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Competitive Spectrophotometric Study of Complexation of Dibenzopyridino-18-crown-6 with Ca^{2+}, Sr^{2+}, and Ba^{2+} in Binary Dimethylsulphoxide–Acetonitrile Solutions

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The complexation of dibenzopyridino-18-crown-6 (DBPY18C6) with Ca^{2+}, Sr^{2+} and Ba^{2+} has been studied in binary dimethylsulphoxide – acetonitrile mixtures at 25°C by a competitive spectrophotometric technique, using murexide as a metal ion indicator. Stoichiometry and stability of the resulting complexes were evaluated by KINFIT program. The stability of 1:1 complexes prepared were found strongly solvent dependent. There is an inverse linear relationship between log K_f and mole fraction of dimethylsulphoxide (DMSO) in the solvent. In all these solvents the increase of %AN increases the stability of DBPY18C6 complexes with alkaline earth cations in the sequence $Ba^{2+} > Sr^{2+} > Ca^{2+}$.

Key words: alkaline earth cations, complexes, spectrophotometry, stability constant

The importance of some alkali and alkaline earth metal ions in life and some industrial processes is evident. In most cases, the role of a given cation is based on the selective complexation and then its transport through synthetic or natural membrane [1,2].

After synthesis and recognition of selectivity behavior of macrocyclic polyethers towards alkali metal ions [3,4], the synthesis and designing of new macrocyclic polyethers became interesting [5–7]. Among the new crowns are pyridino macrocyclic polyethers [7–9], in which the heterocyclic unit changes drastically the behavior of macrocycle towards alkali and alkaline earth metal ions [10–12]. These new compounds have developed the design of ligands for further analytical purposes [13]. One of these pyridino macrocyclic polyethers, *i.e.* dibenzopyridino-18-crown-6 (**I**), was rarely reported [5,6]. Recently, we have studied its chemical reaction in several areas, in which we have compared the behavior of this crown **I** with other 18-crown-6 series [14–17]. We also used this macrocyclic polyether as ion-carrier for Pb^{2+} selective transport through a bulk liquid membrane [18].

In recent years, a competitive spectrophotometric method has been developed [19–22] and used for studying of complexation reaction of colorless ligands [17,23–25]. Continuing our study of crown ether **I**, we studied the complexation re-

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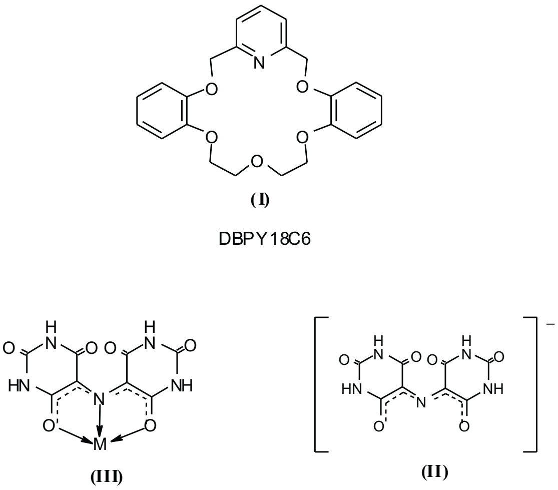
*Author to whom correspondence should be addressed. Fax: + 98- 861- 2770050; E-mail: J-Zolgharnein@araku.ac.ir action of dibenzopyridino-18-crown-6 with some alkaline earth metal ions by a competitive spectrophotometric method in binary dimethylsulphoxide-acetonitrile solution, using murexide as colored ligand. Due to low solubility of the ligand and low values of stability constants in DMSO, the mixed solvent (DMSO-AN) was applied in this work.

EXPERIMENTAL

Reagent grade nitrate salts of calcium, strontium, and barium, dibenzopyridino-18-crown-6 (DBPY18C6, **I**) and murexide (**II**, all from Merck) were of the highest purity available, and used without further purification except for vacuum drying over P_2O_5. Reagent grade dimethylsulphoxide, and acetonitrile (DMSO, AN, all from Merck) were used as received.

All spectra were recorded on a Cecil 3000 spectrophotometer, which was connected to a personal computer. In a typical experiment, 2 ml of murexide (3×10^{-5} M) in DMSO was placed in the spectrophotometer cell, thermostated at 25°C, then a known amount of the metal solution (5.0×10^{-3} M) was stepwise added using a calibrated microsyringe. The spectra of the solution were recorded after attainment of equilibrium. Addition of the metal ion solution was continued until the desired metal to murexide mole ratio was achieved. The same procedure was used when the formation of crown complexes was studied. So, in each experiment 2 ml solution of (3.0×10^{-5} M) of murexide, as colored ligand, and 240 μl of (1.0×10^{-2} M) crown were titrated with a concentrated metal ion solution (5.0×10^{-3} M).



