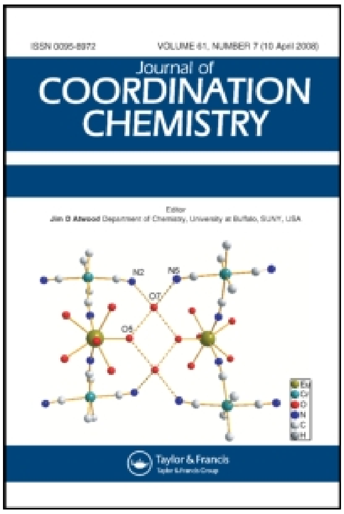


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

LITHIUM-7 NMR STUDY OF THE THERMODYNAMICS OF COMPLEXATION OF LI^{+} ION WITH TETRAETHYLENEGLYCOL-*BIS*-(8-QUINOLYL) ETHER IN NON-AQUEOUS SOLUTION

Madrakian Tayyebeh[a]; Zolgharnein Javad[b]; Shamsipur Mojtaba[b]
[a] Department of Chemistry, Bouali Sina University, Hamadan, Iran [b] Department of Chemistry, Razi University, Kermanshah, Iran

To cite this Article Tayyebeh, Madrakian , Javad, Zolgharnein and Mojtaba, Shamsipur(1996) 'LITHIUM-7 NMR STUDY OF THE THERMODYNAMICS OF COMPLEXATION OF LI^{+} ION WITH TETRAETHYLENEGLYCOL-*BIS*-(8-QUINOLYL) ETHER IN NON-AQUEOUS SOLUTION', Journal of Coordination Chemistry, 40: 1, 121 — 131

To link to this Article: DOI: 10.1080/00958979608022851

URL: http://dx.doi.org/10.1080/00958979608022851

J. Coord. Chem., 1996, Vol. 40, pp. 121–131
Reprints available directly from the publisher
Photocopying permitted by license only

LITHIUM-7 NMR STUDY OF THE THERMODYNAMICS OF COMPLEXATION OF LI$^+$ ION WITH TETRAETHYLENEGLYCOL-*BIS*-(8-QUINOLYL) ETHER IN NON-AQUEOUS SOLUTION

MADRAKIAN TAYYEBEH[a], ZOLGHARNEIN JAVAD[b] and
SHAMSIPUR MOJTABA[b,*]

[a]*Department of Chemistry, Bouali Sina University, Hamadan, Iran;*
[b]*Department of Chemistry, Razi University, Kermanshah, Iran*

(Received 8 March 1996; In final form 23 May 1996)

^{7}Li NMR measurements were used to study the stoichiometry and stability of Li$^+$ complexes with tetraethyleneglycol*bis*-(8-quinolyl)ether (TEGQ) in nitromethane, acetonitrile and their 1:1 (mol:mol) mixture. The resulting chemical shift-mol ratio data revealed the formation of both 1:1 and 2:1 (metal/ligand) complexes in solution. Formation of the two complexes was further supported by monitoring the molar conductance of $LiClO_4$ solutions as a function of TEGQ/Li$^+$ mol ratio. The stepwise formation constants of the 1:1 and 2:1 complexes were evaluated from the computer fitting of the mol ratio data to equations which relate observed ^{7}Li chemical shifts to formation constants. The enthalpy and entropy of complexation in all three solvent systems used were determined from the temperature dependence of the formation constants. Values of ΔH° and ΔS° were found to be solvent dependent. While the stabilities of both 1:1 and 2:1 complexes are of enthalpic origin in nitromethane, they become of entropic origin in acetonitrile solution.

