



## Spectrophotometric Study of Complex Formation Between Iodine and Some Thiacycrown Ethers in Chloroform Solution

MOJTABA SHAMSIPUR\* and MOHAMMAD HOSSEIN MASHHADIZADEH  
*Department of Chemistry, Razi University, Kermanshah, Iran*

(Received 7 September 1999; in final form: 22 November 1999)

**Abstract.** Formation of the charge-transfer complexes between hexathia-18-crown-6, pentathia-15-crown-5, tetrathia-12-crown-4 and iodine in chloroform solution was investigated spectrophotometrically. The molar absorptivities and formation constants of the resulting 1 : 1 molecular complexes were determined. The stability of the iodine complexes increased with the increasing number of donating sulfur atoms in the crown ether ring. The enthalpy and entropy of complexation were determined from the temperature dependence of the formation constants. All molecular complexes formed were enthalpy stabilized, but entropy destabilized. From the thermodynamic data obtained, the  $T\Delta S^\circ - \Delta H^\circ$  plot shows a fairly good linear correlation, which indicates enthalpy-entropy compensation in the reactions.

**Key words:** thiacycrown-iodine complexes, chloroform, stoichiometry, thermodynamics, spectrophotometry.

### 1. Introduction

Crown ethers are macrocyclic polyethers known for their ability to form stable and selective inclusion complexes with many metal ions, including alkali and alkaline earth metal cations [1, 2]. The stability of the resulting 1 : 1 complexes appears to be related to the macrocycle cavity sizes; it is at maximum when the cavity diameter matches the ionic size. The substitution of some oxygen atoms of the crown ethers by sulfur atoms has also been found to alter their complexing ability towards different metal ions [2–5]. The complexing properties of macrocyclic polythiaethers have been widely studied and metal complexes with these ligands have also been isolated and characterized [6–12]. The analytical applications of macrocyclic polythioethers in areas such as solvent-solvent extraction [13–15], solid-phase extraction [16], and PVC-membrane selective electrodes have also been reported in the literature [16–19].

There has been a growing interest in the studies of charge-transfer complexes between macrocyclic crown ethers and a variety of acceptor molecules such as DDQ [20–22], TCNE [20, 21], TCNQ [20], *p*-chloranil [20, 23], TNT [24], picric

---

\* Author for correspondence.

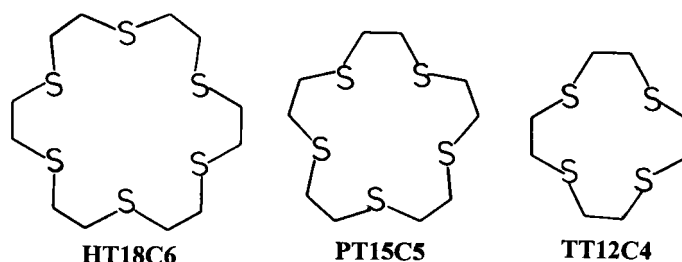


Figure 1. Structures of the thiacrown ethers.

acid [25] and, especially, iodine [26–32]. The cavity formed by the cyclic disposition of donating atoms in the macrocyclic ligands provides a very exciting feature to study their molecular encapsulation properties [33]. It has been clearly shown that the substitution of some of the oxygen atoms in the crown ether ring, by nitrogens, results in a tremendous increase in the stability of their iodine complexes [26, 27, 29, 30] over those of ordinary crowns [23, 28, 31, 33]. However, to the best of our knowledge, there are only a limited number of published reports dealing with the complexation of iodine with thioether crowns in solution [33, 34].

In recent years, we have been involved in spectroscopic study of molecular complexes of iodine with some azacrown ethers [29, 30, 32] and ordinary crowns [31] in chloroform solution. In this paper, we report a spectrophotometric study of the thermodynamics of complexation reactions between iodine and tetrathia-12-crown-4 (TT12C4), pentathia-15-crown-5 (PT15C5) and hexathia-18-crown-6 (HT18C6) in chloroform solution. The structures of the thioether crowns used, are shown in Figure 1.

## 2. Experimental

Reagent grade HT18C6, PT15C5 and TT12C4 (all from Aldrich) were used as received. Reagent grade iodine and chloroform were of the highest purity available and used without any further purification.

All UV-Vis spectra were recorded on a GBC 911 spectrophotometer and the absorbance measurements were made with a Cecil 9000 spectrophotometer using a quartz cell thermostatted at the desired temperature  $\pm 0.1$  °C. Specific details are given in the Results and Discussion section.