(I)

DBPY18C6

(III) **(II)**

Figure 1. Chemical structure of ligands.

The formation constants of the 1:1 complexes of the metal ions used and murexide (Mu, as colored ligand) and DBPY18C6 (as buffer ligand) in binary AN-DMSO solution were determined by absorbance measurements at the λ_{max} of the metal ion-murexide complex. When an alkaline earth ion reacts with murexide and crown **I** to form 1:1 complexes, the corresponding formation constants can be written as

$$M + Mu \rightleftarrows MMu \qquad K_{MMu} = [MMu]/[M][Mu] \qquad (1)$$

$$M + crown \rightleftarrows Mcrown \qquad K_{Mcrown} = [Mcrown]/[M][crown] \qquad (2)$$

(charges are omitted for simplicity). Mass balance equations and the observed absorbance, A_{obs}, are given as

$$C_{Mu} = [Mu] + [MMu] \quad (3) \qquad C_{crown} = [crown] + [Mcrown] \quad (4)$$

$$C_M = [M] + [MMu] + [Mcrown] \quad (5) \qquad A_{obs} = \varepsilon_{Mu}[Mu] + \varepsilon_{MMu}[MMu] \quad (6)$$

where C and ε are the analytical concentration and molar absorptivity of the species indicated, respectively. The mass balance equations can be solved in order to obtain an equation for the free metal ion concentration [M], as follows:

$$K_{MMu}K_{Mcrown}[M]^3 + \{K_{MMu}K_{Mcrown}(C_M - C_{Mu} - C_{crown}) - K_{MMu} - K_{Mcrown}\}[M]^2 - \{K_{Mcrown}(C_M - C_{crown}) + \\ + K_{MMu}(C_{Mu} - C_M) - 1\}[M] - C_M = 0 \quad (7)$$

For evaluation of the formation constants from the absorbance *vs*. C_M/C_{Mu} mole ratios, a non-linear least-squares curve fitting KINFIT program was used [26]. The program is based on the iterative adjustment of calculated values of absorbance to observed values by using either the Wentworth matrix technique [27] or the Powell procedure [28]. Adjustable parameters are the formation constants K_{MMu} and K_{Mcrown} and the molar absorptivities ε_{Mu} and ε_{MMu}. The free metal ion concentration was calculated from (7) by a Newton-Raphson procedure [29]. Once the value of [M] had been obtained, the concentrations of all other species involved were calculated from the mass balance equations (3–5), using the estimated values of the formation constants and molar absorptivities at the current iteration step of the program. Refinement of the parameters was continued until the sum-of-squares of the residuals between the calculated and observed values of absorbance for all experimental points was minimized. The output of the program KINFIT comprises refined parameters, the sum-of-squares and the standard deviation of the data.

RESULTS AND DISCUSSION

Murexide, the ammonium salt of purpuric acid (5-[hexahydroxy-2,4,6-trioxo-5-pyrimidinyl) imino]-2,4,6-(1H,3H,5H) pyrimidinetrione, monoammonium salt, **II**, Figure 1) has been used for many years as a suitable complexing agent for a large number of metal ions over a wide range of experimental conditions [30–32]. The absorption spectra of murexide in various solvent mixtures (AN-DMSO) upon titration with increasing amount of the different metal ions, used in the absence and in the presence of DBPY18C6, were obtained. The absorption spectra of 3.0×10^{-5} M murexide and its complexes with Ca^{2+}, Sr^{2+}, and Ba^{2+} ions in 10% (w/w) AN-DMSO solution are shown in Figure 2. The spectral behavior of the murexide complexes is quite unique in all binary mixtures used. It consists of a large shift (30–70 nm) of maximum towards shorter wavelengths, in comparison to free murexide. The reasons for such strong and ion-specific blue shifts are discussed elsewhere [33]. It is well known, that murexide forms a 1:1 complex with alkali and alkaline earth cations in nonaqueous media [34–36]. Formation of 1:1 complexes of murexide with Ca^{2+}, Sr^{2+}, and Ba^{2+} ions in different AN-DMSO was further confirmed by well-defined isosbestic point in the corresponding murexide spectra during the titration with metal ions and also by excellent computer fitting of the resulting absorbance-mole ratio data to the 1:1 metal ion-murexide stoichiometry. The visible spectra of Sr^{2+}-DBPY18C6 in the presence of the murexide in 10% AN-DMSO solution are shown in Figure 3. Absorbance *vs*. mole ratio plots is also shown in Fig. 4.

