., 49* (1984) 3448; (c) G. T. Szabo, K. Aranyosi and L. Töke, *Acta Chim. Acad. Sci. Hung., 110* (1982) 215, 225.

7 J. Smid, *Angew. Chem., Int. Ed. Engl., 11* (1972) 112.

8 (a) J. Ugelstad, A. Berge and H. Listou, *Acta Chem. Scand., 19* (1965) 208; (b) G. H. Barlow and H. E. Zaugg, *J. Org. Chem., 37* (1972) 2246.

9 (a) E. Santaniello, in L. J. Mathias and C. E. Carraher, Jr. (eds.), *Crown Ethers and Phase Transfer Catalysis in Polymer Science,* Plenum, New York, 1984, p. 397; (b) E. Santaniello, A. Fiecchi, A. Manzocchi and P. Ferraboschi, *J. Org. Chem., 48* (1983) 3074.

10 (a) A. Berge and J. Ugelstad, *Acta Chem. Scand., 19* (1965) 742; (b) L. M. Thomassen, T. Elligsen and J. Ugelstad, *Acta Chem. Scand., 25* (1971) 3024.

11 W. T. Reichle, *J. Org. Chem., 37* (1972) 4254.

12 (a) E. Buncel, E. J. Dunn, R. A. B. Bannard and J. G. Purdon, *J. Chem. Soc., Chem. Commun.,* (1984) 162; (b) E. Buncel and M. J. Pregel, *J. Chem. Soc., Chem. Commun.,* (1989) 1566; (c) E. J. Dunn and E. Buncel, *Can. J. Chem., 67* (1989) 1440; (d)E. J. Dunn, R. Y. Moir, E. Buncel, J. G. Purdon and R. A. B. Bannard, *Can. J. Chem., 68* (1990) 1837; (e) M. J. Pregel, E. J. Dunn and E. Buncel, *Can. J. Chem., 68* (1990) 1846; (f) *J. Am. Chem. Soc.,* in press; (g) Ng. van Truong and E. Buncel, unpublished results; (h) E. Buncel, E. J. Dunn, Ng. van Truong, R. A. B. Bannard and J. G. Purdon, *Tetrahedron Lett., 31* (1990) 6513.

13 (a) C. J. Pedersen, *J. Am. Chem. Soc., 89* (1967) 7017; (b) R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, J. J. Christensen and D. Sen, *Chem. Rev., 85* (1985) 271; (c) J. D. Lamb, R. M. Izatt, C. S. Swain and J. J. Christensen, *J. Am. Chem. Soc., 102* (1980) 475; (d) G. Michaux and J. Reisse, *J. Am. Chem. Soc., 104* (1982) 6895; (e) L. Echegoyen, A. Kaifer, H. D. Durst and G. W. Gokel, *J. Org. Chem., 49* (1984) 688; (f) B. L. Haymore, J. D. Lamb, R. M. Izatt and J. J. Christensen, *Inorg. Chem., 21* (1982) 1598.

14 (a) G. W. Gokel, D. M. Goli, C. Minganti and L. Echegoyen, *J. Am. Chem. Soc., 105* (1983) 6786; (b) I. M. Kolthoff and M. K. Chantooni, Jr., *Anal. Chem., 52* (1980) 1039; (c) I. O. Sutherland, *Chem. Soc. Rev., 15* (1986) 63; (d) Y. Takeda, Y. Kudo and S. Fujiwara, *Bull. Chem. Soc. Jpn., 58* (1985) 1315.

15 (a) J.-M. Lehn, *Struct. Bonding (Berlin), 16* (1973) 1; *Acc. Chem. Res., 11* (1978) 49; (b) J.-M. Lehn and J. P. Sauvage, *J. Am. Chem. Soc., 97* (1975) 6700.

16 (a) B. G. Cox, J. Garcia-Rosas and H. Schneider, *J. Am. Chem. Soc., 103* (1981) 1384; (b) B. G. Cox, Ng. van Truong and H. Schneider, *J. Am. Chem. Soc., 106* (1984) 1273; (c)B. G. Cox, J. Garcia-Rosas, H. Schneider and Ng. van Truong, *Inorg. Chem., 25* (1986) 1165; (d)

M. H. Abraham and H. C. Ling, *J. Chem. Soc., Faraday Trans. I, 80* (1984) 3445; (e) A. F. D. de Namor and L. Ghousseini, *J. Chem. Soc., Faraday Trans. I, 80* (1980) 2843; *81* (1981) 781.

17 B. G. Cox, Ng. van Truong, J. Rzeszotarska and H. Schneider, *J. Chem. Soc., Faraday Trans. I, 80* (1984) 3275; (b) B. G. Cox, Ng. van Truong, J. Rzeszotarska and H. Schneider, *J. Am. Chem. Soc., 106* (1984) 5965; (c) W. Burgermeister and R. Winkler-Oswatitsch, *Top. Curr. Chem., 69* (1977) 91.

18 (a) F. Vögtle and E. Weber, *Angew. Chem., Int. Ed. Engl., 18* (1979) 753; (b) J. Grandjean, P. Laszlo, F. Vögtle and H. Sieger, *Angew. Chem., Int. Ed. Engl., 17* (1978) 856.

19 (a) D. K. Cabbiness and D. W. Margerum, *J. Am. Chem. Soc., 91* (1969) 6540; (b) H. F. Frensdorf, *J. Am. Chem. Soc., 93* (1971) 600; (c) C. J. Pederson and

H. F. Frensdorf, *Angew. Chem., Int. Ed. Engl., 11* (1972) 16; (d) N. O. Okoroafor and A. I. Popov, *Inorg. Chim. Acta, 148* (1988) 91.

20 M. Pinkerton and L. K. Steinrauf, *Mol. Biol., 49* (1970) 533.

21 (a) W. K. Lutz, H. K. Wipf and W. Simon, *Helv. Chim. Acta, 53* (1970) 1741; (b) W. L. Duax, G. D. Smith and P. D. Strong, *J. Am. Chem. Soc., 102* (1980) 6725.

22 B. G. Cox, Ng. van Truong, J. Garcia-Rosas and H. Schneider, *J. Phys. Chem., 88* (1984) 996.

23 R. M. Noyes, *J. Am. Chem. Soc., 84* (1962) 513.

24 G. R. Hedwig, D. A. Owensby and A. J. Parker, *J. Am. Chem. Soc., 97* (1975) 3888.

25 M. H. Abraham and Y. Marcus, *J. Chem. Soc., Faraday Trans. I, 82* (1986) 3255.