Iranian Int. J. Sci. ***2****(2) 2001*

Thermodynamic Study of a Thiophen Derived Schiff's Base and Its Complexes with Some Transition and Heavy Metal Ions in Acetonitrile Solution

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(received: 24/2/2001; accepted:18/4/2001)

Abstract

A conductance study of the interaction between Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} and Hg^{2+} ions with thiophen derived schiff's base in acetonitrile solution has been carried out at different temperatures. Formation constants of the resulting 1:1 complexes were determined from the molar conductance – mole ratio data and found to vary in the sequence $Pb^{2+} > Hg^{2+} > Cd^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+}$.

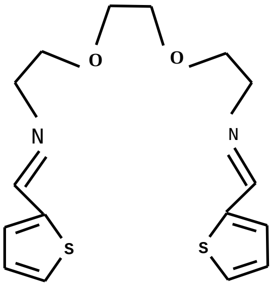
The enthalpy and entropy of complexation were determined from the temperature dependence of the formation constant. In all cases, the complexes were found to be enthalpy stabilized but entropy destabilized.

Keywords: *complexes, schiff's base, thermodynamic, conductometry, transition metal ions.*

Introduction

The polydentate schiff's base ligands are known to form very stable complexes with transition and heavy metal ions (Jones, *et al.*, 1979; Tajmir-Riahi, 1983; Arena, *et al.*, 1986; Calligaris, *et al.*, 1987; Martell, & Sawyer,1988; Atwood, 1997). The resulting complexes have attracted increasing attention, mainly due to their peculiar properties (Tajmir-Riahi, 1983; Arena, *et al.*, 1986; Calligaris, *et al.*, 1987; Atwood, 1997). Schiff's base complexes of transition metals have been frequently used as catalysis in such diverse processes as oxygen –and atom-transfer(Rihter, *et al.,* 1993), enantioselective epoxidation (Zhang, *et al.,* 1990) and aziridation (Li, *et al,.* 1993), mediating organic redox reactions (Fry,1993) and as mediators in other oxidation processes (Aurangzeh, *et al.,*1992). Despite extensive scientific reports on the synthesis, characterization and crystalline structure of the transition metal-schiff's base complexes (Jones, *et al.,* 1979; Tajmir-Riahi, 1983; Arena, *et al.,* 1986; Calligaris, *et al.,* 1987; Martell, & Sawyer,1988; Atwood, 1997; Rihter, *et al.,* 1993; Zhang, *et al.,* 1990; Li, *et al,.* 1993; Fry,1993; Aurangzeh, *et al.,*1992) To the best of our knowledge, there is no report on the values of K_f, ? H^0 and ?oS^0 for the complexation of recently synthesized (Hashemi, *et al.,* 2000) ethaneamine 2,2@?*ethylene bis(oxy)]N,N?*-bis(2-thienyl methylene) (L) and transition and heavy metal ions in acetonitrile solution.

We have recently reported the successful use of this schiff's base (L) as an excellent neutral complexing agent in solid phase extraction and determination of ultra-trace amounts of Pb^{2+} by octadecyl silica membrane disks (Hashemi, *et al.,* 2000). In this paper we report a conductance of Co^{2+},Ni^{2+}, Cu^{2+},Zn^{2+}, Hg^{2+}, Pb^{2+} and Cd^{2+} complexes with the schiff's base (L), in acetonitrile at different temperatures in order to investigate the stoichiometry, stability, selectivity and thermodynamic parameters ?|H^0 and ?|S^0 of the resulting complexes in solution.