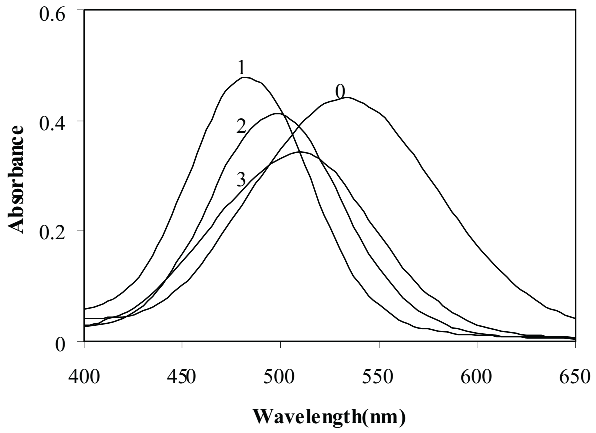


Figure 2. Visible spectra for complexation of 3×10^{-5} M murexide (0), with Ca^{2+} (1), Sr^{2+} (2), and Ba^{2+} (3) in 10% AN-DMSO solution.

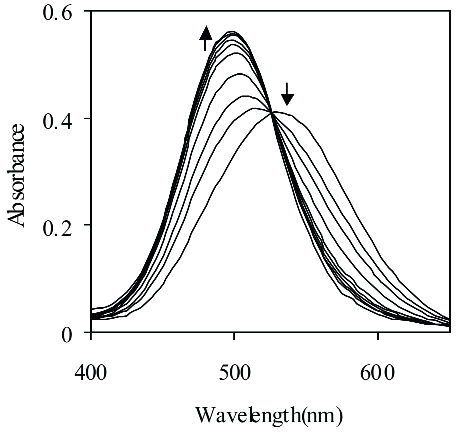


Figure 3. Visible spectra for complexation of 1.07×10^{-3} M DBPY18C6 and 3×10^{-5} M murexide with gradual addition of 5×10^{-3} M Sr^{2+} in 10% AN-DMSO at 25°C.

The resulting data (Table 1) show that the sequence of stability of the murexide complexes with the alkaline earth cations in DMSO and other mixed solvents (DMSO-AN) follows the effective ionic radii sequence [37]. However, among these metal ions the Ca-purpurate complex has the highest stability in DMSO and in its mixture with AN. This is probably due to the proper size of Ca^{2+} ion, which could favor a suitable fit with the donating atoms of the murexide (bridging nitrogen atom and neighboring oxygen atoms **II, III**, Figure 1) [33,38]. Therefore, the stability of murexide complexes varies in the order $Ca^{2+} > Sr^{2+} > Ba^{2+}$, for reasons discussed elsewhere [34–36]. The formation constants obtained for the murexide-Sr^{2+} complexes in mixed AN-DMSO solvent is in a fair agreement with that reported in literature. These results are also shown in Table 1 [39].

Table 1. Logarithm of stability constants (Log K_f $\pm\sigma$*) for resulting complexes of murexide and dibenzopyridino-18-crown-6 with some alkaline earth cations in various mixture solvents at 25°C.

Ligand	Ion	Log K_f $\pm\sigma$			
		0%	10%	25%	40% AN(w/w)
Murexide	Ca^{2+} (1.00 Å)^a	4.10±0.01	4.27±0.01	4.57±0.01	4.81±0.01
	Sr^{2+} (1.18 Å)^a	3.83±0.01	4.10±0.01	4.43±0.01	4.53±0.01
	Ba^{2+} (1.33 Å)^a	3.68±0.01	3.90±0.01	4.16±0.01	4.19±0.01
	Sr$^{2+\,b}$	3.83±0.02	3.92±0.01	4.17±0.02	4.31±0.02
DBPY18C6	Ca^{2+} (1.00 Å)^a	1.98±0.01	2.30±0.01	2.70±0.01	3.23±0.01
	Sr^{2+} (1.18 Å)^a	2.86±0.01	3.01±0.01	3.15±0.01	3.41±0.01
	Ba^{2+} (1.33 Å)^a	2.93±0.01	3.37±0.01	3.81±0.01	3.94±0.01

*: Standard deviation, a: ref. [37], b: ref. [39].

