

Conductance Study of the Thermodynamics of Some Transition and Heavy Metal Complexes with Aza-18-crown-6 in Dimethylformamide Solution

¹MOJTABA SHAMSPUR* AND ²HAMID REZA POURETEDAL

¹Department of Chemistry, Razi University, Kermanshah, Iran

²Department of Chemistry, Shiraz University, Shiraz, Iran

(Received 6th April, 1998, revised 22nd August, 1998)

Summary: A conductance study of the interaction between Tl^+ , Ag^+ , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} ions and aza-18-crown-6 in dimethylformamide solution has been carried out at various temperatures. The formation constants of the resulting 1:1 complexes were determined from the molar conductance-mole ratio data and found to vary in the order $Tl^+ > Ag^+ > Pb^{2+} > Cd^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+}$. The enthalpy and entropy of complexation reactions were determined from the temperature dependence of the formation constants. In the case of all M^{2+} -A18C6 systems studied, the resulting complexes are both enthalpy and entropy stabilized. While, in the case of Ag^+ and Tl^+ ions, the resulting complexes with A18C6 are enthalpy stabilized but entropy destabilized.

Introduction

Since the first synthesis of crown ethers [1], the studies of these macrocyclic ligands and their metal ion complexes have become a very popular field of research [2-4], mainly due to their similarities in many respects to the naturally occurring ionophores [5,6]. The thermodynamics of complexation of crown ethers has been mainly studied with alkali and alkaline earth cations in water and in various nonaqueous solvents [3,4]. However, in comparison, the systematic investigation of the thermodynamics of transition and heavy metal ion complexes with macrocyclic ligands in various solvents has received much less attention.

There are at least four factors which can make significant contributions to the stability of the metal ion complexes with macrocyclic ligands: (1) the cavity size-cation diameter ratio (2) the nature and number of donating atoms participating in cation binding, (3) conformations of the free and complexed crown ethers and (4) the ionic solvation of the charged species involved. It has been clearly shown the substitution of some of the donating oxygen atoms of crown ether by -S- [7,8] and -NH- groups [9-11] drastically alters the complexing ability of the ligands toward different metal ions.

Since the first report on the facile synthesis of monoaza crown ethers [12], the syntheses and properties of their derivatives have been under

investigation [4,13,14]. The macrocycle aza-18-crown-6 (A18C6, I) was first used by Frensdorf [7] in the study of the effect of donor atoms of the macrocyclic ring on the stability of their complexes with metallic cations. Since then, however, there are only some limited reports on the complexation of Na^+ , K^+ and NH_4^+ ions in methanol solution [15-17].

We have recently involved in the thermodynamic study of the complexation of macrocyclic ligands with some metal cations and ammonium ion in nonaqueous and mixed solvent [18-22]. In this paper we report a conductance study of the thermodynamics of Ag^+ , Tl^+ , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} complexes with A18C6 in dimethylformamide (DMF) solution.

Results and Discussion

In order to evaluate the influence of adding A18C6 on the molar conductance of the cations used in DMF solution, the conductivity at a constant salt concentration (in the range 7.15×10^{-5} - $2.42 \times 10^{-4}M$) was monitored while increasing the macrocycle at four different temperatures. The resulting molar conductance vs. A18C6/cation mole ratio plots are shown in Figures 1-3. It is obvious that, with the exception of Ag^+ ion, addition of the macrocyclic ligand to the cation solution caused a rather large and continuous decrease in the molar conductance of the solutions, indicating the lower mobility of the

*To whom all correspondence should be addressed.