(L)

Experimental

Reagents: Reagent grade $Co(NO_3)_2$ $6H_2O$, $Ni(NO_3)_2$ $6H_2O$, $Cu(NO_3)_2$

$3H_2O$, $Zn(NO_3)_2$ $4H_2O$, $Cd(NO_3)_2$ 4H2O, $Pb(NO_3)_2$ and $Hg(NO_3)_2$ $2H_2O$ were of the highest purity available and used without further purification except for vacuum drying over P_2O_5. Reagent grade acetonitrile (AN, Merck) was purified and dried by the previously reported method (Greenberg & Popov, 1975). The conductivity of the solvent was $<1.0\times10^{-7}$ S^{-1} cm^{-1}. Thiophen-2-carbaldehyde and 1,3-diamine-3,6-dioxaoctane were purchased from Fluka. Schiff's base (L) was synthesized and purified as described elsewhere (Hashemi, *et al.*, 2000).

Apparatus: Conductivity measurements were carried out with a Metrohm 660 conductivity meter. A dip-type conductivity cell, made of platinum black, with a cell constant of 0.8300 cm^{-1} was used. In all measurements, the cell was thermostated at the desired temperature $\pm0.05^0C$ using a Phywe immersion thermostat.

Procedure: In a typical run, 15 cm^3 of a metal nitrate solution($1.0\times10^{-5}M$) was placed in a water-jacketed cell equipped with a magnetic stirrer and connect to the thermostat circulating water at the desired temperature. In order to keep the electrolyte concentration constant during the titration, both the starting solution and the titrant had the same metal ion concentration. Conductance of the initial solution was measured after thermal equilibrium had been reached. Then, a known amount of the ligand solution was added in stepwise manner using a calibrated micropipette. The conductance of the solution was measured after each addition. Addition of the ligand was continued until the desired ligand-to-cation mole ratio was achieved.

Results

In order to evaluate the influence of adding (L) on the molar conductance of the metal ions used in AN solution, the conductivity at a constant salt concentration($1.0\times10^{-5}M$) was monitored while increasing the L concentration at different temperatures. The resulting molar conductance vs. L/cation mole ratio plots at 10 and 35^0C are shown in Figures 1 and 2, respectively. From Figures 1 and 2 it is seen that, in all cases studied, addition of the L to the metal ion solution caused a rather large and continuous decreased in the molar conductance of the solution, indicating that the complexed metal ions are less mobile than the corresponding solvated M^{2+} ions.

As can be seen from Figures 1 and 2, in the case of Hg^{2+}, Pb^{2+} and Cd^{2+} ions addition of L to metal ion solution in AN causes a continuous linear decrease in molar conductance which begins to level off at a mole ratio of *ca*. unity indicating, the formation of relatively stable 1:1 complexes, at all temperature studied. However, in other cases, and especially at higher temperatures, although the molar conductance does not show and tendency for leveling off even at a mole ratio of 3, the corresponding mole ratio plots show a considerable change in their slopes at a mole ratio of *ca*. unity, emphasizing the formation of some weaker 1:1 complexes.

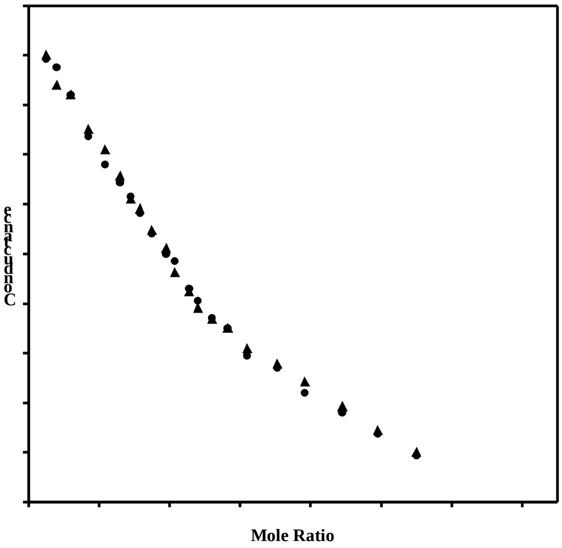


Figure 1. Computer fit of molar conductance (?^{a1}cm^{2} mol^{-1})-mole ratio data for metal ions (M^{n+})-thiophen Derived Schiff's Base in acetonitrile at 25$^{?}$C (?)Experimentalpoin; (?y) calculated point.

