DALTON

Spectrophotometric study of the complexation of iodine with macrocycles in chloroform solution

Abolfazl Semnani[a] **and Mojtaba Shamsipur** *[,b]

[a] *Department of Chemistry, Shiraz University, Shiraz, Iran*
[b] *Department of Chemistry, Razi University, Kermanshah, Iran*

The complex-formation reactions between iodine and aza-18-crown-6 (1,4,7,10,13-pentaoxa-16-azacyclooctadecane), 7,16-diaza-18-crown-6 (1,4,10,13-tetraoxa-7,16-diazacyclooctadecane and 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (cryptand C222) have been studied spectrophotometrically in chloroform solution at various temperatures. In the cases of 7,16-diaza-18-crown-6 and cryptand C222 the resulting 1:2 (macrocycle to iodine) molecular complex is formulated as (macrocycle $\cdots$ I^+)I_3^-, while with aza-18-crown-6 a 2:2 molecular complex of the type [(macrocycle)$_2$ $\cdots$ I^+]I_3^- is formed. The spectrophotometric results, as well as conductance measurements, revealed that the gradual release of triiodide ion from its contact ion pair in the molecular complex into solution is the rate-determining step of the reaction. The formation constants of the resulting molecular complexes were evaluated from computer fitting of absorbance *vs.* mole ratio data and found to vary in the order cryptand C222 > 7,16-diaza-18-crown-6 > aza-18-crown-6. The enthalpy and entropy of complexation of iodine with aza- and 7,16-diaza-18-crown-6 were determined from the temperature dependence of the formation constants. In both cases, the complexation reactions are enthalpy stabilized, but entropy destabilized.

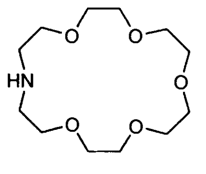
Since the first synthesis of crown ethers[1] and cryptands[2] there has been intensive research on the thermodynamics and kinetics of complexation of these compounds with various cations in a wide variety of solvent systems.[3,4] However, the complexation of macrocycles with neutral molecules is a relative young area of research. Interest in such molecular complexes is strongly stimulated by their possible applications in areas such as separation processes, biomimetic receptors, catalysis of chemical reactions and conversion of chemical reactions into optical or electronic signals.[5] Despite these interesting features, there are few thermodynamic[5,6–10] or kinetic[11–13] data available on such processes. Such data would be helpful in identifying and understanding reaction driving forces and in the characterization of the molecular complexes.

During the past few decades the complexation of iodine with a wide variety of donors has been the subject of extensive research.[14–17] More recently, some attention has been paid to iodine complexes with macrocyclic crown ethers and their aza derivatives in various solvents.[6,7,18–21] It has been shown that the substitution of the oxygen atoms in a crown ether ring by NH groups results in a drastic increase in the stability of the iodine complexes[19,20] over those of ordinary crowns.[6,18]

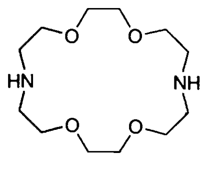
We have recently commenced a spectroscopic study of molecular complexes of crown ethers with different neutral molecules.[22,23] In this paper we report the results of a spectrophotometric investigation of the stoichiometry, thermodynamics and kinetics of complex formation of iodine with 1,4,7,10,13-pentaoxa-16-azacyclooctadecane (aza-18-crown-6), 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (7,16-diaza-18-crown-6) and 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]hexacosane (cryptand C222) in chloroform solution.

Experimental

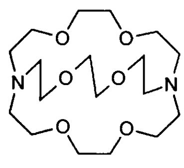
The macrocycles (Merck) were recrystallized from reagent-grade hexane and dried under vacuum over P_2O_5. Reagent-grade iodine and chloroform (Merck) were used without further purification.



aza-18-crown-6



7, 16-diaza-18-crown-6



cryptand **C222**

All UV/VIS spectra were recorded on a Philips PUB 700 spectrophotometer and the absorbance measurements were made with a Philips PUB 875 spectrophotometer at various temperatures (±0.5 °C). Conductance measurements were carried out with a Metrohm 660 conductivity meter. Specific details are given in the Results and Discussion section.