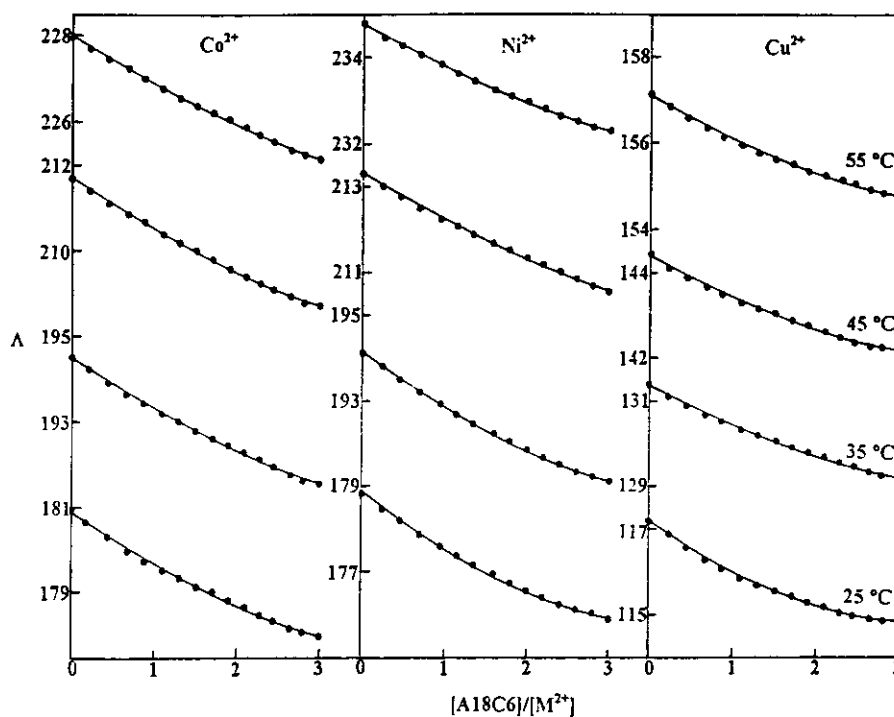


Fig. 1: Molar conductance ($\text{S cm}^2 \text{ mol}^{-1}$) vs. $[\text{A18C6}]/[\text{M}^{2+}]$ for Co^{2+} , Ni^{2+} and Cu^{2+} ions in DMF at various temperatures.

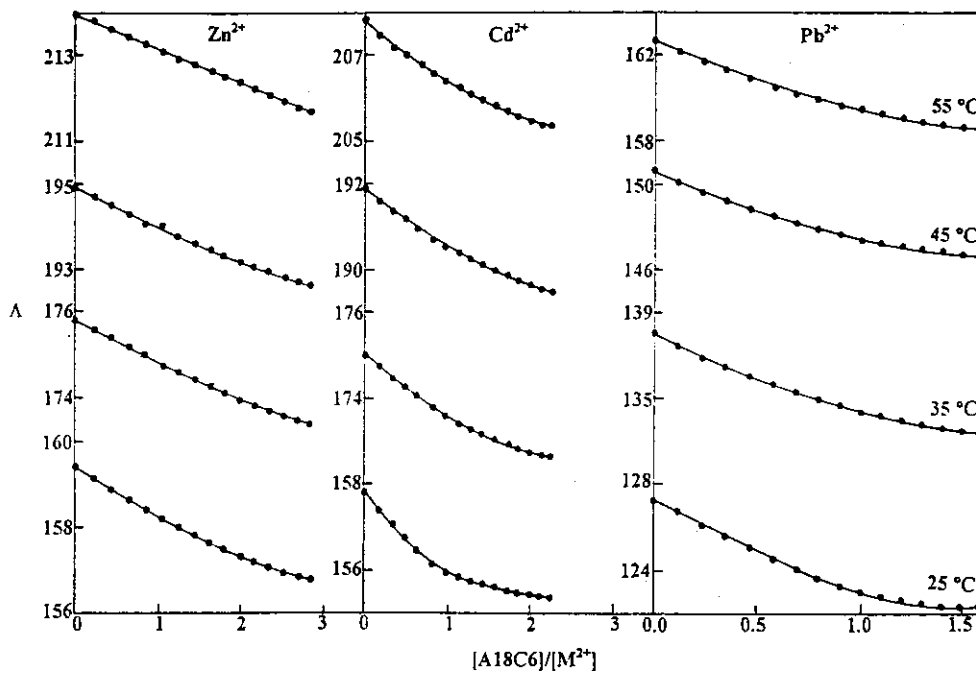


Fig. 2: Molar conductance ($\text{S cm}^2 \text{ mol}^{-1}$) vs. $[\text{A18C6}]/[\text{M}^{2+}]$ for Zn^{2+} , Cd^{2+} and Pb^{2+} ions in DMF at various temperatures.

