Bull. Chem. Soc. Ethiop. **2008**, 22(2), 287-294. ISSN 1011-3924
Printed in Ethiopia

THERMODYNAMIC STUDY OF CHARGE-TRANSFER COMPLEX OF IODINE WITH HT18C6 IN CHLOROFORM SOLUTION

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(Received September 29, 2007; revised November 28, 2007)

ABSTRACT. A spectrophotometric study concerning the interaction between HT18C6 as n-donor and I_2 as σ-acceptor has been performed in chloroform solution at different temperatures. The results are indicative of the formation 1:1 complex through equilibrium reaction. The stability constant of the complex at 7, 13, 19 and 25 ^oC is obtained by the computer-fitting of absorbance-mole ratio data in MATLAB software. The ΔH^o and ΔS^o values are obtained by the Vant Hoff method. The obtained data show that the complex is enthalpy stabilized and entropy destabilized. The entropy destabilitization is attributed to the decrease of the entropy of the free donor upon complexation. Comparison of the data from this work with those of previous works done on 18C6-I_2 and HA18C6-I_2 is indicative of different stability, stoichiometry and products. The possible reasons for such differences are discussed.

KEY WORDS: Charge-transfer complex, Iodine, HT18C6, Stability constant, Thermodynamic data, Spectrophotometry, Chloroform

INTRODUCTION

The formation of molecular complexes between electron donors and electron acceptors has long been recognized as an important phenomenon in many biological processes [1, 2]. Macrocyclic polyethers, a class of compounds that first synthesized by Pedersen [3], have been shown to bind cation much more strongly than monofunctional and liner polyfunctional ethers of similar basicity [4, 5]. More recently, the potential of complexing ability of these macrocycles toward neutral molecules has been investigated [6, 7]. Interest in such molecular complexes has been strongly stimulated by possibility of their application in such broad areas as separation sciences, catalysis of chemical reactions and conversion of chemical reactions into electronic or optical signals [6, 7].

Moreover, the charge-transfer involvement in bimolecular interactions can be better demonstrated by studying simple multi-site donors which would serves model compounds of biomolecules [8]. The complexing properties of macrocyclic polythiaethers have been widely studied and metal complexes with these ligands have also been isolated and characterized [9-13]. The analytical applications of macrocyclic polythiaethers in areas such as solvent-solvent extraction [14-15], solid phase extraction [16] and PVC-membrane selective electrodes have also been reported in the literature [16-18].

However, to the best of our knowledge, there are only a limited number of published reports dealing with the complexation of iodine with thiacrown ethers in solution [19-21]. In connection with our previous studies made on the charge-transfer complexes of iodine with crown ethers and their aza derivatives in various solvents [22-28], in this work, we report the results of spectrophotometric study concerning the interaction of iodine with HT18C6 in chloroform solution.

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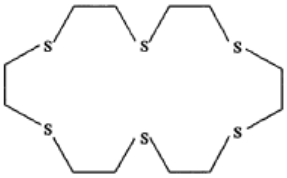
EXPERIMENTAL

Reagent grade of HT18C6 (1,4,7,10,13,16-hexathiacyclooctadecane) from Aldrich Company (CAS Number 296-41-3) was used as received. Reagent grade iodine and chloroform were of the highest purity available and used without any further purification.



HT18C6

The UV-Vis spectra were recorded on a UV-Vis Cary spectrophotometer model 150 at 25.0±0.03 ^{o}C and the absorbance measurements were made with the same instrument at various temperatures (± 0.03 ^{o}C).

In order to obtain UV-Vis spectra of HT18C6 in the presence of varying concentrations of iodine, 3 mL of 1.00 x 10^{-3} M solution of HT18C6 was transferred to a quartz cell and titrated with a 0.27 M solution of iodine by a 10 μL Hamiltonian syringe. Pure chloroform was used as reference solution. Each spectrum was recorded after addition of 2 μL of concentrated iodine solution and the addition was continued until the total added volume was 22 μL. Thus, the spectra were due to solutions in which the iodine to HT18C6 mole ratios were 0.00, 0.18, 0.36, 0.54, 0.72, 0.90, 1.08, 1.26, 1.44, 1.62, 1.80 and 1.98, respectively. As the volume change during whole titration was 22 μL, therefore, the volume correction of spectra was not necessary. Same procedure was followed for the obtaining of absorbance vs. iodine to HT18C6 mole ratio data. For obtaining the spectra of iodine in the presence of varying quantities of HT18C6, several solutions containing constant concentration of iodine (1.00 x 10^{-4} M) and different quantities of HT18C6 (0.00, 1.50 x 10^{-5}, 3.40 x 10^{-5}, 4.80 x 10^{-5}, 6.60 x 10^{-5}, 8.50 x 10^{-5}, 1.02 x 10^{-4}, 1.20 x 10^{-4}, 1.38 x 10^{-4}, 1.54 x 10^{-4} and 1.78 x 10^{-4} were prepared and the corresponding spectra were recorded. Thus, the spectra were due to solutions in which the mole ratio of HT18C6 to iodine solutions were 0.00, 0.15, 0.34, 0.48, 0.66, 0.85, 1.02, 1.20, 1.38, 1.54, and 1.78, respectively. In all cases, pure chloroform was employed as reference solution. For employment of Job's method, two equimolar solutions of donor and acceptor (1.00 x 10^{-3} M) were made and the needed solutions were prepared by mixing appropriate volumes of stock solutions in 5 mL volumetric flasks.