## 3. Results and Discussion

The electronic absorption spectra of iodine ( $1.0 \times 10^{-4}$  M) in the presence of excess amount of TT12C4, PT15C5 and HT18C6 in chloroform at 25 °C are shown in Figure 2. As seen, the resulting thiacrown-iodine complexes have a rather sharp absorption at 310 nm and a weaker and broader absorption at about 425 nm. None of the initial reactants show any measurable absorption in the 290–450 nm region.

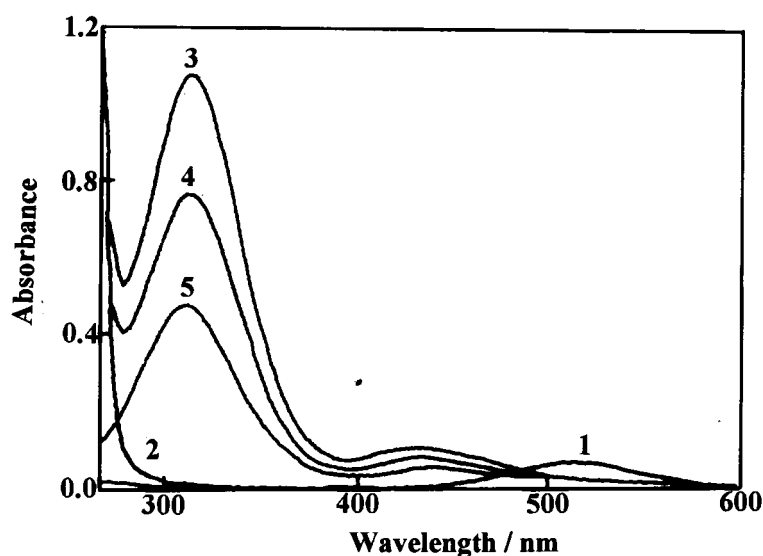


Figure 2. Electronic absorption spectra of iodine (1), thiocrown ethers (2), HT18C6-I<sub>2</sub> (3), PT15C5-I<sub>2</sub> (4) and TT12C4-I<sub>2</sub> (5) in chloroform solution at 25 °C.

Thus, the existence of these new bands must be associated with the formation of donor-acceptor molecular complexes between the thiocrown ethers used and iodine in chloroform solution [34–37].

The stoichiometry of the molecular complexes, determined by the continuous variations method [38], was 1 : 1 (thiocrown : I<sub>2</sub>) in all cases. Moreover, the existence of a well defined isosbestic point at 485 nm in the spectra of iodine upon titration with the thiocrown ethers (seen Figure 3 as an example) is also a good indication for a simple 1 : 1 complexation equilibrium in solution. It is noteworthy that a 1 : 1 stoichiometry between iodine and different thiocrown ethers has already been reported in solution [33, 34].

Formation constants of the resulting 1 : 1 donor-acceptor complexes were determined by measuring the absorbance at 310 nm for a series of nine solutions with varying concentration of thiocrowns and constant iodine concentration ( $1.0 \times 10^{-4}$  M) in chloroform. Since both donor and acceptor concentrations are very low and comparable, the following modification of the Benesi–Hildebrand equation was used [39]:

$$\frac{C_A^{\circ} C_D^{\circ}}{\text{Abs}} = \frac{1}{K_f \epsilon_{DA}} + \frac{C_A^{\circ} + C_D^{\circ}}{\epsilon_{DA}}, \quad (1)$$

where  $C_A^{\circ}$  and  $C_D^{\circ}$  are the initial concentrations of I<sub>2</sub> and thiocrown, respectively,  $K_f$  is the complex formation constant and  $\epsilon_{DA}$  is the molar absorptivity of the complex. According to Equation (1), a plot of  $C_A^{\circ} C_D^{\circ} / \text{Abs}$  vs.  $C_A^{\circ} + C_D^{\circ}$  will result in a straight line from the slope and intercept of which the  $\epsilon_{DA}$  and  $K_f$  values can be computed, respectively. Sample  $C_A^{\circ} C_D^{\circ} / \text{Abs}$  vs.  $C_A^{\circ} + C_D^{\circ}$  plots are shown in Figure 4,