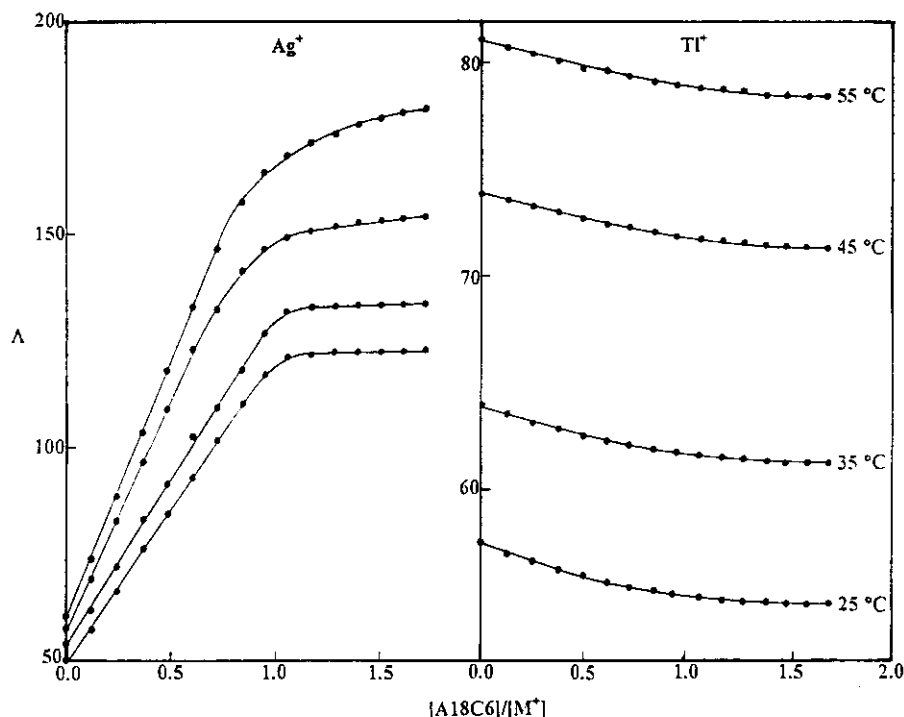


Fig. 3: Molar conductance ($\text{S cm}^2 \text{mol}^{-1}$) vs. $[\text{A18C6}]/[\text{M}^n]$ for Ag^+ and Tl^+ ions in DMF at various temperatures.

complexed cations compared to the free ones. However, in the case of Ag^+ ion, an opposite conductance behaviour is observed (Figure 3). This could be due to the lower mobility of the solvated cation and/or existence of some ion pairing in the initial salt, as it is pointed out elsewhere [23].

From Figures 1-3 it is seen that, in the case of Ag^+ , Tl^+ , Cd^{2+} and Pb^{2+} ions (and, especially, at lower temperatures), the slopes of the corresponding molar conductance-mole ratio plots change sharply at the point where the ligand to cation mole ratio is one, emphasizing the formation of relatively stable 1:1 complex between A18C6 and the cations used. However, in other cases, the relatively large decrease in molar conductance of the cations upon addition of the macrocyclic ligands does not show any tendency of leveling off even at mole ratios of about 3, indicating the formation of weaker complexes. It is noteworthy that, in all cases studied, an increase in temperature will result in expected increased molar conductance of solutions as well as the decreased curvature of the mole ratio plots at a mole ratio of about 1. This is indicative of the diminished stability of the resulting complexes at higher temperatures.