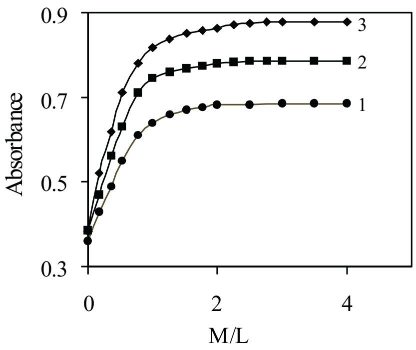


Figure 4. Absorbance *vs*. mole-ratio plots for complexation of 1.07×10^{-3} M DBPY18C6 (L) and 3×10^{-5} M murexide with (M); Ca^{2+} (1, λ_{max} = 480 nm), Sr^{2+} (2, λ_{max} = 500 nm), and Ba^{2+} (3, λ_{max} = 515 nm) in 40% AN-DMSO at 25°C.

As seen in Table 1, the stability of the Ca^{2+}, Sr^{2+}, and Ba^{2+} ions complexes with DBPY18C6 in the solvents used decreases in the order Ba^{2+} > Sr^{2+} > Ca^{2+}. Barium ion with an ionic radius of 1.35 Å [37] nicely fits inside the cavities of DBPY18C6 with radii of 1.3–1.6 Å [40]. Other cations with smaller ionic sizes are too loose for the cavities of this ligand, resulting in weaker complexes. On the other hand, the presence of three aromatic moieties in this macrocycle substantially reduced the affinity of the donor atoms towards the metal ion. Introducing the pyridyl unit into the 18-ring decreases both the flexibility and the affinity of the macrocycle to alkaline earth metal ions [10–12]. The pyridino nitrogen, as a "soft" base, is not able to interact strongly with "hard" alkaline earth cations. But among the alkaline earth metal ions, the Ba^{2+} is relatively softer than others, thus, due to HSAB (hard and soft acid and base) principle the stronger interaction between crown **I** and Ba^{2+} is expected [41,42]. Therefore, relatively moderate stability constants for complexation of DBPY18C6 with other alkaline metal ions are observed. Recently, we have compared the chemical behaviors of crown **I** in a series of 18-crown-6 complexation reaction with alkaline earth cations in methanol by competitive potentiometric method and we have shown that the stability constants varied in the order DCY18C6 > 18C6 > DB18C6 > DBPY18C6 (logarithm of stability constant of DBPY18C6 with: Ca^{2+} = 3.04±0.03, Sr^{2+} = 4.03 ±0.02, Ba^{2+} = 4.64±0.01) [16]. We also compared the complexation reaction of DBPY18C6 with other 18-crown-6 toward lanthanide(III) ions by competitive spectrophotometric method in DMSO solution and have shown that the sequence of resulted complexes varies as 18C6 > DCY18C6 > DB18C6 > DBPY18C6 (logarithm of stability constant of DBPY18C6 with: La^{3+} = 1.94 ±0.01, Ce^{3+} = 1.89 ±0.01, Pr^{3+} = 1.68 ±0.01, and Er^{3+} = 1.62±0.01) [17].

However, it should be noted that the thermodynamic stability constants are not just a measure of the absolute strength of the complexes, an idea from "ion-in-the-hole" model [5], but they are a measure of the relative strength, as compared to the ionic solvation. Thus, it is only for the weakly solvated larger ions (such as Ba^{2+}), that the cation size can be considered primarily responsible for the complexing characteristics. In the case of smaller cations, like Ca^{2+} ion, the cation is relatively stronger solvated and considerably more energy must be expended in the desolvation step than for the larger cations. Contributions of the cation-solvent, complex-solvent, and even ligand-solvent interactions on the stability of the resulting complexes cannot be ignored [43].