By comparison of the molar conductance – mole ratio plots for all L-M^{2+} systems obtained at different temperatures (Figs. 2.and 3), two trends are observed which deserve attention. First, as is expected, the corresponding molar conductances increased rapidly with temperature, owing to the decreased viscosity of the solvent and, consequently, the enhanced mobility of the charged species present. Secondly, for each cation used, the curvature of the corresponding mole ratio plot decreases with increasing temperature, indicating the formation of weaker complexes at high temperatures.

The 1:1 binding of transition and heavy metal ions (M^+) with (L), can be expressed by the following equilibrium:

$$M^+ + L \underset{}{\overset{K_f}{\rightleftarrows}} ML^+ \qquad (1)$$

The corresponding equilibrium constant, $K_{f,}$ is given by

$$K_f = \frac{ML^+]}{[M^+][L]} \times \frac{f(ML^+)}{f(M^+)\, f(L)} \qquad (2)$$

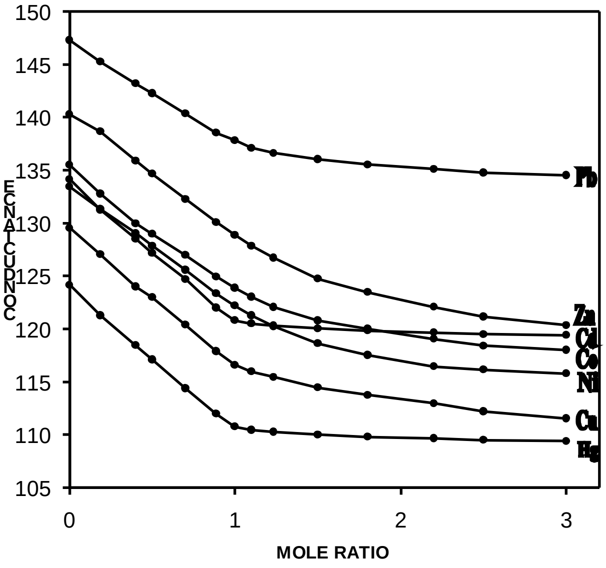


Figure 2. Molar conductance (?$^{\sim1}$cm^2 mol^{-1}) vs [L] / [metal ions] curves in acetonitrile solution at 10 ^{0}C

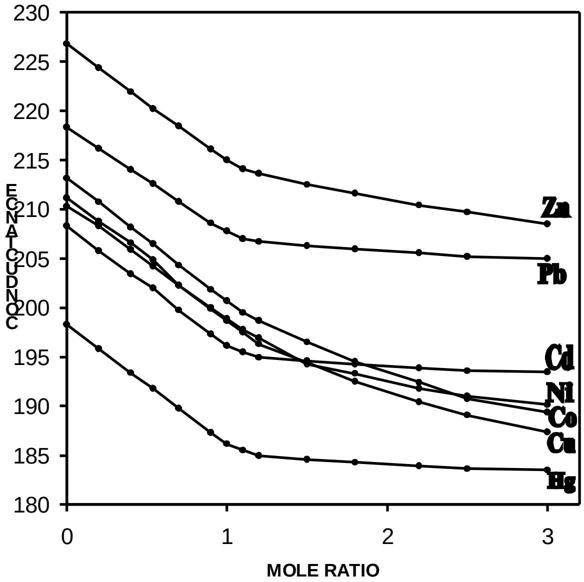


Figure 3. Molar conductance (?V^{-1}cm^{2} mol^{-1}) vs [L] / [metal ions] curves in acetonitrile solution at 35 ^{0}C.

Where $[ML^+]$, $[M^+]$, $[L]$ and f represent the equilibrium molar concentration of complexes, free cation, free ligand and the activity coefficient of the species indicated, respectively.