Results and Discussion

The electronic absorption spectra of iodine (1.23×10^{-4} mol dm^{-3}) in the presence of increasing amounts of aza-18-crown-6 and cryptand C222 in chloroform solution at 25 °C are shown in Figs. 1 and 2, respectively. The corresponding spectra for 7,16-diaza-18-crown-6 are very similar to those with aza-18-crown-6 and thus are not included. While none of the initial reactants show any measurable absorption in the 250–450 nm region, addition of the macrocycles to iodine results in two strong absorptions in this region, presumably due to the formation of iodine–macrocycle complexes. As it is seen from Figs. 1 and 2, in the case of aza-18-crown-6 (and also 7,16-diaza-18-crown-6), the absorption bands appear at 262 and 390 nm, while the cryptand C222 complex shows two absorptions at 292 and 364 nm. This latter spectrum resembles that of a 1:1

J. Chem. Soc., Dalton Trans., 1996, Pages 2215–2218

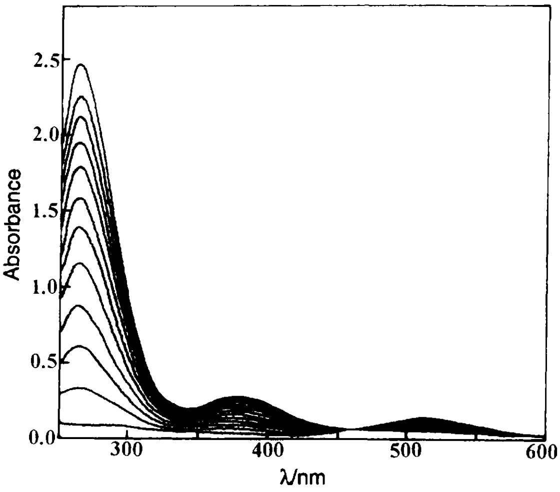


Fig. 1 Absorption spectra of 1.23 × 10^{-4} mol dm^{-3} iodine in chloroform in the presence of various concentrations of aza-18-crown-6. The macrocycle : I_2 mole ratios from the bottom to the top spectrum are 0.00, 0.12, 0.24, 0.36, 0.48, 0.60, 0.72, 0.84, 0.96, 1.08, 1.20 and 1.44 : 1

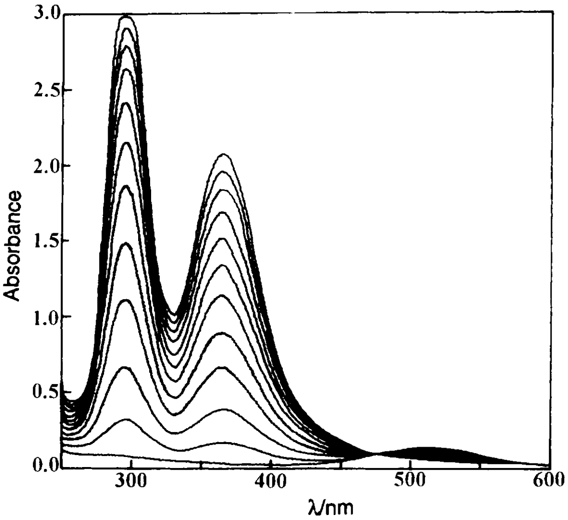


Fig. 2 Absorption spectra of 1.23 × 10^{-4} mol dm^{-3} iodine in chloroform in the presence of various concentrations of cryptand C222. The macrocycle : I_2 mole ratios from the bottom to the top spectrum are 0.00, 0.11, 0.22, 0.34, 0.45, 0.56, 0.67, 0.78, 0.90, 1.01, 1.12 and 1.23 : 1

mixture of tetrabutylammonium iodide and chloroform. It should be noted that the bands of 292 and 364 nm are characteristic for the formation of triiodide ion, I_3^-, in the process of complex formation between iodine and different electron-pair donor ligands.[6,19,20,24–26] Interestingly, it was found that, after about 5–7 h, the absorption bands of the aza- and 7,16-diaza-18-crown-6 complexes with iodine at 262 and 390 nm shift to new positions at 292 and 364 nm, respectively.