Keywords: TEGQ; Li$^+$; complexes; formation constants; thermodynamics; ^{7}Li NMR

INTRODUCTION

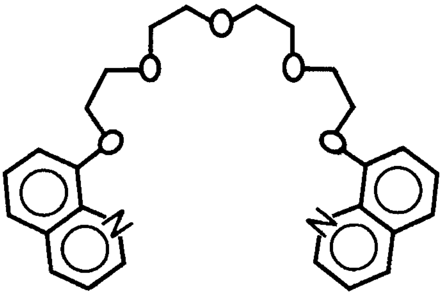
Since the first report on complexation of open-chain polyethylene glycols with alkali metal ions,[1] there has been a growing interest in the coordination chemistry of these ligands and their metal ion complexes.[2–9] This is due to the similarities of the ligands in many respects to synthetic and naturally occurring

---

[*] Author for correspondence.

polyether ionophores. However, much less thermodynamic data is available on the complexation of open chain polyethylene glycols, in comparison with those reported for macrocyclic crown ethers and cryptands in different solvent systems.[10–11]

In recent years we have employed nuclear magnetic resonance spectrometry as a very sensitive technique to investigate the thermodynamics and exchange kinetics and mechanism of a number of metal ion-macrocycle complexes in non-aqueous and mixed solvents.[12–18] In this paper we report the use of the lithium-7 NMR technique in nitromethane, acetonitrile and their 1:1 (mol:mol) mixture to investigate the thermodynamics of complexation of Li^+ ion with tetraethyleneglycol*bis*-(8-quinolyl)ether (TEGQ, I), a polyether molecule which resembles the noncyclic nigercin antibiotics with respect to molecular flexibility.[3,19]



I

EXPERIMENTAL

Reagent grade tetreaethyleneglycol*bis*-(8-quinolyl)ether (TEGQ, Fluka) was used without any further purification except for vacuum drying over P_2O_5 for 72 h. Lithium perchlorate (Merck) was purified and dried by a previously reported method.[20] Spectroscopic grade nitromethane (NM, Reidel) and acetonitrile (AN, Merck) were used as received.

All nuclear magnetic resonance measurements were carried out on a JEOL FX 90 Q FT-NMR Spectrometer with a field strength of 21.13 kG. At this field, lithium-7 resonates at 33.4 MHz. A 4.0 M aqueous LiCl solution was used as external reference and the reported ^7Li chemical shifts referred to this solution. Paramagnetic (down field) shift from the reference is designated as being positive. The concentration of all $LiClO_4$ solutions used was 5.0×10^{-3} M. Temperature of the probe was adjusted at the desired value ± 0.1°C with a temperature control unit using a sensitive heating element. To reach the equilibrium temperature, each sample tube was left in the probe for at least 10 min before measurements began.

Conductivity measurements were carried out with a Metrohm 712 conductometer. A dip-type conductivity cell with platinum black electrodes and with a cell constant of 0.8540 cm^{-1} was used. In all measurements the cell was thermostatted at 25.00 ± 0.05°C using a Haake D1 thermostat.

RESULTS AND DISCUSSION

^{7}Li chemical shifts were monitored as a function of TEGQ/Li^+ mol ratio at various temperatures in NM, AN and 1:1 NM-AN solutions. All resulting chemical shift-mol ratio data are summarized in Table I and sample plots of δ *vs* [TEGQ]/[Li^+] in pure NM and AN solutions at 27°C are shown in Figure 1. In all cases studied, only one population average resonance of Li^+ ion was observed, indicating that exchange of the metal ion between solvated and complexed sites is fast on the NMR time scale.

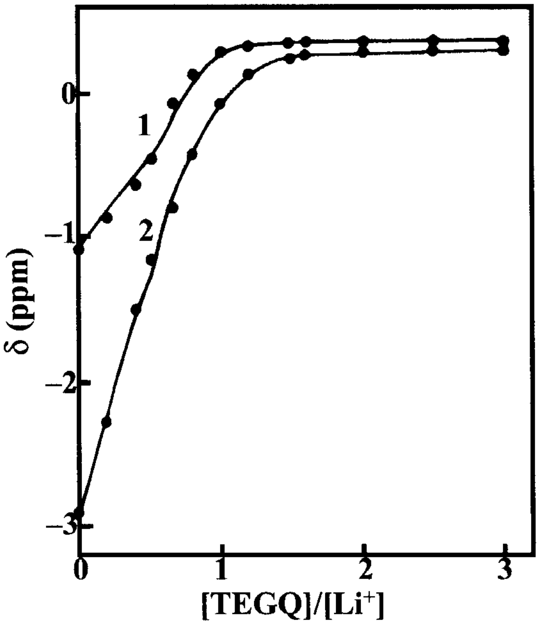


FIGURE 1 Lithium-7 chemical shift as a function of TEGQ/Li^+ mol ratio at 27°C in NM (1) and AN (2) solutions; solid lines are the calculated points and the filled circles are the experimental points.