Under the dilute condition we used, the activity coefficient of the unchanged ligand, f(L) can be reasonably assumed as unity (Ganjali, *et al.*, 1996). The use of Deby-Hückel limiting law (Rouhollahi, *et al.*, 1999; Deby & Huckel, 1928) lead to the conclusion that $f(M^+)$?0 $f(ML^+)$, so the activity coefficients in equation (2) cancel. Thus the complex formation constant in term of the molar conductance can be expressed as (Takeda, 1983; Zollinger *et al.*, 1987).

$$K_f = \frac{[ML^+]}{[M^+][L]} = \frac{(?\tilde{A}_{M} - ?\ddagger_{obs})}{(?\text{þ}_{obs} - ?\ddagger_{ML})[L]} \qquad (3)$$

where

$$[L] = C_L - \frac{C_M\,(?\hat{a}_{M} - ?\ddagger_{obs})}{(?_{M} - ?\ddagger_{ML})} \qquad (4)$$

Here, $?_{M}$ is the molar conductance of the metal ion before addition of ligand, $?\neg_{ML}$ the molar conductance of the complexed ion, $?\neg_{obs}$ the molar conductance of the solution during titration, C_L the analytical concentration of the L added, and C_M the analytical concentration of the salt. The complex formation constant, K_f and the molar conductance of complex, $?\text{ç}_{ML}$, were obtained by computer fitting of equations (3) and (4) to the molar conductance-mole ratio data using a non-linear least-squares program KINFIT (Nicely & Dye, 1971). A simple computer fit of the resulting mole ratio data is shown in Figure1.

The assumed 1:1 stoichiometry for the resulting complexes was further supported by the fair agreement between the observed and calculated molar conductances in the process of computer fitting of the mole ratio data. It should be noted that, in acetonitrile as a solvent of intermediate donor number (DN=14.1) and dielectric constant (?≭38.0) (Gutmann, 1987), it was assumed that the association to ion pairs is negligible under the highly dilute experimental conditions used (Janz & Tomkins, 1972; Hassani & Shamsipur, 1994). The ligand (L) concentration in solution was also sufficiently low ($< 1.4\times10^{-4}$ mol dm^{-3}) to avoid corrections for viscosity changes. All calculated formation constants are summarized in Table 1. Of note, it was found that, at different total analytes concentrations (in the range 1.0×10^{-4}-1.0×10^{-5} mole dm^{-3}), the K_f values obtained for a given L-M^{2+} system are essentially the same within their experimental error, once again supporting the existence of negligible ion-pairing of the metal nitrate used in AN solution.

Comparison of the formation constants given in Table1 revealed that the stability of the ligand (L) varies in the sequence $Pb^{2+} > Hg^{2+} > Cd^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+}$.

It is known that both the relative size of the cations to the cavity of (L) and the hard-soft acid-base character of the cations and the donating sites of the ligand are among the most important parameters affecting the stability of cation-(L) complexes (Smetana, & Popov, 1979; Takeda, 1983; Pedersen,1967; Pedersen, 1970).

Initial estimates of geometry of structures were obtained by the MMX molecular mechanics method implemented in PCMODEL software (Serena). Full minimization was done by using the semi empirical AM (Dewar *et al.*, 1985) Hamiltonian available in Mopac 6.0 (Dewar) computer program. All structures were characterized as stationary points and true minima on the potential energy surface by using the FORCE keyword.

Table 1. Formation constants for different M^{2+}-L complexes

Cations	**$LogK_f$**			
	$10^{0}C$	***$15^{0}C$***	***$25^{0}C$***	***$35^{0}C$***
Pb^{2+}(1.19Å)	6.16±0.05	5.80±0.06	5.41±0.05	5.11±0.06
Hg^{2+}(1.19Å)	5.90±0.04	5.61±0.05	5.27±0.05	5.01±0.05
Cd^{2+}(0.95Å)	5.88±0.05	5.57±0.05	5.22±0.04	4.97±0.03
Cu^{2+}(0.77Å)	4.58±0.03	4.37±0.02	4.13±0.04	3.93±0.04
Co^{2+}(0.75Å)	4.42±0.06	4.23±0.06	4.05±0.03	3.86±0.03
Ni^{2+}(0.69Å)	4.39±0.03	4.20±0.05	4.03±0.02	3.85±0.02
Zn^{2+}(0.74Å)	3.90±0.04	3.59±0.03	3.30±0.04	3.02±0.06