Fig. 3 shows the plots of absorbance *vs.* macrocycle: I_2 mole ratio for all three compounds, obtained at λ_{max} of iodine (508 nm). The plots are clearly indicative of the formation of a 1 : 2 (macrocycle-to-iodine) complex in the case of 7,16-diaza-18-crown-6 and cryptand C222, and a 2 : 2 adduct in the case of aza-18-crown-6, in chloroform solution. Moreover, the existence of a well defined isosbestic point in the spectra of iodine upon titration with the macrocycles (see Figs. 1 and 2) further supports the occurrence of a simple complexation equilibrium in solution. It is interesting that the curvature of absorbance *vs.* mole ratio plots in Fig. 3 decrease in the order cryptand C222 > 7,16-diaza-18-crown-6 > aza-18-crown-6 which reflects a decrease in the stability of the resulting iodine complexes in this sequence.

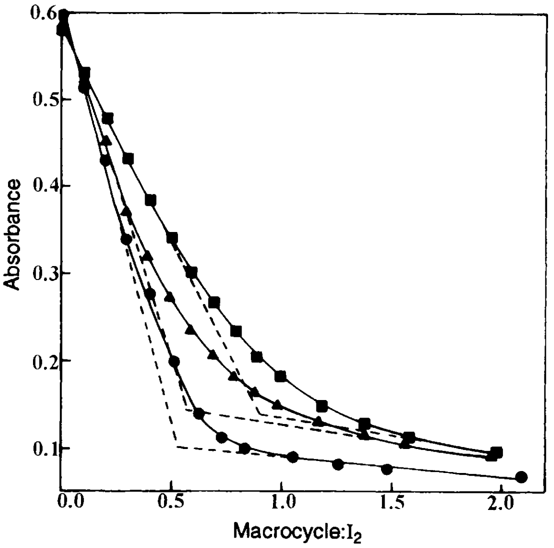


Fig. 3 Plots of absorbance *vs.* macrocycle : I_2 mole ratio in chloroform solution obtained at 508 nm and 25 °C: (■) aza-18-crown-6, (▲) 7,16-diaza-18-crown-6, (●) cryptand C222

Based on the observed spectral behaviours for the iodine complexes with 7,16-diaza-18-crown-6 and cryptand C222, the formation of triiodide ion can be reasonably assumed to occur in two steps. The first involves the formation of a molecular complex (macrocycle $\cdots I^+$)I_3^- in the form of a contact ion pair [equation (1)]. Evidence for the formation of such

$$\text{macrocycle} + 2I_2 \rightleftharpoons (\text{macrocycle} \cdots I^+)I_3^- \quad (1)$$

molecular complexes has been reported previously.[27] In the second step, which is actually rate determining for the formation of triiodide ion, the resulting molecular complex is decomposed to release free I_3^- ion (or solvent separated I_3^- ion) into the chloroform solution [equation (2)]. However, in

$$(\text{macrocycle} \cdots I^+)I_3^- \longrightarrow \text{macrocycle} \cdots I^+ + I_3^- \quad (2)$$

the case of aza-18-crown-6, the resulting molecular complex with iodine is formulated as [2 macrocycle $\cdots I^+$]I_3^-, most probably due to the strong affinity of the I^+ ion for the soft NH group of the macrocyclic ring which results in the formation of such a sandwich adduct.