TABLE I Lithium-7 chemical shift *vs* TEGQ/Li$^+$ mol ratio data in different non-aqueous solutions at various temperatures

[TEGQ]/[Li⁺]	*δ(ppm)*											
mole ratio[a]	*NM*				*NM-AN*				*AN*			
	27°C	*37°C*	*57°C*	*67°C*	*27°C*	*37°C*	*57°C*	*67°C*	*27°C*	*37°C*	*57°C*	*67°C*
0.00	−1.07	−1.17	−1.19	−1.23	−2.89	−2.89	−2.88	−2.85	−2.90	−2.90	−2.90	−2.90
0.20	−0.85	−0.88	−0.91	−0.93	−2.38	−2.39	−2.40	−2.39	−2.29	−2.31	−2.34	−2.37
0.40	−0.66	−0.67	−0.70	−0.72	−1.73	−1.74	−1.73	−1.73	−1.45	−1.48	−1.53	−1.57
0.50	−0.45	−0.46	−0.47	−0.48	−1.53	−1.53	−1.54	−1.54	−1.16	−1.21	−1.26	−1.30
0.65	−0.06	−0.05	0.00	−0.03	−0.92	−0.93	−0.93	−0.94	−0.79	−0.83	−0.90	−0.95
0.80	−0.02	−0.01	0.04	0.01	−0.61	−0.62	−0.62	−0.63	−0.43	−0.48	−0.57	−0.64
1.00	0.27	0.30	0.37	0.34	0.03	0.01	0.01	−0.04	−0.07	−0.14	−0.24	−0.33
1.20	0.33	0.35	0.43	0.41	0.19	0.18	0.15	0.13	0.10	0.05	−0.05	−0.13
1.50	0.35	0.37	0.44	0.41	0.22	0.23	0.23	0.22	0.21	0.17	0.10	0.04
1.60	0.36	0.37	0.44	0.41	—	—	—	—	0.22	0.18	0.11	0.06
2.00	0.37	0.44	0.44	0.41	0.27	0.28	0.29	0.28	0.26	0.22	0.18	0.14
2.50	0.36	0.38	0.45	0.42	0.28	0.29	0.30	0.29	0.28	0.26	0.24	0.20
3.00	0.36	0.38	0.45	0.42	0.28	0.29	0.30	0.30	0.29	0.27	0.25	0.22

[a] Concentration of $LiClO_4$ in all cases is 5.0×10^{-3} M.

As is obvious from Figure 1, the resulting shift *vs* mol ratio plots in NM and AN show two distinct inflection points at ligand/metal ion mol ratios of 0.5 and 1, indicating the formation of two complexes with the respective stoichiometries of TEGQ.2Li$^+$ and TEGQ.Li$^+$ in solution. Evidence for the formation such 1:1 and 2:1 (metal/ligand) adducts between TEGQ and Na$^+$, K$^+$ and Mg^{2+} in methanol solution involving absortion changes in the electronic spectra of the ligand have been reported in the literature.[3]

In order to get further information about TEGQ interactions with Li$^+$ ion in NM and AN solutions, we studied the molar conductance of metal ion solutions (1.0 × 10^{-4} M) as a function of the ligand concentration relative to the concentration of Li$^+$ ion. The resulting molar conductance *vs* TEGQ to lithium ion mol ratio plots in NM and AN solutions at 25°C are shown in Figure 2. Interestingly, both plots show two sharp inflection points at ligand to metal ion mol ratios of 0.5 and 1 a fact which strongly supports the NMR data. We have previously observed similar conductance behaviour for the formation of DA18C6.NH$_3^+$ and DA18C6.2NH$_3^+$,[21] as well as 18C6.H$_3$O$^+$ and 2(18C6).NH$_3^+$ in non-aqueous solution.[22–23]