The cavity size of the ligand (L) was determined by using this program. The most stable structure for ligand (lower energetic level) showed a cavity size of about 4.0 Å (which is close to the size of 18C6). This acyclic hexadentate bis-schiff's base contains six donor atoms from which two are hard base, two soft and two intermediate, these mix donor atom provide flexibility, in acid – base behavior, to the ligand. The first row transition metal ions Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} are all small for the cavity of ligand (L) and, moreover, they have brodeline acid character according to the HSAB principle of Pearson (Hancock & Martell, 1996; Pearson, 1963). Thus their L-complexes are considerably weaker than those with the heavy metal ions used. It is interesting that the stability sequence of the first transition series complexes with (L) (i.e. $Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+}$) nicely follows the

Irving Williams order [37], which generally holds for the equilibrium constants of the transition metals (Alizadeh & Shamsipur, 1993; Ghasemi & Shamsipur, 1995; Ghasemi & Shamsipur, 1980).

On the other hand, both Pb^{2+} and Hg^{2+} ions, with the same ionic radius (Izatt *et al.,* 1986), seem to have the best size to fit well inside the cavity of the ligand used (Izatt *et al.,* 1986; Pedersen, 1970). However, the Pb^{2+} ion forms a more stable complex than does the Hg^{2+} ion, obviously due to its less softer acid character than the mercury ion (Hancock & Martell, 1996; Pearson, 1963). The Cd^{2+} ion possesses a softer acid character than does the Pb^{2+} ion, and therefore stability of its 1:1 complexe with ligand (L) is lower than of ligand-$Pb^{2+.}$

In order to have a better understanding of the thermodynamics of complexation reactions discussed, it is useful to consider the enthalpic and the entropic contributions to these reactions. The ?^{1}H^0 and ?^{1}S^0 values for the complexation reaction were evaluated from the corresponding logK_f- temperature data by applying a linear least – squares analysis according to the Van't Hoff equation. Plot of logK_f vs I/T for different L- M^{2+} systems were linear for all cases studied (Figure 4).

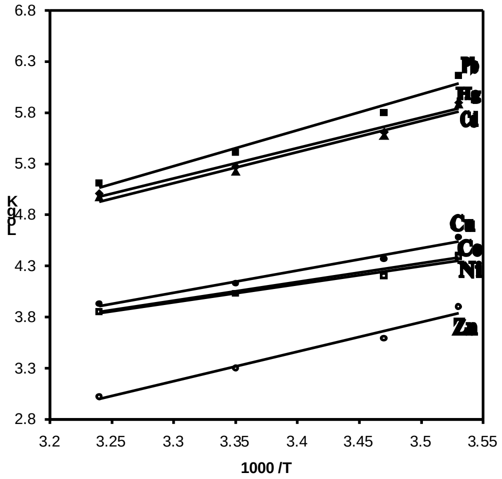


Figure 4. Log K_f vs.1000/T for different metal ions / (L) complexes in acetonitrile solution

The enthalpies and entropies of complexation were determined in the usual manner from the slope and intercepts of the plots and the results are summarized in Table2.. It is noteworthy that the validity of ?S^0 and, especially, ?H^0 values was checked by using the modified Van’tHoff equation suggested by Hepler (Hepler, 1981) in which the correct calculation of ?H^0 and ?C_p^0 and ?V^0 from temperature dependence of equilibrium constants is presented. The ?G^0 Values, calculated from ?G^0=-RTlnK_f at 25^{0}C are also included in Table 2. It should be noted that, to the best of our knowledge, there are no published values of $K_{f,}$?H^0 and ?S^0 for the complexation of L available to be able to compare with the results obtained here.