The 1:1 binding of the metal ions used with A18C6 can be expressed by the following equilibrium



The corresponding equilibrium constant, K_f , is given by

$$K_f = \frac{[\text{MA18C6}^{n+}] \times f(\text{MA18C6}^{n+})}{[\text{M}^{n+}][\text{A18C6}] f(\text{M}^{n+})f(\text{A18C6})} \quad (2)$$

where $[\text{MA18C6}^{n+}]$, $[\text{M}^{n+}]$, $[\text{A18C6}]$ and f represent the equilibrium molar concentrations of complex, free cation, free ligand and the activity coefficients of the species indicated, respectively. Under the highly dilute conditions we used, the activity coefficients of uncharged ligand, $f(\text{A18C6})$, can be reasonably assumed as unity [11,19,21-25]. The use of the Debye-Huckel limiting law [26] leads to the conclusion that $f(\text{M}^{n+}) \approx f(\text{MA18C6}^{n+})$, so the activity coefficients in equation (2) cancel. Thus the

complex formation constant in terms of the molar conductance can be expressed as [21-23,27,28].

$$K_f = \frac{[MA18C6^{n+}]}{[M^{n+}][A18C6]} = \frac{(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})[A18C6]} \quad (3)$$

where

$$[A18C6] = C_{A18C6} - \frac{C_M(\Lambda_M - \Lambda_{obs})}{(\Lambda_M - \Lambda_{ML})} \quad (4)$$

Here, Λ_M is the molar conductance of the metal nitrate before addition of A18C6, Λ_{obs} the molar conductance of solution during titration, Λ_{ML} the molar conductance of the complex, C_{A18C6} the analytical concentration of the macrocycle added and C_M the analytical concentration of the metal salt.

The complex formation constant, K_f , and the molar conductance of the complex, Λ_{ML} , were evaluated by computer fitting of equation (3) and (4) to the molar conductance-mole ratio data using a non-linear least-squares program KINFIT [29]. All the resulting values are summarized in Table-1. A sample computer fit of the resulting mole ratio data is also shown in Figure 4. The assumed 1:1 stoichiometry for the A18C6 complexes seems reasonable in the light of the fair agreement between the observed and calculated molar conductances.

In order to have a better understanding of the thermodynamics of the complexation reactions of the metal ions used with A18C6, it is useful to consider the enthalpic and entropic contributions to these reactions. The ΔH° and ΔS° values in DMF solution were determined by measuring the formation constants as a function of temperature. The formation constants of all M^{n+} -A18C6 complexes in DMF at various temperatures, obtained by computer fitting of the mole ratio data, are listed in Table-1. Plots of $\log K_f$ vs. $1/T$ for different M^{n+} -A18C6 were linear for all cases studied (Figure 5). The enthalpies and entropies of complexation were determined in the usual manner from the slopes and intercepts of the plots, respectively, and the results are also included in Table-1.

Comparison of the formation constants reported for Ni^{2+} -18C6 [30], Tl^+ -18C6 [11,31] and

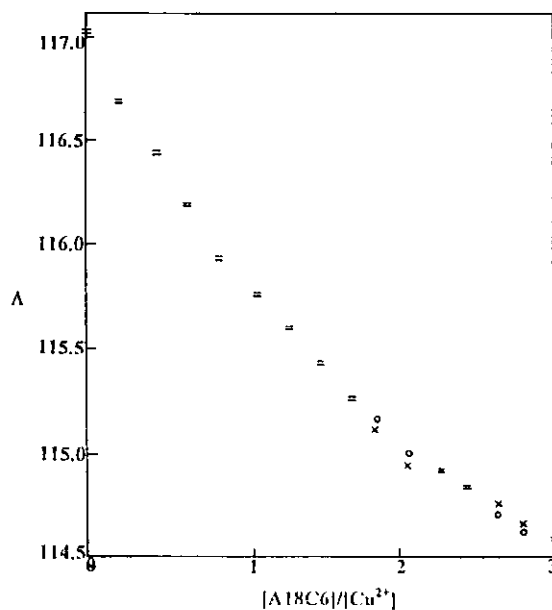


Fig. 4: Computer fit of molar conductance-mole ratio data for Cu^{2+} -A18C6 in DMF at $25^\circ C$ (x) experiment point (o) calculated point; (=) experimental and calculated points are the same within the resolution of the plot.

Ag^+ -18C6 [11] in DMF solution with those of the corresponding complexes with A18C6 obtained in this study (Table-1) reveals a considerable increase (one to three orders of magnitude) in the stability of the later complexes in DMF solution. It is well known that the substitution of some oxygen atoms of 18C6 by -NH-groups drastically decreases the formation constant of its alkali and alkaline earth complexes [3,4,10], while it may greatly enhance the stability of its transition and heavy metal complexes [3,4,32]. This is because the nitrogen atom of A18C6 ring, as a soft base, would interact more strongly with the transition and heavy metal ions used as soft or intermediate acids [33] than oxygen atoms, as hard bases.