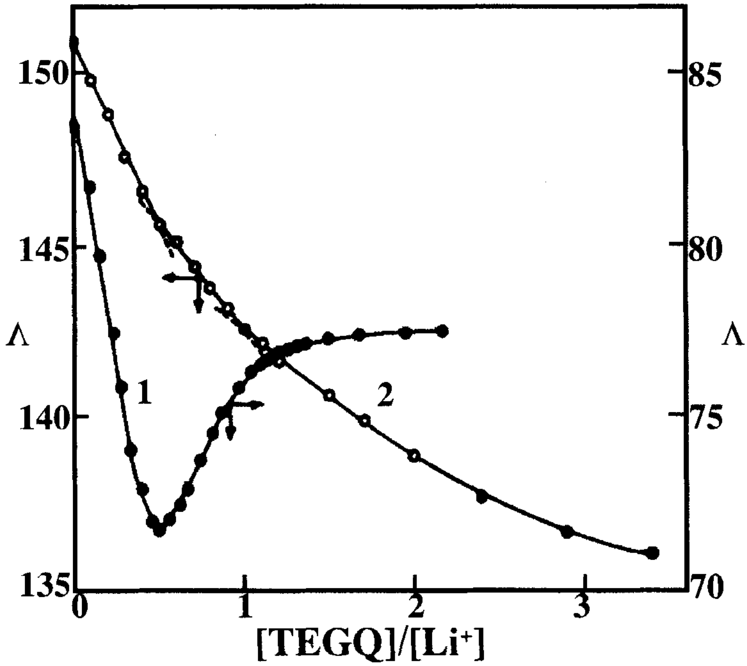


FIGURE 2 Molar conductance (S^{-1} cm^2 mol^{-1}) as a function of TEGQ/Li$^+$ mol ratio at 25°C in NM(1) and AN(2) solutions.

When both 1:1 and 2:1 (metal/ligand) complexes are formed, *i.e.*,

$$M + L = ML \qquad K_1 = [ML]/[ML][L] \qquad (1)$$

$$ML + M = M_2L \qquad K_2 = [M_2L]/[ML][M] \qquad (2)$$

(the charges are omitted for simplicity), the mass balance equations can be written as

$$C_M = [M] + [ML] + 2[M_2L] \qquad (3)$$

$$C_L = [L] + [ML] + [M_2L] \qquad (4)$$

where C_M and C_L are the analytical concentrations of the metal ion and ligand, respectively. Then, the mass balance equations can be solved to obtain an equation for the free metal ion concentration, [M], as in (*5*).

$$K_1K_2[M]^3 + [K_1K_2(2C_L - C_M) + K_1][M^2] + [1 + K_1(C_L - C_M)]$$

$$[M] - C_M = 0 \qquad (5)$$

The observed chemical shift of ^{7}Li is also given by

$$\delta_{obs} = [M]\delta_M/C_M + [ML]\delta_{ML}/C_M + [M_2L]\delta_{M2L}/C_M \qquad (6)$$

where δ_M, δ_{ML} and δ_{M2L} are the respective chemical shifts of the free, 1:1 complexed and 2:1 complexed lithium ion. For evaluation of the stepwise formation constants from the chemical shift-mol ratio data, a non-linear, least-squares curve fitting program, KINFIT, was used.[24] Adjustable parameters are the stepwise formation constants and the corresponding chemical shifts (*i.e.*, K_1, K_2, δ_{ML} and δ_{M2L}).

During the fitting process, the free metal ion concentration, [M], was calculated from equation (*5*) by means of a Newton-Raphson procedure. Once the value of [M] had been obtained, the concentrations of all other species involved were calculated from the mass balance equations (*3*) and (*4*), using estimated values of formation constants at the current iteration step of the program. Refinement of the parameters was continued until the sum-of-squares of the residual between the observed and calculated (from equation (*6*)) chemical shifts for all experimental points was minimized. The output of the program KINFIT comprises the refined parameters, the sum-of-squares and the standard deviation of the data. All the calculated stepwise formation constants are summarized in Table II. Our assumption of 1:1 and 2:1 stoichiometries for the resulting complexes seems reasonable in the light of fair agreement between the observed and calculated chemical shifts (see Figure 1).