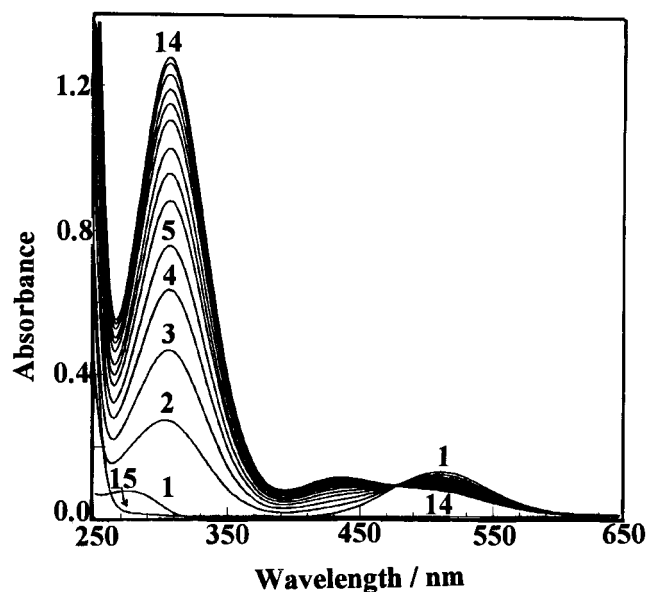


Figure 3. Electronic absorption spectra of  $1.0 \times 10^{-4}$  M of iodine in the presence of increasing concentration of PT15C5 at 25 °C. The PT15C5/I<sub>2</sub> mole ratio are: 1, 0; 2, 10; 3, 20; 4, 30; 5, 40; 6, 50; 7, 60; 8, 70; 9, 80; 10, 90; 11, 100; 12, 110; 13, 120; 14, 130; 15, PT15C5 alone.

Table I. Formation constants ( $K_f/M^{-1}$ ) and molar absorptivities ( $\epsilon/M^{-1} \text{ cm}^{-1}$ ) for different thiacycrown-I<sub>2</sub> complexes in chloroform at various temperatures

Macrocycle	283 K		290 K		298 K		306 K	
	$K_f$	$\epsilon$	$K_f$	$\epsilon$	$K_f$	$\epsilon$	$K_f$	$\epsilon$
HT18C6	$201 \pm 3$	$3.8 \times 10^4$	$137 \pm 2$	$3.2 \times 10^4$	$101 \pm 2$	$2.6 \times 10^4$	$69 \pm 1$	$2.1 \times 10^4$
PT15C5	$145 \pm 3$	$3.5 \times 10^4$	$113 \pm 2$	$2.8 \times 10^4$	$83 \pm 2$	$2.4 \times 10^4$	$60 \pm 1$	$2.0 \times 10^4$
TT12C4	$104 \pm 2$	$3.0 \times 10^4$	$84 \pm 2$	$2.3 \times 10^4$	$64 \pm 2$	$1.7 \times 10^4$	$51 \pm 1$	$1.4 \times 10^4$

which further support the 1 : 1 stoichiometric ratio. All the formation constants and molar absorptivities evaluated for different thiacycrown-iodine complexes at various temperatures are listed in Table I.

In order to have a better understanding of the thermodynamics of the molecular complexation reactions, it is useful to consider the enthalpic and entropic contributions to these reactions. The  $\Delta H^\circ$  and  $\Delta S^\circ$  values for the complexation reactions were evaluated from the corresponding  $\log K_f$  and temperature data by applying a linear least-squares analysis according to the equation

$$2.303 \log K_f = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}. \quad (2)$$