Hence, dimethylsulfoxide as the solvent removes difficulties associated with metal ion hydrolysis, but some restrictions, such as low solubility of this crown ether and low stability constants of the resulted complexes in DMSO forced us to choose a mixed AN-DMSO solvent. Mixed solvents are interesting, because a solvent with quite different properties may result, both physically (dielectric constant, density, and viscosity) and chemically (acid-base and donor – acceptor properties). By mixing solvents of different polarity in proper ratios, the dielectric constant of the medium, and at the same time the solvating power can be varied [44]. From Table 1, it is immediately obvious that the using of mixed solvents has a very important effect on the stability of resulting complexes. In all cases, the stability of the resulting complexes for both murexide and DBPY18C6 increases with increasing weight percent of AN in the mixed solvent. It is well known, that the Gutmann donating ability of solvent [45] plays a key role in different complexation reactions [23–25,34–36]. DMSO is a solvent with a high solvating ability (DN = 29.8), which can strongly compete with murexide and crown ether for metal ions. Thus, it is not surprising that addition of AN, as a relatively low donor solvent (DN = 14.1) to DMSO, increases the stability of both murexide and crown ether complexes. It should be noted that the somewhat lower dielectric constant of AN ($\varepsilon = 38.0$) in comparison with that of DMSO ($\varepsilon = 45.0$) would cause an increase of electrostatic contribution to the bond formation with increasing amount of AN in the solvent mixture.

It is interesting to note that there exists a linear relationship between logs K of the murexide and crown complexes and the mole fraction of acetonitrile (X_{AN}) in the mixed solvent (Figs 5 and 6). It is reasonably to assume, that the preferential solva-

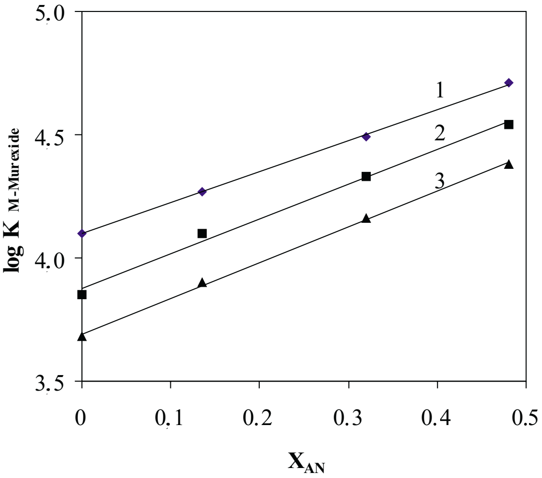


Figure 5. Log K *vs*. X_{AN} plots for complexation of murexide with: Ca^{2+} (1), Sr^{2+} (2), and Ba^{2+} (3), at 25°C.

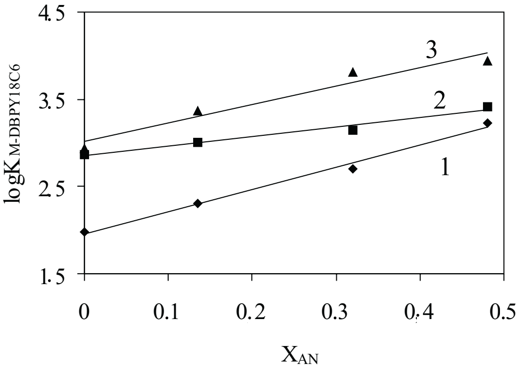


Figure 6. Log K *vs*. X_{AN} plots for complexation of DBPY18C6: Ca^{2+} (1), Sr^{2+} (2), and Ba^{2+} (3), at 25°C.

tion of the cations by DMSO is mainly responsible for such a monotonic dependence of stability constants of resulted complexes on the solvent composition.

This paper shows that the main factors responsible for specifity and affinity of complexation reaction of DBPY18C6 with alkaline metal ions are: substituted pyridyl unit in 18 membered ring, the size of cations (type of interaction) and solvating power of mixed solvents.