From the data given in Table2, it is readily obvious that all L-M^{2+} complexes formed in AN solution are enthalpy stabilized but entropy destabilized. It should be noted that others and we previously observed similar behavior, in both aqueous and non-aqueous solutions (Zollinger *et al.*, 1987; Hassani & Shamsipur, 1994; Izatt *et al.*, 1985; Lamb *et al.*, 1980; Ghasemi & Shamsipur, 1980; Hepler, 1981; Kaufman *et al.*, 1981; Shamsipur & Popov, 1979).

Table 2. Enthalpy, Entropy and ?G values for different M^{2+}-L complexation reaction.

Cations	**?H^0**	**?S^0**	**?G^0**
Pb^{2+}	70.46	133.35	30.72
Hg^{2+}	60.39	102.45	29.85
Cd^{2+}	61.12	105.58	29.65
Cu^{2+}	43.53	67.97	23.36
Co^{2+}	39.51	55.00	23.01
Ni^{2+}	35.66	43.50	22.70
Zn^{2+}	58.31	132.88	18.71

In aqueous solutions, it was assumed that the decrease in entropy was largely due to the rearrangement of water structure upon the metastasis of a small inorganic cation into a large hydrophobic organic cations (Kaufman *et al.*, 1981). While this explanation is quit feasible for aqueous solutions, it cannot be carried out over to the much less structured organic solvent used in this investigation. It seems reasonable to assume that the main reason for the negative entropy of complexation is the decreased in the conformational entropy of the schiff's base brought about upon complexation from a rather flexible free state to a relative structured rigid complex (Zollinger *et al.*, 1987; Ghasemi & Shamsipur, 1995; Cooper & Rawle, 1991; Alberto *et al.*, 1996). Thus, it is not surprising to observed that the Pb^{2+} ion with best fitting condition for the cavity of L will resulting the most negative ?ŒH^{0} and ?ŒS^{0} values in the series.

Reference

Alberto, R., Nef, W., Smith, A., Kaden, T.A., Neuburger, M., Zehnder, M., Frey, A., Abram, U., Augest, O., Schubiger, P., (1996) Inorg. Chem., **35**, 3420.

Alizadeh, N., Shamsipur, M., (1993) Talanta, **40**, 503.

Arena, F., Floriani, C., Chiesi-Villa, A., Gausstini, C., (1986) Inorg. Chem., **25**, 4589.

Atwood, D.A., (1997) Coord. Chem. Rev., **65**, 256.

Aurangzeh, M., Hume, C.E., McAuliffe, C.A., Richard, R.C.,Watkinson, A., Gareia-Deibe., Bermejo M.R., Sousa A., (1992) J. Chem. Soc. Chem. Commun., 1524.

Blake, A.J., Schrder, M., (1990) Adv. Inorg. Chem., **1**, 35.

Calligaris, M., Randaccio, R., In: Wilkinson, G. Gillard, R.D., (1987) McCleverty(eds) Comprehensive Coordination Chemistry, Oxford. London, Vol. **l2**, Chap. 20.

Cooper, S.R., Rawle, S.C., (1991) Struct. Bonding (Berlin), **72**.

Deby, P. and Huckel, H., (1928) Phys. Z., **24**, 305.

Dewar, M. J.S., Zeobish, E.G., Healy, E.F., and Stewart, J.J.P., (1985) J. Am. Chem. Soc., **107**, 3902.

Frendsdorff, H.K., (1971) J.Am.Chem.Soc., **93**, 600.

Fry, A. J., Fry, F.F., (1993) J. Org. Chem., **58**, 3496.

Ganjali, M. R., Rouhollahi, A., Moghimi, A., Shamsipur, M., (1996) Polish J. Chem., **70**, 1172.