As it is seen from the data given in Table-1, the stability of the resulting A18C6 complexes vary in the order $Tl^+ > Ag^+ > Pb^{2+} > Cd^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+}$. The sequence of the first transition series complexes with A18C6 (i.e. $Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$) follows the Irving-Williams order [34], which generally holds for the equilibrium constants of transition metals [22,32]. However, since the ionic size of Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} ions is too small for

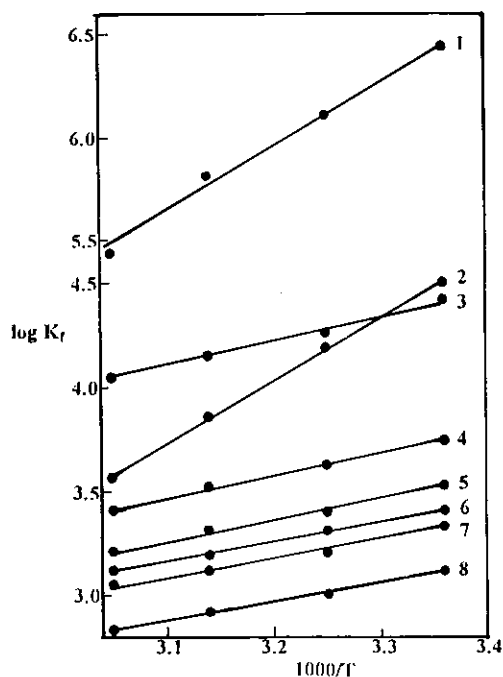
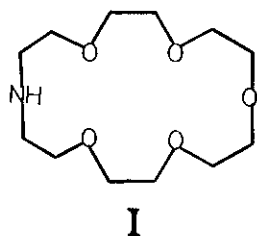


Fig. 5: Van't Hoff plots for different M^{n+} -A18C6 systems in DMF M^{n+} is 1, Ag^+ ; 2, Tl^+ ; 3, Pb^{2+} ; 4, Cd^{2+} ; 5, Cu^{2+} ; 6, Ni^{2+} ; 7, Co^{2+} ; 8, Zn^{2+} .

the cavity of 18C6 with a size of 2.6 - 3.2 Å [35], the resulting complexes are significantly weaker than those of the other cations used.

On the other hand, despite its single positive charge, Tl^+ ion with the ionic size of 3.0 Å [36] forms the most stable complex with A18C6 in the series, mainly because of the best fitting conditions of this cation inside the macrocyclic ligand's cavity. Based on the above argument, the greater stability of the A18C6 complexes with Pb^{2+} and Cd^{2+} ions over those of the first transition metal ions is not unexpected. It is also interesting to note that Ag^+ ion with about the same ionic size of Pb^{2+} ion [36] forms a much more stable complex with A18C6 than lead ion. This behavior is not only due to the larger soft character of Ag^+ [33], but also probably reflects the fact that this cation has a much lower charge density than Pb^{2+} ion, and therefore, it is rather weakly solvated by the solvent molecules. Thus, competition between the ligand and solvent molecules for the Pb^{2+} ion is stronger than that for the Ag^+ ion, which in turn, causes the weakening of the Pb^{2+} -A18C6 complex.

The thermodynamic data given in Table-1 reveal that, in the case of all A18C6- M^{2+} systems studied, the resulting 1:1 complexes are both enthalpy and entropy stabilized. Here, the desolvation of strongly solvated bivalent cations seems to be mainly responsible for the positive ΔS° values in DMF solution [1-3]. While, in the case of Ag^+ and Tl^+ ions, the resulting complexes are enthalpy stabilized but entropy destabilized. It should be noted that similar behaviour was previously observed for many crown ether complexes with different univalent cations in nonaqueous solutions [2-4]. It has been reasonably assumed that the decrease in entropy upon complexation is related to a change in the conformational entropy of the macrocyclic ligand, from a rather flexible structure in the free state to a rigid conformation in the