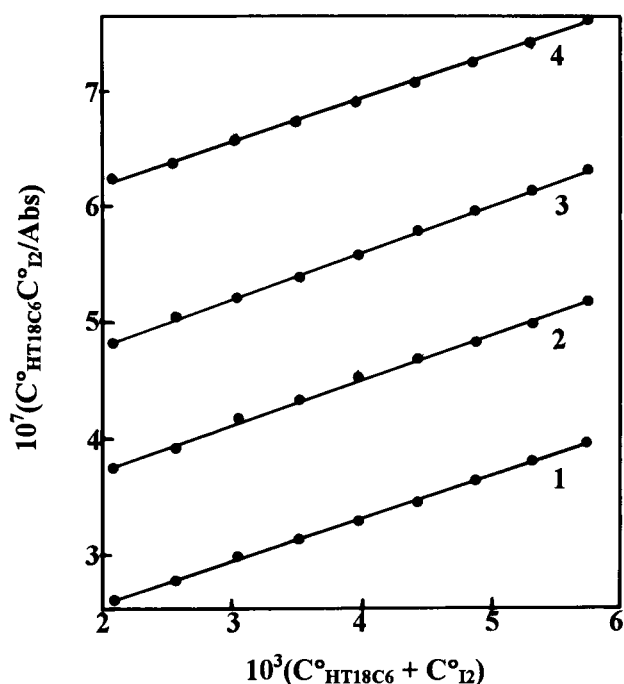


Figure 4. Plots of  $C_{I_2}^{\circ}C_{HT18C6}^{\circ}/Abs$  vs.  $C_{I_2}^{\circ} + C_{HT18C6}^{\circ}$  at various temperatures: 1, 10 °C; 2, 17 °C; 3, 25 °C; 4, 33 °C.

Table II. Thermodynamic parameters  $\Delta H^{\circ}$ ,  $\Delta S^{\circ}$  and  $\Delta G^{\circ}$  for different thiacycrown- $I_2$  complexes in chloroform solution

Macrocycle	$\Delta H^{\circ}/kJ mol^{-1}$	$\Delta S^{\circ}/J mol^{-1} K^{-1}$	$\Delta G^{\circ}/kJ mol^{-1}$
HT18C6	$-32.9 \pm 1.6$	$-72 \pm 6$	$-11.4 \pm 0.6$
PT15C5	$-27.7 \pm 1.6$	$-56 \pm 6$	$-10.9 \pm 0.6$
TT12C4	$-22.3 \pm 0.8$	$-40.2 \pm 2$	$-10.3 \pm 0.5$

Plots of  $\log K_f$  vs.  $1/T$  for different thiacycrown- $I_2$  systems were linear for all cases studied (Figure 5). The enthalpies and entropies of molecular complexation were determined in the usual manner from the slopes and intercepts of the plots and the results are summarized in Table II.

The data given in Table I clearly indicated that the stability and molar absorptivity of the molecular complexes of iodine with the crown ethers used, vary in the order HT18C6 > PT15C5 > TT12C4. It is well known that the crown ether cavity size and the number of donating atoms available play an important role in the stability of the resulting donor-acceptor complexes with iodine [26–34]. Since, in the process of molecular complexation of iodine, it is reasonably assumed that the

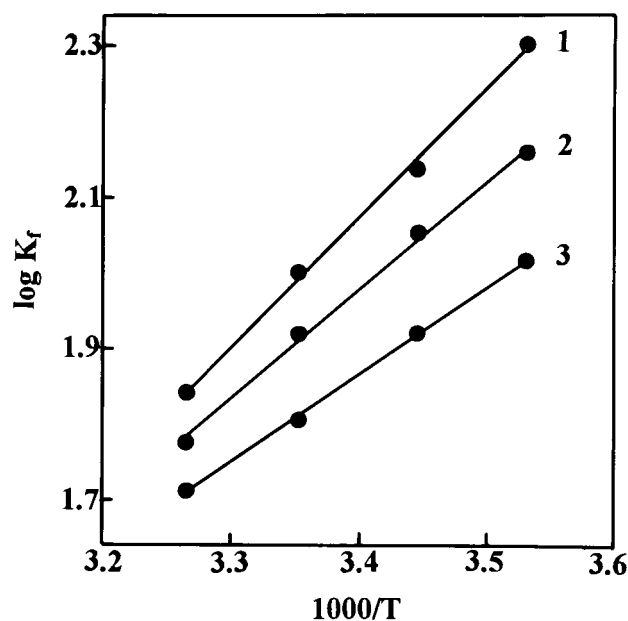


Figure 5. Van't Hoff plots for iodine complexes with different thiacycrown ethers in chloroform solution: 1, HT18C6; 2, PT15C5; 3, TT12C4.

charge density is donated from the base (thiacycrown ether sulfur atoms) to the  $b_{2\sigma u}$  antibonding molecular orbital of iodine [40, 41], the increased number of crown sulfurs in the ring as well as their proper spatial positions are expected to increase the crown-iodine interaction in solution [33, 34, 42].