Ghasemi, J. and Shamsipur, M., (1980) J. Solution Chem., **7**, 701.

Ghasemi, J. and Shamsipur, M., (1995) J. Coord. Chem., **36**, 183.

Greenberg, M.S., Popov, A.I., (1975) Spectrochim. Acta, **31a**, 697.

Gutmann, V., (1987). *The Donor-Acceptor Approach to Molecular Interaction*, Plenum Press, New York.

Hancock, R.D., Martell A.E., (1996) J. Chem. Educ, **73**, 654.

Hashemi, O.R., Raoufi, F., Ganjali, M.R., Moghimi, A., Kargar- Razi, M., and Shamsipur, M., (2000) Anal. Sci., In the press.

Hassani, M. and Shamsipur, M., (1994) J. Solution Chem., **23**, 721.

Hepler, L.G., (1981) Thermochim. Acta, **50**, 69.

Irving, H., Williams, R.J.P., (1953) J. Chem. Soc., 3192.

Izatt, R.M., Bradshaw, J.S., Nielsen, S.A., Lamb, J.D., Christensen, J.J., (1986) Sep. Purif. Methods, **15**, 21.

Izatt, R.M., Bradshaw, J.S., Nielsen, S.A., Lamb, J.D., Christensen, J.J. and Sen, D., (1985) Chem. Rev., **85**, 271.

Janz, G.J. and Tomkins R.P.T., (1972) *Nonaqueous Electrolytes Handbook*, Vol 1, Academic Press, New York.

Jones, R.D., Summerville, D.A., Basolo, F., (1979) Chem Rev., **79**, 139.

Kaufman, J., Lehn, J. M., Saurage, J.P, (1981) Helv. Chim. Acta, **59**, 1099.

Lamb, J.D., Izatt, R.M, Swain C.S., Christensen J.J., (1980) J.Am.Chem.Soc, **102**, 475.

Li, Z., Conser, K.R., Jacobsen, E.N., (1993) J.Am.Chem.Soc., **115**, 5326.

Martell, A.E., Sawyer, O.T., (1988) *Oxygen complexes and oxygen Activation by Transition Metals*. Plenum Press, New york.

Nicely, V.A. and Dye, J.I., (1971) J. Chem. Educ., **48**, 443.

Pearson, R.G., (1963) J. Am. Chem. Soc., **85**, 3533.

Pedersen, C.J., J. Am. Chem. Soc., (1967) **89**, 7017.

Pedersen, C.J., (1970) J. Am. Chem. Soc., **92**, 386.

Rihter, B., Srittari, S., Hunter, S., Masnovi, J., (1993) J.Am. Chem. Soc.,**115**, 3918.

Rouhollahi, A., Ganjali, M. R., Moghimi, A., Buchanan, G. W., and Shamsipur, M., (1999) J. Incl. Phenom., **33**, 361.

Rounaghi, G., Popov, A.I., (1981) J.Inorg.Nucl.Chem., **43**, 911.

Serena Software, BOX 3076, Bloomington, IN.

Shamsipur, M. and Popov, A.I., (1979) J. Am. Chem. Soc., **101**, 405.

Smetana, A.J. and Popov, A.I., (1979) J. Chem. Thermodyn., **11**, 1145.

Stewart, J.J.P., QCPE 581, Department of Chemistry, Indiana University, Bloomington, IN.

Tajmir-Riahi, H.A., (1983) Polyhedron, **3**, 723.
Takeda, Y., (1983) Bullten. Chem. Soc.Jpn., **56**, 3600.
Tawarah, K.M. and Mizyed, S.A., (1989) J. Solution Chem., **18**, 387.
Zhang, W., Loehach, J.L., Wilson, S.R., Jacobsen, E.N., (1990) J. Am. Chem. Soc., **112**, 2801.
Zollinger, D.P., Bult. E., Christenhuse, A., Bos, M. and Vander Linden, W.E., (1987) Anal. Chim. Acta, **198**, 207.