Table-1: Formation constants at various temperatures and enthalpy and entropy values for different transition and heavy metal ion complexes with A18C6 in DMF solution

Cation*	log K_f				$-\Delta H^\circ$ (kJ mole ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
	25°C	35°C	45°C	55°C		
Co^{2+} (1.50)	3.33 ± 0.08	3.30 ± 0.06	3.12 ± 0.05	3.05 ± 0.03	17 ± 1	6 ± 3
Ni^{2+} (1.38)	3.41 ± 0.07	3.32 ± 0.07	3.19 ± 0.05	3.12 ± 0.05	19 ± 1	3 ± 2
Cu^{2+} (1.54)	3.53 ± 0.09	3.40 ± 0.06	3.32 ± 0.07	3.31 ± 0.07	19.5 ± 0.8	2 ± 2
Zn^{2+} (1.48)	3.12 ± 0.06	3.00 ± 0.05	2.92 ± 0.05	2.84 ± 0.04	17.2 ± 0.7	2 ± 2
Cd^{2+} (1.90)	3.75 ± 0.06	3.63 ± 0.08	3.53 ± 0.06	3.41 ± 0.07	20.9 ± 0.5	1 ± 1
Pb^{2+} (2.38)	4.42 ± 0.09	4.24 ± 0.06	4.15 ± 0.07	4.05 ± 0.08	23 ± 2	9 ± 4
Ag^+ (2.30)	6.43 ± 0.10	6.11 ± 0.13	5.84 ± 0.13	5.42 ± 0.16	62 ± 2	-83 ± 8
Tl^+ (3.00)	4.49 ± 0.09	4.20 ± 0.08	3.86 ± 0.06	3.57 ± 0.09	58 ± 1	-108 ± 3

*The values in parentheses are the ionic sizes in Å [36].

complexes form [37]. The degree of macrocycle flexibility in the free state would vary with its size as well as the macrocycle-solvent interaction [38].

Experimental

Reagent grade nitrate salts of thallium, silver, cobalt, nickel, copper, zinc, cadmium and lead (Merck) were of the highest purity available and used without further purification except for vacuum drying over P₂O₅. DMF (Merck) was purified and dried by the previously reported method [39]. The conductivity of the solvent was less than $1.0 \times 10^{-7} \text{ S}^{-1} \text{ cm}^{-1}$. A18C6 (Merck) was recrystallized from reagent grade n-heptane and vacuum dried for 72 h.

Conducance measurements were carried out with a Metrohm 660 conductivity meter. A dip-type conductivity cell made of platinum black was used. The cell constant at the different temperatures used was determined by measuring the conductivity of a 0.010 M solution of analytical grade KCl (Merck) in triply distilled deionized water. The specific conductance of this solution at various temperatures have been reported in the literature [40]. In all measurements, the cell was thermostated at the desired temperature $\pm 0.03 \text{ }^\circ\text{C}$ using a Lo-Temprol 154 Precision Scientific thermostat.

In a typical experiment, 15 cm³ of the desired metal salt solution (7.15×10^{-5} - 2.43×10^{-4} M) was placed in the titration cell, thermostated to the desired temperature and the conductance of the solution was measured. Then, a known amount of the concentrated crown ether solution was added in a stepwise manner using a calibrated micropipette. The conductance of the solution was measured after each addition. Addition of the ligand solution was continued until the desired ligand to cation mole ratio was achieved.