As can be seen from Table II, the thiacycrown-12 complexes studied are all enthalpy stabilized, but entropy destabilized. Similar behavior was previously observed for macrocycle complexes with iodine [30, 33]. As seen, the negative  $\Delta H^\circ$  and  $\Delta S^\circ$  values both increase with increasing cavity size and donating sulfur atoms of the thiacycrown ethers. The more comfortable overlapping of the molecular orbitals of donor and acceptor partners in the process of charge-transfer complexation, the more negative the  $\Delta H^\circ$  values. On the other hand, although a detailed interpretation of all parameters including solvation-desolvation of the reaction partners is not possible, it is very likely that a main part of the unfavorable entropy contribution is related to a decrease in the conformational entropy of thiacycrown ethers upon formation of charge-transfer complexes with iodine. Large thiacycrown molecules should be rather flexible in the free state. The extent of flexibility is expected to vary with the size of macrocycle as well as the extent of macrocycle-solvent interaction. Interaction of iodine molecules with the flexible thiacycrown molecules presumably results in the formation of a rigid charge-transfer adduct in which the preferred conformation of the two component molecules for maximum overlap will lead to a negative entropy change during the complexation reaction [30, 43, 44]. Thus, it is not surprising to observe the largest negative  $\Delta S^\circ$  values for HT18C6, with the

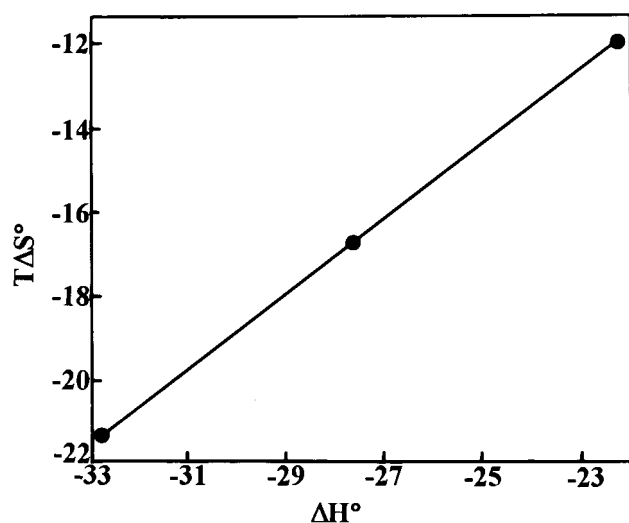


Figure 6. Plot of  $T\Delta S^\circ$  (kJ mol<sup>-1</sup>) vs.  $\Delta H^\circ$  (kJ mol<sup>-1</sup>) for different thiacrown-iodine complexes.

largest conformational change in the series during the complexation reaction with I<sub>2</sub>, and the smallest for TT12C4.

The data given in Table II revealed that a weaker thiacrown-iodine binding is associated with an enthalpic loss which is partially compensated by a simultaneous entropic gain due to the greater degree of freedom of the resulting complex. The existence of such a compensating effect between  $\Delta H^\circ$  and  $\Delta S^\circ$  values, which is frequently observed for a variety of metal-ligand [45–49] and charge-transfer complexes [35, 36], would cause the overall change in the complex stability ( $\Delta G^\circ$ ) to be smaller than might be expected from the change in either  $\Delta H^\circ$  or  $\Delta S^\circ$ , independently.

There is actually a fairly good linear correlation between the  $T\Delta S^\circ$  and  $\Delta H^\circ$  values obtained in this study (Figure 6) with the regression equation.

$$T\Delta S^\circ = T\Delta S_0^\circ + \alpha\Delta H^\circ, \quad (3)$$

in which  $T\Delta S_0^\circ = 8.1$  kJ mol<sup>-1</sup>,  $\alpha = 0.9$  and  $r = 0.9999$ . Equation (3) suggests that the entropic change consists of two components. The first component is independent of the enthalpy change ( $T\Delta S_0^\circ$ ) and the second is proportional to it ( $\alpha\Delta H^\circ$ ). The proportionality factor,  $\alpha$ , might be considered as a quantitative measure of the enthalpy-entropy compensation. The  $\alpha$  value of 0.9 indicates that only 10% of the increase in  $\Delta H^\circ$  contributes to the increase in the complex stability. The positive  $T\Delta S_0^\circ$  value of 8.1 kJ mol<sup>-1</sup> (the intrinsic entropic gain) emphasizes that the charge-transfer complex formation is favored even in the absence of any enthalpic gain (i.e.,  $\Delta H^\circ = 0$ ). This intrinsic entropic gain indicates the important role of the solvent properties in the process of complexation reaction. Since, during the com-

Table III. Thermodynamic data for the formation of molecular complexes between iodine and some 18-crowns in chloroform

Macrocycle	$\log K_f$	$\Delta H^\circ/\text{kJ mol}^{-1}$	$\Delta S^\circ/\text{J mol}^{-1} \text{K}^{-1}$	Ref.
18C6	0.69	-13.7	-32.6	[41]
HT18C6	2.00	-32.9	-72.2	This work
A18C6	4.33	-80	-187	[30]
DA18C6	7.1	-53	-41	[30]

plexation of iodine molecule by a thiacycrown ether, most of the associated solvent molecules are replaced by the donating sulfur atoms of the ligand, the increased degree of freedom due to the desolvation of iodine may result in some positive entropic gain.