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REFRENCES

1. Fraustoda Silva J.J.R. and Williams R.J.P., *Struct. Bonding (Berlin)*, **29**, 67 (1970).
2. Dietrich B., *J. Chem. Educ.*, **62**, 954 (1985).
3. Pedersen C.J., *J. Am. Chem. Soc.*, **89**, 7017 (1967).
4. Lehn J.M., *Struct. Bonding*, **16**, 1 (1973).
5. Izatt R.M., Bradshaw J.S., Nielsen S.A., Lamb J.D. and Christensen J.J., *Chem. Rev.*, **85**, 271 (1985).
6. Izatt R.M., Pawlak K., Bradshaw J.S. and Bruening R.L., *Chem. Rev.*, **91**, 1721 (1991).
7. Hancock R.D. and Martell A.E., *Chem. Rev.*, **89**, 1875 (1989).
8. Newcomb M., Gokel G.W. and Cram D.J., *J. Am. Chem. Soc.*, **96**, 6810 (1974).
9. Newcomb M., Timko J.M., Walba D.M. and Cram D.J., *J. Am. Chem. Soc.*, **99**, 6392 (1977).
10. Staveren C.J. van., Aarts V.M.L.J., Grootenhuis P.D.J., Droppers J. van Edren, Harkema S. and Reinhoudt D.N., *J. Am. Chem. Soc.*, **110**, 8134 (1988).
11. Lamb J.D., Izatt R.M., Swain C.S. and Christensen J.J., *J. Am. Chem. Soc.*, **102**, 475 (1980).
12. Zhang X.X., Bordunov A.V., Kou X., Dalley N.K. and Izatt R.M., *J. Am. Chem. Soc.*, **36**, 2586 (1997).
13. Zoltov Yu.A., Macrocyclic Compound in Analytical Chemistry, Wiley & Sons Inc, NY, 1997.
14. Zolgharnein J. and Shamsipur M., *Polish J. Chem.*, **72**, 248 (1998).
15. Shamsipur M. and Zolgharnein J., *J. Incl. Phenom.*, **40**, 41 (2001).
16. Zolgharnein J., Tahmasebi H., Habibi M. and Amain S., *J. Incl. Phenom.*, submitted.
17. Zolgharnein J., Riahhi F. and Amani S., *J. Incl. Phenom.*, (in press) (2003).
18. Zolgharnein J., Hossini S., Sangi M.R., Dadfarnia S. and Shamsipur M., *Chem. Anal. (Warsaw)*, **48**, (in press) (2002).
19. Loyola V.M., Pizer R. and Wilkins R.G., *J. Am. Chem. Soc.*, **99**, 7183 (1997).
20. Ohyoshi E., *Anal. Chem.*, **57**, 446 (1985).
21. Gholivand M.B., Kashanian S. and Shamsipur M., *Polyhedron*, **6**, 535 (1987).
22. Colston B.J. and Robinson V.J., *Analyst*, **122**, 1451 (1997).
23. Shamsipur M. and Alizadeh N., *Talanta*, **40**, 503 (1993).
24. Ghasemi J. and Shamsipur M., *J. Coord. Chem.*, **31**, 265 (1994).
25. Khajesharifi H. and Shamsipur M., *J. Coord. Chem.*, **35**, 289 (1995).
26. Nicely V.A. and Dye J.L., *J. Chem. Educ.*, **48**, 443 (1971).
27. Wentworth W.E., *J. Chem. Educ.*, **42**, 96 (1962).
28. Powel M.J.D., *Comput.*, **7**, 155 (1964).
29. Legget D.J., Computational Methods for the Determination of Formation Constants., Plenum Press, NY, 1985.
30. Schwarzenbach G. and Gysling H., *Helv. Chim. Acta*, **32**, 1314 (1949).
31. Geier G., *Helv. Chim., Acta*, **50**, 1879 (1967).
32. Hulanicki A., Glab S. and Ackermann G., *Pure Appl. Chem.*, **55**, 1137 (1983).
33. Diebler H., Eigen M., Ilegenfritz G., Maass G. and Winkeler R., *Pure Appl. Chem.*, **51**, 94 (1968).
34. Kashanian S., Gholivand M.B., Madaaeni S., Nikrahi A. and Shamsipur M., *Polyhedron.*, **7**, 1227 (1988).
35. Shamsipur M., Madanei S. and Kashanian S., *Talanta*, **36**, 773 (1989).
36. Shamsipur M. and Alizadeh N., *Talanta*, **39**, 1209 (1992).
37. Shannon D., *Acta Cryst.*, **32**, 751 (1976).
38. Shannon D. and Prewitt C.T., *Acta Cryst.*, **B26**, 1076 (1970).
39. Azimi G. and Shamsipur M., *J. Coord. Chem.*, **47(4)**, 581 (1998).
40. Frensdorff H.K., *J. Am. Chem. Soc.*, **93**, 600 (1971).
41. Pearson R.G., *J. Am. Chem. Soc.*, **85**, 3533 (1963).
42. Pearson R.G., *Inorg. Chem.*, **27**, 734 (1988).
43. Gutmann V., Coordination Chemistry in Nonaqueous Solvents, Springer-Verlag, Vienna, 1968.
44. Baggesgaard-Rasmussen H., *Z. Analyt. Chem.*, **105**, 269 (1936).
45. Gutmann V., The Donor-Acceptor to Molecular Interactions, Plenum, NY, 1978.