References

1. C.J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017 (1967).
2. A.I. Popov and J.M. Lehn in "Coordination Chemistry of Macrocyclic Compounds", G.A. Melson, Ed., Plenum, New York (1979).
3. R.M. Izatt, J.S. Bradshaw, S.A. Nielsen, J.D. Lamb, J.J. Christensen and D. Sen, *Chem. Rev.*, **85**, 271 (1985).
4. R.M. Izatt, K. Pawlak, J.S. Bradshaw and R.L. Bruening, *Chem. Rev.*, **91**, 1721 (1991).
5. Yu. A. Ovchinnikov, V.T. Ivanov and A.M. Shkrob, "Membrane-Active Complexiones", Elsevier, Amsterdam (1974).
6. K.A. Rubinson, *J. Chem. Educ.*, **54**, 345 (1977).
7. H.K. Frensdorff, *J. Am. Chem. Soc.*, **93**, 600 (1971).
8. G. Rounaghi and A.I. Popov, *J. Inorg. Nucl. Chem.*, **43**, 911 (1981).
9. M. Shamsipur and A.I. Popov, *Inorg. Chim. Acta*, **43**, 243 (1980).
10. S. Kashanian and M. Shamsipur, *Inorg. Chim. Acta*, **155**, 203 (1989).
11. A. Jabbari, M. Hasani and M. Shamsipur, *J. Incl. Phenom.*, **15**, 329 (1993).
12. H. Maeda, Y. Nakatsuji and M. Okahara, *J. Chem. Soc. Chem. Commun.*, 471 (1981).
13. A. Masuyama, Y. Nakatsuji, I. Ikeda and M. Okahara, *Tetrahedron Lett.*, **22**, 4665 (1981).
14. H. Tsukube, *Talanta*, **40**, 1313 (1993).
15. R. Schultz, E. Schlegel, D.M. Dishong and G.W. Gokel, *J. Chem. Soc., Chem. Commun.*, 242 (1982).
16. W. Offerman and E. Weber, *Chem. Ber.*, **117**, 234 (1984).
17. R.A. Schultz, B.D. White, D.M. Dishong, K.A. Arnold and W.G. Gokel, *J. Am. Chem. Soc.*, **107**, 6659 (1985).
18. J. Ghasemi and M. Shamsipur, *J. Coord. Chem.*, **31**, 265 (1994).
19. M. Hasani and M. Shamsipur, *J. Solution Chem.*, **23**, 721 (1994).
20. H. Khajesharifi and M. Shamsipur, *J. Coord. Chem.*, **35**, 289 (1995).
21. M. Shamsipur and J. Ghasemi, *J. Incl. Phenom.*, **20**, 157 (1995).
22. J. Ghasemi and M. Shamsipur, *J. Solution Chem.*, **25**, 485 (1996).
23. M.K. Amini and M. Shamsipur, *Inorg. Chem. Acta*, **183**, 65 (1991).
24. A.J. Smetana and A.I. Popov, *J. Chem. Thermodyn.*, **11**, 1145 (1979).
25. K.M. Tawarah and S.A. Mizyed, *J. Solution Chem.*, **18**, 387 (1989).
26. P. Debye and H. Huckel, *Phys. Z.*, **24**, 305 (1928).
27. Y. Takeda, *Bull. Chem. Soc. Jpn.*, **56**, 3600 (1983).

28. D.P. Zollinger, E. Bulten, A. Christenhuse, M. Bos and W.E. van der Linden, *Anal. Chim. Acta*, **198**, 207 (1987).
29. V.A. Nicely and J.L. Dye, *J. Chem. Educ.*, **38**, 3443 (1971).
30. R.D. Boss and A.I. Popov, *Inorg. Chem.*, **24**, 3660 (1985).
31. E. Lada, S. Filipek and M.K. Kalinowski, *Aust. J. Chem.*, **41**, 437 (1988).
32. N. Alizadeh and M. Shamsipur, *Talanta*, **40**, 503 (1993).
33. R.G. Pearson, *J. Am. Chem. Soc.*, **84**, 3533 (1963).
34. H. Irving and R.J.P. Williams, *J. Chem. Soc.*, 3192 (1953).
35. C.J. Pedersen, *J. Am. Chem.Soc.*, **92**, 386 (1970).
36. R.D. Shannon, *Acta Crystallorg.*, **32A**, 751 (1976).
37. M. Shamsipur and A.I. Popov, *J. Am. Chem .Soc.*, **101**, 4051 (1979).
38. R.M. Izatt, J.S. Bradshaw, K. Pawlak, R.L. Bruening and B.J. Tarbet, *Chem. Rev.*, **92**, 1261 (1992).
39. M.S. Greenberg and A.I. Popov, *Spectrochim. Acta*, **31A**, 697 (1975).
40. H.J. Buschmann, *J. Incl. Phenom.*, **7**, 581 (1989).