In Table III, the thermodynamic parameters obtained for the HT18C6-iodine complex are compared with those reported for the corresponding ordinary crown and aza-substituted crown complexes in chloroform solution. It is readily seen that, despite the tremendous difference between the stability of the resulting iodine complexes, in all cases they are enthalpy stabilized, but entropy destabilized, as discussed before. The stability of iodine complexes vary in the order DA18C6  $\gg$  A18C6  $\gg$  HT18C6  $\gg$  18C6; the difference between  $K_f$  of two adjacent complexes being 2–3 orders of magnitude. Ordinary crown ethers form very weak iodine complexes mainly due to the decreased interaction between I<sub>2</sub> as a soft acceptor and the ring oxygens as hard donors [50].

As expected, the substitution of the hard oxygens of the ring by the soft sulfur or nitrogen atoms will result in enhanced stability of their iodine complexes. However, it should be mentioned that both the stoichiometry and stability of the azacycrown-iodine system are totally different from those of thiacycrown-iodine complexes; the azacycrown : I<sub>2</sub> ratio is 1 : 2 (in the form of azacycrown-I<sup>+</sup>.I<sub>3</sub><sup>-</sup>) and its formation constant is much larger than the 1 : 1 thiacycrown-I<sub>2</sub> complex. The formation of a triiodide ion and the increased stability in the case of azacycrown ethers, could be related to the much higher donor ability of its nitrogen atoms, compared with that of the sulfurs in the thiacycrowns [34, 50].

## References

1. R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, J. J. Christensen, and D. Sen: *Chem. Rev.* **85**, 271 (1985).
2. R. M. Izatt, K. Pawlak, J. S. Bradshaw, and R. L. Bruening: *Chem. Rev.* **91**, 1721 (1991).
3. H. K. Frensdorff: *J. Am. Chem. Soc.* **93**, 900 (1971).
4. G. Rounaghi and A. I. Popov: *J. Inorg. Nucl. Chem.* **43**, 911 (1981).
5. R. M. Izatt, G. A. Clark, J. S. Bradshaw, J. D. Lamb, and J. J. Christensen: *Sep. Purif. Methods* **15**, 121 (1986).