In order to have a better understanding of the thermodynamics of complexation between TEGQ and Li^+ ion, it is useful to consider the enthalpic and entropic contributions to these reactions. The enthalpy and entropy of the complexation reactions were determined by measuring the stepwise formation constants of the resulting 1:1 and 2:1 complexes as a function of temperature (see Table II). The van't Hoff plots of log K *vs* 1/T for the 1:1 and 2:1 complexes in various non-aqueous solutions used were linear (Figure 3). ΔH° and ΔS° values were evaluated in the usual manner from the slopes and intercepts of the plots, respectively, and results are also included in Table II.

From the data given in Table II it is obvious that the nature of solvent plays an important role in complex formation. At all temperatures, complex stability decreases in the order NM > NM-AN > AN. It should be noted that, while NM and AN have about the same dielectric constants, their solvating abilities, as expressed by the Gutmann donor number,[25] are quite different (*i.e.*, $\varepsilon = 35.9$ and DN = 2.7 for NM and $\varepsilon = 36.1$ and DN = 14.1 for AN). It is well known that the donating ability of solvent plays a key role in different complexation reactions.[12–18, 20–23] AN as a solvent of higher solvating ability can compete more with TEGQ for Li^+ than can NM as a poor solvating solvent. Thus, it is not unexpected to have the most stable TEGQ-Li^+ complex in NM and the least stable in AN solution.

The thermodynamic data presented in Table II clearly illustrate the fact that the enthalpy and entropy changes obtained for both 1:1 and 2:1 complexes vary very significantly with the nature of non-aqueous solutions used. It is seen that, while the stabilities of both complex adducts are of enthalpic origin in NM and NM-AN mixture, they become of entropic origin in pure AN. This would be mainly due to

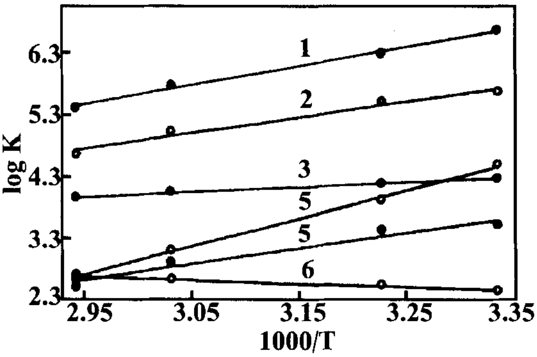


FIGURE 3 Van't Hoff plots for Li^+ ion complexes with TEGQ in different non-aqueous solutions; (1) log K, in NM, (2) log K_1 in NM-AN, (3) Log K_1 in AN, (4) log K_2 in NM, (5) log K_2 in NM-AN, (6) log K_2 in AN.

TABLE II Stepwise formation constants and enthalpy and entropy values for Li^+ complexes with TEGQ in various non-aqueous solutions[a]

Solvent	*Stoichiometry*	*log K*				ΔH^o	ΔS^o
		27°C	*37°C*	*57°C*	*67°C*	*(kJ/mol)*	*(J/molK)*
NM	1:1	6.65 ± 0.03	6.25 ± 0.02	5.76 ± 0.09	5.38 ± 0.06	-60 ± 2	-72 ± 7
	2:1	4.48 ± 0.03	3.91 ± 0.05	3.08 ± 0.08	2.14 ± 0.07	-88 ± 4	-207 ± 12
NM+AN	1:1	5.7 ± 0.1	5.49 ± 0.05	5.0 ± 0.4	4.6 ± 0.2	-49 ± 4	-55 ± 14
(50% by mol)	2:1	3.5 ± 01	3.4 ± 02	2.9 ± 0.3	2.5 ± 0.3	-50 ± 6	-96 ± 18
AN	1:1	4.3 ± 0.2	4.1 ± 0.2	4.0 ± 0.3	3.9 ± 0.3	-16 ± 1	30 ± 2
	2:1	2.45 ± 0.05	2.5 ± 0.5	2.6 ± 0.5	2.7 ± 0.5	10 ± 1	81 ± 2

[a] The errors associated with all thermodynamic parameters are given as ± SD.

the solvation-desolvation behaviour of the reactants and products as well as the change in flexibility of TEGQ brought about upon its complexation with Li^+ ion.