Consequently, the two absorption maxima observed at 262 and 390 nm can be reasonably assigned to I_3^- in the contact ion pair, while those of 292 and 364 nm belong to the free (or solvent-separated) triiodide ion. The existence of such a two-step mechanism for the formation of I_3^- ion was further supported by conductivity measurements of a 3.32 × 10^{-4} mol dm^{-3} solution of iodine in chloroform before and after addition of the macrocycles (1.4 × 10^{-3} mol dm^{-3}). While, just after addition of aza- and 7,16-diaza-18-crown-6 to the iodine solution (having negligible conductivity) the molar conductance of the solution rises to about 3.0 S cm^2 mol^{-1}, addition of cryptand C222 causes a very large increase in molar conductance to Λ = 79.0 S cm^2 mol^{-1}, similar to that of a corresponding NBu_4I–I_2 mixture in chloroform solution (Λ = 82.6 S cm^2 mol^{-1}). However, after 7 h the molar conductances of the 18-crown-6 systems increase to 79.2 and 81.3 S cm^2 mol^{-1}, respectively, indicating gradual release of I_3^- from its molecular complexes.

On the other hand, from the spectral behaviour and the conductance data obtained for the cryptand C222–I_2 system, it is obvious that, in this case, the second step of the reaction is quite fast, presumably due to the inclusion of I^+ ion inside the cryptand cavity which facilitates release of I_3^- ion from its contact ion pair.

In order to investigate the kinetics of triiodide formation, the absorbance at 364 nm was monitored as a function of time in a chloroform solution containing the reactants in I_2 : macrocycle mole ratio of about 16 : 1 (analytical concentration of I_2 = 8.0×10^{-4} mol dm^{-3}) at 25 °C. The absorbance changes were found to be in accord with first-order kinetics. The rate constants were calculated by the Guggenheim method using the relationship $\ln(A_\infty - A_t) = -K(t_\infty - t_0) + \ln(A_\infty - A_0)$. The values obtained from the slopes of the corresponding linear plots of $\ln(A_\infty - A_t)$ *vs.* $(t_\infty - t_0)$, are given in Table 1. As is seen, the rate constants vary in the order cryptand C222 > 7,16-diaza-18-crown-6 > aza-18-crown-6, which is consistent with the spectral and conductance data discussed above, and the proposed two-step mechanism.

For the evaluation of the formation constants of the resulting molecular complexes, K_f, from the absorbance–mole ratio data, the non-linear least-squares curve-fitting program KINFIT was used.[28] The program is based on the iterative adjustment of calculated to observed absorbance values by using either the Wentworth matrix technique[29] or the Powell procedure.[30] Adjustable parameters are K_f and ε, where ε is the molar absorption coefficient of iodine.

The observed absorbance of an iodine solution in chloroform at its λ_{max} is given by equation (3). The mass-balance equations can be written as (4) and (5), and the formation constant of the

$$A_{obs} = \varepsilon l[I_2] \quad (3)$$

$$c_I = [I_2] + 2[(\text{macrocycle} \cdots I^+)I_3^-] \quad (4)$$

$$c_{macrocycle} = [\text{macrocycle}] + [(\text{macrocycle} \cdots I^+)I_3^-] \quad (5)$$

complex as in (6). Substitution of equations (4) and (5) into (6) and rearrangement yields (7). In the case of the 2 : 2 complex, the corresponding equation is (8). The free iodine concentrations, $[I_2]$, were calculated from either equation (7) or (8) by means of

$$K_f = [(\text{macrocycle} \cdots I^+)I_3^-]/[\text{macrocycle}][I_2]^2 \quad (6)$$

$$K_f[I_2]^3 + K_f(2c_{macrocycle} - c_I)[I_2]^2 + [I_2] - c_I = 0 \quad (7)$$

$$K_f[I_2]^2 + [1 + K_f(c_{macrocycle} - c_I)][I_2] - c_I = 0 \quad (8)$$

a Newton–Raphson procedure. Once the value of $[I_2]$ had been obtained the concentrations of all other species involved were calculated from the corresponding mass-balance equations by using the estimated value of K_f at the current iteration step of the program. Refinement of the parameters was continued until the sum-of-squares of the residuals between calculated and observed absorbance values for all experimental points was minimized. The output of the program KINFIT comprises the refined parameters, the sum of squares and the standard deviations of the data.