6. S. R. Cooper: *Acc. Chem. Res.* **21**, 141 (1988).
7. W. N. Setzer, Y. Tang, G. J. Grant, and D. G. VanDerveer: *Inorg. Chem.* **30**, 3652 (1991).
8. P. B. Savage, S. K. Holmgren, J. M. Sessler, and S. H. Gellman: *Pure Appl. Chem.* **65**, 461 (1993).
9. R. Alberto, W. Net, A. Smith, T. A. Kaden, M. Neuberger, M. Zehnder, A. Frey, U. Abram, and P. A. Schubiger: *Inorg. Chem.* **35**, 3420 (1996).
10. D. Sellmann, D. Haüssinger, F. Knock, and M. Moll: *J. Am. Chem. Soc.* **118**, 5368 (1996).
11. K. B. Yatsimirskii and V. V. Pavlishchuk: *J. Coord. Chem.* **37**, 341 (1996).
12. P. Comba, A. Fath, A. Kühner, and B. Nuber: *J. Chem. Soc., Dalton Trans.* 1889 (1997).
13. K. Saito, S. Murakami, A. Muromatsu, and E. Sekido: *Anal. Chim. Acta* **237**, 3533 (1990).
14. K. Saito, S. Murakami, A. Muromatsu, and E. Sekido: *Polyhedron* **12**, 1587 (1993).
15. B. A. Moyer, L. H. Delmau, G. N. Case, S. Bajo, and C. F. Baes, Jr.: *Sep. Sci. Technol.* **30**, 1047 (1995).
16. Y. Yamini, N. Alizadeh, and M. Shamsipur: *Anal. Chim. Acta* **355**, 69 (1997).
17. S. Kamata, K. Yamasaki, M. Higo, A. Bhale, and Y. Fukunaga: *Analyst.* **113**, 43 (1988).
18. D. Siswanta, K. Nagat, H. Yamada, K. Kumakura, H. Hisamoto, Y. Shichi, K. Toshima, and K. Suzuki: *Anal. Chem.* **68**, 4166 (1996).
19. A. R. Fakhari, M. R. Ganjali, and M. Shamsipur: *Anal. Chem.* **69**, 3693 (1997).
20. A. M. Nour El-Din: *Spectrochim. Acta* **42A**, 637 (1986).
21. A. Semnani and M. Shamsipur: *Spectrochim. Acta* **49A**, 411 (1993).
22. M. Hasani and M. Shamsipur: *J. Incl. Phenom.* **28**, 39 (1997).
23. L. J. Andrews and R. M. Keefer: *J. Org. Chem.* **53**, 337 (1988).
24. Y. Jayathirth and Krishnan: *Indian J. Chem.* **20A**, 249 (1981).
25. A. H. Rady: *Spectrosc. Lett.* **25**, 327 (1992).
26. E. M. Nour and L. A. Shahada: *Spectrochim. Acta* **44A**, 1227 (1988).
27. E. M. Nour: *Spectrochim. Acta* **47A**, 743 (1991).
28. W. Hirsch, J. Greenman, and R. Pizer: *Can. J. Chem.* **71**, 2171 (1993).
29. A. Semnani and S. Shamsipur: *J. Incl. Phenom.* **22**, 99 (1995).
30. A. Semnani and M. Shamsipur: *J. Chem. Soc., Dalton Trans.* 2215 (1996).
31. A. Semnani and M. Shamsipur: *Polish J. Chem.* **71**, 134 (1997).
32. S. Sadeghi, M. Shamsipur, and M. Elahi: *Polish J. Chem.* **71**, 1594 (1997).
33. R. M. Izatt, J. S. Bradshaw, K. Pawlak, R. L. Bruening, and B. J. Taret: *Chem. Rev.* **92**, 1261 (1992).
34. E. M. Nour, L. A. Shahada, and Sh. S. Alkaabi: *Bull. Soc. Chim. Fr.* 727 (1989).
35. P. Balasubramanian, K. Ramaraj, and V. P. Senthilnathan: *Spectrochim. Acta* **34A**, 449 (1978).
36. A. Suszka: *J. Chem. Soc., Perkin Trans. 2* 531 (1985).
37. M. M. Ayad: *Spectrochim. Acta* **50A**, 671 (1994).
38. P. Job: *Ann. Chim. (Paris)* **9**, 113 (1928).
39. N. J. Rose and R. S. Drago: *J. Am. Chem. Soc.* **81**, 6138 (1959).
40. R. S. Mulliken: *J. Am. Chem. Soc.* **74**, 811 (1952).
41. H. P. Hopkins, D. V. Jahagirdar, and F. J. Windler: *J. Phys. Chem.* **82**, 1254 (1978).
42. F. A. L. Anet, J. Krane, J. Dale, K. Daasvatn, and P. O. Kristians: *Acta Chem. Scand.* **27**, 3395 (1973).
43. M. Shamsipur and A. I. Popov: *J. Am. Chem. Soc.* **101**, 4051 (1979).
44. M. R. Ganjali, A. Rouhollahi, A. R. Mardan, and M. Shamsipur: *J. Chem. Soc., Faraday Trans.* **94**, 1959 (1998).
45. Y. Inou, F. Amano, N. Okada, H. Inada, M. Ouchi, A. Taio, and T. Hakushi: *J. Chem. Soc., Perkin Trans. 2* 1239 (1990).
46. Y. Inou, T. Hakushi, Y. Liu, L.-H. Tong, B.-J. Shen, and D. S. Jin: *J. Am. Chem. Soc.* **115**, 475 (1993).
47. M. Shamsipur and J. Ghasemi: *J. Incl. Phenom.* **20**, 157 (1995).

48. E. Grunwald and C. Steel: *J. Am. Chem. Soc.* **117**, 5687 (1995).
49. J. Ghasemi and M. Shamsipur: *J. Solution Chem.* **25**, 485 (1996).
50. R. D. Hancock and A. E. Martell: *J. Chem. Educ.* **73**, 654 (1996).