In NM, as a poorly solvating solvent, both 1:1 and 2:1 complexes are enthalpy stabilized but entropy destabilized. Very negative ΔH° values in this solvent emphasize the more comfortable stronger interactions between the weakly solvated cation and the free donating groups of the ligand. In this case, the positive contribution due to desolvation of the reactants in the entropy changes of the system is expected to be negligible. On the other hand, it seems reasonable to assume that the main reason for the negative entropy of complexation is the decrease in the conformational entropy of the ligand upon formation of a metal complex.[26–28] Large polyethers such as TEGQ should be rather flexible in the free state. The degree of flexibility would vary with the solvent, *i.e.*, with the extent of ligand-solvent interaction. Formation of a rigid complex with the cation should decrease the conformational entropy of the ligand and thus, possibly, give rise to a negative value.

On the other hand, in AN, as a relatively highly solvating solvent, ΔH° values become much more positive than those in NM at the expense of a considerable increase in ΔS° values. AN can not only strongly solvate the Li^+ ion, but also may have some considerable interaction with the ligand itself, such as that observed for the case of 18C6 in AN solution.[29] Thus, an unfavourable ΔH° value for the TEGQ- Li^+ system is not surprizing. Moreover, in this case, the positive contribution of both ligand and cation desolvation to the overall ΔS° of the system seems to be so high that it can overcome the negative contribution of conformational entropy of the ligand brought about upon complexation. Such a positive entropy values for the complexation of silver[30] and lead ions with TEGQ in methanol as a solvent of about the same order of solvating ability as AN[29] have already been reported in the literature.

It is interesting to note that, in NM-AN mixture, the thermodynamic behaviour of the Li^+-TEGQ system more resembles that in pure nitromethane, although the solvent components are present in 1:1 (mol/mol) composition. These results seem to be inconsistent with the preferential solvation of Li^+ ion with AN in the solvent mixture.[32] However, as was pointed out before, not only the cation and ligand desolvation contributes to the ΔS° value, but ligand conformational changes upon complexation may also have a very significant role in the thermodynamic behaviour of complexation. In a recent publication on the mechanism of complexation of Li^+ and Na^+ ions with tetraglyme in nitromethane, Petrucci and co-workers have clearly shown that they follow the Eigen-Winkler mechanism.[33]

$$M^+ + C \underset{k_0}{\overset{k_0}{=\!=\!=\!=\!=}} M....C^+ \underset{k_{-1}}{\overset{k_1}{=\!=\!=\!=\!=}} MC^+ \underset{k_{-2}}{\overset{k_1}{=\!=\!=\!=\!=}} (MC)^+$$

where M^+ is the solvated cation, C is the free solvated glyme and $M...C^+$, MC^+ and $(MC)^+$ are three different conformations of the complex. Based on ultrasonic relaxation data, they concluded that the initial rearrangement of the ligand is rate determining for faster processes, and the flexibility of tetraglyme affects both the fast process (through k_{-1}) and the slow process (through k_2). Consequently, overall values of the enthalpies and entropies of complexation are sums of contributions of several processes, all of which are influenced by the nature of solvent to some extent. Thus, it seems reasonable to assume that the observed thermodynamic behaviour of the Li^+-TEGQ system in NM + AN mixture is mainly related to the flexibility of TEGQ in its possible conformations, during the course of complexation. However, the TEGQ conformation in each step (and especially the ligand-solvent interaction) must be much better known before the nature of thermodynamic behaviour can be elucidated.