In order to have a better understanding of the thermodynamics of the complexation reactions of iodine with the macrocycles used it is useful to consider the enthalpic and entropic contributions to these reactions. The enthalpy and entropy in chloroform solution were determined by measuring the formation constants as a function of temperature.[31,32] The formation constants of all molecular complexes in chloroform at various temperatures, obtained by computer fitting of the corresponding absorbance *vs.* mole ratio data (see, for example, Fig. 4), are listed in Table 1. A sample computer fit of the mole ratio data for the 7,16-diaza-18-crown-6–I_2 system is shown in Fig. 5. The fair agreement between the observed and calculated absorbances further supports the occurrence of a 1 : 2 complexation between the macrocycles used and I_2 in chloroform solution. It is interesting that Nour[20] recently reported the formation of a 1 : 3 (crown to iodine) molecular complex between 1,10-diaza-18-crown-6 and I_2 in 1,2-dichloroethane, based on the elemental analysis data for the solid complex. However, extrapolations of the two linear parts of his reported plots of absorbance *vs.* I_2: crown mole ratio, obtained at 290 and 360 nm in 1,2-dichloroethane solution, intersect exactly at a mole ratio of 2 : 1 indicating the formation of a 2 : 1 molecular complex in solution. However, the stability constant of the resulting complex was not reported.

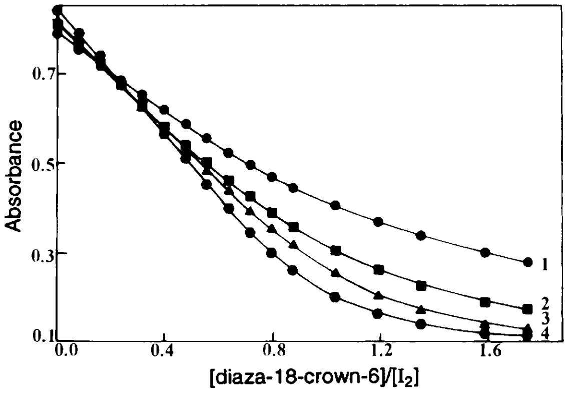


Fig. 4 Plots of absorbance *vs.* 7,16-diaza-18-crown-6 : I_2 mole ratio in chloroform solution at 508 nm and various temperatures: 1, 40; 2, 30; 3, 20; 4, 10 °C

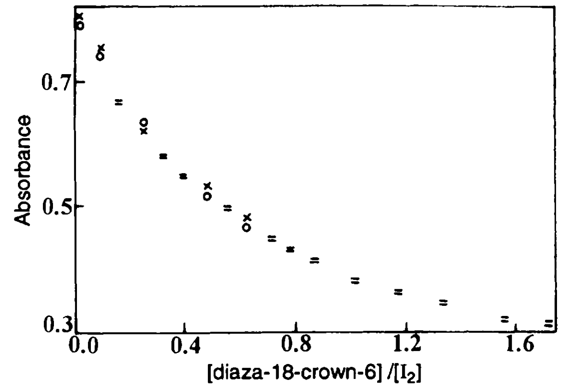


Fig. 5 Computer fit of the plot of absorbance *vs.* 7,16-diaza-18-crown-6 : I_2 mole ratio obtained at 508 nm and 40 °C: (×), experimental points; (○), calculated points; (=), experimental and calculated points are the same within the resolution of the plot

Plots of $\log K_f$ *vs.* $1/T$ were linear for the cases studied. The enthalpies and entropies of complexation were determined in the usual manner from the slopes and intercepts (free enthalpies) of the plots, respectively, and the results are also included in Table 1. It should be noted that the method described above for the evaluation of the formation constant from the absorbance–mole ratio data generally becomes unreliable for very strong complexes with $K_f > 10^8$. Thus, no exact value for the formation constant of the cryptand of C222–I_2 complex is reported in the table. The reported thermodynamic data for the 18-crown-6–I_2 system in cyclohexane[6] are included for comparison.

As the data in Table 1 indicate, the stability of the aza-18-crown-6 and, especially, the 7,16-diaza-18-crown-6 complexes with iodine are several orders of magnitude larger than that reported for 18-crown-6–I_2.[6] It is obvious that the substitution of some oxygen atoms of 18-crown-6 ring with NH groups results in a tremendous increase in the stability of the iodine complexes, most probably due to the strong soft–soft interactions between iodine and nitrogen atoms in solution.[33] Evidence for the formation of such strong complexes between iodine and some aza-substituted crown ethers has been reported previously.[7,19]

It is interesting that the stability of iodine complexes with the macrocycles used varies in the order cryptand C222 > 7,16-diaza-18-crown-6 > aza-18-crown-6. As was suggested in the foregoing paragraphs, the molecular complex formation

Table 1 Rate constants and thermodynamic data for the formation of molecular complexes between iodine and macrocycles in chloroform solution

Macrocycle	k/min^{-1}	log K_f 10 °C	20 °C	25 °C	30 °C	40 °C	$\Delta H°$/ kJ mol^{-1}	$\Delta S°$/ J K^{-1} mol^{-1}
Aza-18-crown-6	(5.5 ± 0.1) × 10^{-3}	4.95 ± 0.01	4.56 ± 0.02	4.33 ± 0.09	3.89 ± 0.05	3.60 ± 0.05	−80 ± 5	−187 ± 18
7,16-Diaza-18-crown-6	(1.61 ± 0.03) × 10^{-2}	7.5 ± 0.2	7.3 ± 0.2	7.1 ± 0.1	6.9 ± 0.1	6.6 ± 0.1	−53 ± 3	−41 ± 10
Cryptand C222	(5.9 ± 0.1) × 10^{1}	> 8	> 8	> 8	> 8	> 8	—	—
18-Crown-6*		—	—	0.69	—		−13.7	−32.6

* Data taken from ref. 6.

between I_2 and the macrocycles is associated with the penetration of I^+ inside the macrocyclic cavity which facilitates the formation of a contact (or solvent-separated) triiodide ion in solution. Since all three macrocycles used in this study have about the same cavity radius of 1.4 Å,[34] other structural features of the macrocycles such as their dimensions and number of nitrogen atoms in the ring are expected to play an important role in the stability of the resulting complexes. Although the size of I^+ having an ionic radius of 0.83 Å[35] is too small for the cavity of macrocyclic ligands used, it can form a more or less rigid cryptate-type inclusion complex with the three-dimensional cryptand C222.[34,36] Consequently, the cryptand C222–I_2 system shows a sharp cryptate effect compared with the two-dimensional 7,16-diaza-18-crown-6–I_2 complex in solution which involves a large enhancement in complex stability.[36] As expected, the 2:2 complex of aza-18-crown-6 with I_2 is the least stable in the series.

As can be seen in Table 1, the iodine complexes with aza and 7,16-diaza-18-crown-6 are both enthalpy stabilized but entropy destabilized. Similar behaviour was previously observed for macrocycle complexes with iodine.[6,37] Based on the proposed mechanism for the formation of macrocycle–iodine molecular complexes, it seems reasonable to assume that the main reason for the relatively large negative entropy of complexation is the decrease in the conformational entropy of the macrocycle upon formation of the $(\text{macrocycle}\cdots I^+)I_3^-$ complex. Large macrocycles such as aza- and 7,16-diaza-18-crown-6 should be rather flexible in the free state. The extent of flexibility would vary with their interaction with chloroform, *i.e.*, with the extent of macrocycle–solvent interaction. The formation of a rigid and stable wraparound structure between I^+ and the macrocyclic ring should considerably decrease the conformational entropy of the macrocycle and thus give rise to a negative entropy of complexation.[31,38,39]