References

[1] L.L. Chen and J. Smid, *J. Am. Chem. Soc.*, **89**, 4547 (1967); *ibid*, **90**, 4654 (1968).
[2] U. Takaki and J. Smid, *J. Am. Chem. Soc.*, **96**, 2588 (1974).
[3] B. Tümmler, G. Maass, E. Weber, W. Wehner and F. Vögtle, *J. Am. Chem. Soc.*, **99**, 4683 (1977).
[4] B. Tümmber, G. Maass, F. Vögtle, H. Sieger, U. Heimann and E. Weber, *J. Am. Chem. Soc.*, **101**, 2588 (1979).
[5] H.J. Buschmann, *Inorg. Chim. Acta*, **108**, 241 (1985).
[6] Y. Hirashima, K. Kanetsuki, I. Yonezu, N. Isobe and J. Shiokawa, *Bull. Chem. Soc. Jpn.*, **59**, 25 (1986).
[7] H.J. Buschmann, *Inorg. Chim. Acta*, **118**, 77 (1986).
[8] E. Buncel, H.S. Shin, Ng. van Truong, R.A.B. Bannard and J.G. Purdon, *J. Phys. Chem.*, **92**, 4176 (1988).
[9] Ng. van Truong, A.R. Norris, H.S. Shin, E. Buncel, R.A.B. Bannard and J.G. Purdon, *Inorg. Chim. Acta*, **184**, 59 (1991).
[10] R.M. Izatt, J.S. Bradshaw, S.A. Nielsen, J.D. Lamb, J.J. Christensen and D. Sen, *Chem. Rev.*, **85**, 271 (1985).
[11] R.M. Izatt, K. Pawlak, J.S. Bradshaw and R.L. Bruening, *Chem. Rev.*, **91**, 1721 (1991).
[12] M. Shamsipur and A.I. Popov, *J. Phys. Chem.*, **92**, 147 (1988).
[13] M. Shamsipur and M.K. Amini, *Iran. J. Chem., Chem. Eng.*, **10**, 40 (1991).
[14] M.K. Amini and M. Shamsipur, *J. Phys. Chem.*, **95**, 9601 (1991).
[15] A. Rouhollahi, M.K. Amini and M. Shamsipur, *J. Solution Chem.*, **23**, 63 (1994).
[16] E. Karkhaneei, A. Afkhami and M. Shamsipur, *Polyhedron*, **15**, 1989 (1996).
[17] T. Madrakian, A. Afkhami, J. Ghasemi and M. Shamsipur, *Polyhedron*, in press.
[18] E. Karkhaneei, A. Afkhami, M. Shamsipur, *J. Coord. Chem.*, in press.
[19] W. Wehner and F. Vögtle, *Tetrahedron Lett.*, 2603 (1976).
[20] M. Shamsipur and A.I. Popov, *Inorg. Chim. Acta*, **43**, 243 (1980).
[21] M. Hasani and M. Shamsipur, *J. Inclus. Phenom.*, **16**, 123 (1993).
[22] M.K. Amini and M. Shamsipur, *J. Solution Chem.*, **21**, 275 (1992).
[23] M.K. Amini and M. Shamsipur, *Iran. J. Chem. Eng.*, **11**, 12 (1992).

[24] V.A. Nicely and J.L. Dye, *J. Chem. Educ.*, **49**, 443 (1971).
[25] V. Gutmann, The *Donor-Acceptor Approach to Molecular Interactions*. (Plenum, New York, 1978).
[26] M. Shamsipur, G. Rounaghi and A.I. Popov, *J. Solution Chem.*, **9**, 701 (1980).
[27] M. Shamsipur and J. Ghasemi, *J. Inclus. Phenom.*, **20**, 157 (1995).
[28] H. Khajesharifi and M. Shamsipur, *J. Coord. Chem.*, **35**, 289 (1995).
[29] J.A.A. DeBoer, D.M. Reinhoudt, S. Harkema, G.J. van Hummel and F. de Jong, *J. Am. Chem. Soc.*, **104**, 4073 (1982).
[30] H.J. Buschmann, *Inorg. Chim. Acta*, **102**, 95 (1985).
[31] H.J. Buschmann, *Inorg. Chim. Acta*, **198**, 43 (1985).
[32] Y. Marcus, *Ion Solvation*, (Wiley and Sons, Chichester, 1985).
[33] P. Firman, E.M. Eyring and S. Petrucci, *J. Phys. Chem.*, **98**, 147 (1994).