References

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

2 B. Dietrich, J. M. Lehn and J. P. Sauvage, *Tetrahedron Lett.*, 1969, 2885, 2889.

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

4 R. M. Izatt, K. Pawlak, J. S. Bradshaw and R. L. Bruening, *Chem. Rev.*, 1991, **91**, 1721.

5 R. M. Izatt, J. S. Bradshaw, K. Pawlak, R. L. Bruening and B. J. Tarbet, *Chem. Rev.*, 1992, **92**, 1261.

6 H. P. Hopkins, D. V. Jahagirdar and F. Windler, *J. Phys. Chem.*, 1978, **82**, 1254.

7 L. Shahada, S. Alkaabi and E. M. Nour, *Acta Chim. Hung.*, 1990, **127**, 297.

8 R. Malini and V. Krishnan, *J. Phys. Chem.*, 1980, **84**, 551.

9 R. Malini and V. Krishnan, *Spectrochim. Acta, Part A*, 1984, **40**, 323.

10 C. J. van Staveren, V. M. L. Aarts, and P. D. J. Grootenhuis, *J. Am. Chem. Soc.*, 1986, **108**, 5271.

11 J. Muchova and V. Holba, *Z. Chem.*, 1984, **24**, 289.

12 J. Muchova and V. Holba, *Collect. Czech. Chem. Commun.*, 1983, **48**, 1158.

13 R . Pizer, *J. Am. Chem. Soc.*, 1978, **100**, 4239.

14 L. J. Andrews and R. M. Keefer, *Molecular Complexes in Organic Chemistry*, Holden-Day, New York, 1964.

15 M. Tamres and J. Yarwood, *Spectroscopy and Structure of Molecular Complexes*, Plenum, New York, 1974, ch. 3.

16 P. T. Trotter and P. A. White, *Appl. Spectrosc.*, 1978, **32**, 232.

17 N. Kulevsky and K. N. Butamina, *Spectrochim. Acta, Part A*, 1991, **46**, 79.

18 L. J. Andrews and R. M. Keefer, *J. Org. Chem.*, 1987, **52**, 2690.

19 E. M. Nour and L. A. Shahada, *Spectrochim. Acta, Part A*, 1988, **44**, 1277.

20 E. M. Nour, *Spectrochim. Acta, Part A*, 1991, **47**, 473.

21 W. Hirsch, J. Greenman and R. Pizer, *Can. J. Chem.*, 1993, **71**, 2171.

22 A. Semnani and M. Shamsipur, *Spectrochim. Acta, Part A*, 1993, **49**, 411.

23 A Semnani and M. Shamsipur, *J. Inclusion Phenom.*, 1995, **22**, 99.

24 R. P. Lang, *J. Phys. Chem.*, 1974, **78**, 1657.

25 L. J. Andrews, E. S. Prochaska and A. Loewenschuss, *Inorg. Chem.*, 1980, **19**, 463.

26 M. Mizuno, J. Tanaka and I. Harada, *J. Phys. Chem.*, 1981, **85**, 1789.

27 Y. A. Serguchev and T. I. Petrenko, *Teor. Eksp. Khim.*, 1977, **13**, 705.

28 V. A. Nicely and J. L. Dye, *J. Chem. Educ.*, 1971, **48**, 443.

29 W. E. Wentworth, *J. Chem. Educ.*, 1962, **42**, 96, 162.

30 M. J. D. Powell, *Comput. J.*, 1964, 7, 155.

31 M. Shamsipur, G. Rounaghi and A. I. Popov, *J. Solution Chem.*, 1980, **9**, 701.

32 M. Hasani and M. Shamsipur, *J. Inclusion Phenom.*, 1993, **16**, 123.

33 R. G. Pearson, *Struct. Bonding* (*Berlin*), 1993, **80**, 1.

34 J. M. Lehn, *Struct. Bonding* (*Berlin*), 1973, **16**, 1.

35 P. Labbe, R. Le Goaller, H. Handel, G. Pierre and J. L. Pierre, *Electrochim. Acta*, 1982, **27**, 257.

36 J. M. Lehn and J. P. Sauvage, *J. Am. Chem. Soc.*, 1975, **97**, 6700.

37 Yu. A. Serguchev, A. B. Khotkevich, V. N. Kalinin and V. M. Timoshenko, *Theor. Exp. Chem.* (*Engl. Transl.*), 1988, **24**, 716.

38 M. Shamsipur and A. I. Popov, *J. Am. Chem. Soc.*, 1979, **101**, 4051.

39 J. Ghasemi and M. Shamsipur, *J. Inclusion Phenom.*, 1995, **20**, 157.

Received 3rd *January* 1996; *Paper* 6/00170J