RESULTS AND DISCUSSION

Absorption spectra of 1.00 x 10^{-3} M of HT18C6 in the presence of varying concentrations of I_2 in chloroform solution are shown in Figure 1. As seen upon stepwise addition of iodine two new bands appear at 510 and 310 nm. The 510 nm band is the well known band of iodine in chloroform [22, 23]. On the other hand the 310 nm band is the charge-transfer absorption band and can be attributed to the formation of charge-transfer complex between iodine as σ-acceptor and HT18C6 as n-donor [29]. The appearance of free iodine band at 510 nm (Figure 1) indicates that the interaction of donor and acceptor is not complete and merely a small fraction of iodine is consumed [30]. Figure 2 shows the absorption spectra of iodine in the presence of varying

quantities of HT18C6. The appearance of an isosbestic point at 350 nm, indicate that the interaction of iodine and HT18C6 follows through equilibrium pathway [30].

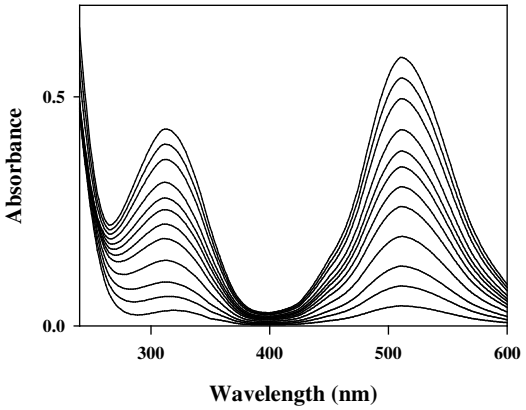


Figure 1. Absorption spectra of 1.00 x 10^{-3} M HT18C6 in the presence of varying concentrations of I_2 in chloroform solution. The $[I_2]$/[HT18C6] mole ratios from bottom to top are 0.00, 0.18, 0.36, 0.54, 0.72, 0.90, 1.08, 1.26, 1.44, 1.62, 1.80 and 1.98, respectively.

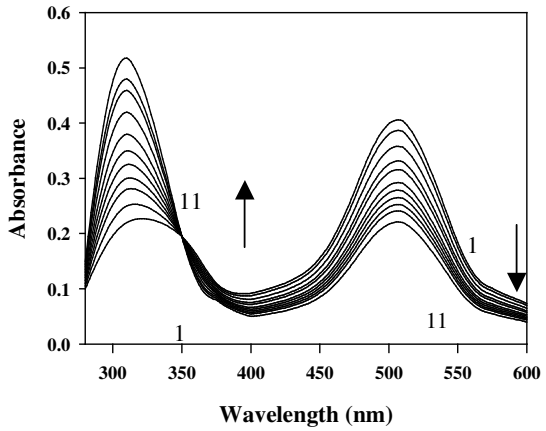


Figure 2. Absorption spectra of 3.50 x 10^{-4} M iodine in the presence of varying concentrations of HT18C6 in chloroform solution. The [HT18C6]/$[I_2]$ mole ratios are 1; 0.00, 2; 0.15, 3; 0.34, 4; 0.48, 5; 0.66, 6; 0.85, 7; 1.02, 8; 1.20, 9; 1.38, 10; 1.54 and 11; 1.78.

In order to determine stoichiometry of the reaction, the Job's [31] and mole ratio methods [32] were followed. The corresponding plots are shown in Figures 3 and 4, respectively. The appearance of a maximum at $X_{macrocycle}$ = 0.5 in Job's plot (Figure 3) fairly confirms 1:1 stoichiometry. However, because of weak interaction, an obvious break in mole ratio plot (Figure 4) is not seen and upon stepwise addition of HT18C6 to iodine solution in the range of 0.0-2.1 only steady increase in absorbance is observed. Based on the spectral evidences (Figures

1 and 2) and the results of Job's method (Figure 3) the following equation is suggested for the interaction of HT18C6 and I_2:

$$HT18C6+I_2 \leftrightarrows HT18C6.I_2 \quad (1)$$

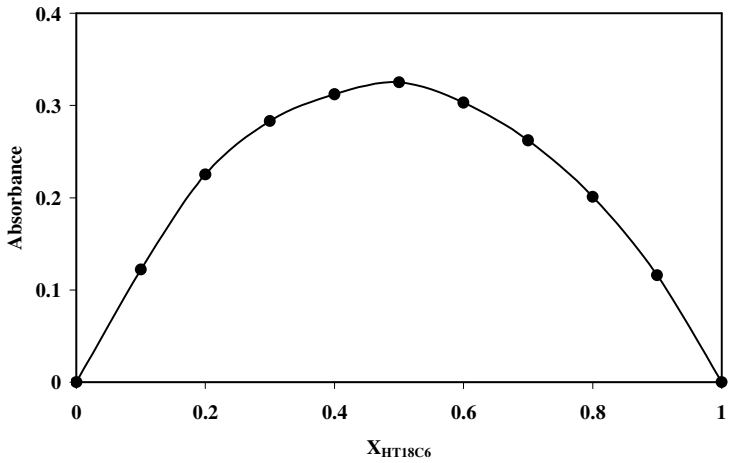


Figure 3. Plot of absorption vs. mole fraction of HT18C6 in $CHCl_3$ at 310 nm and 25 °C.

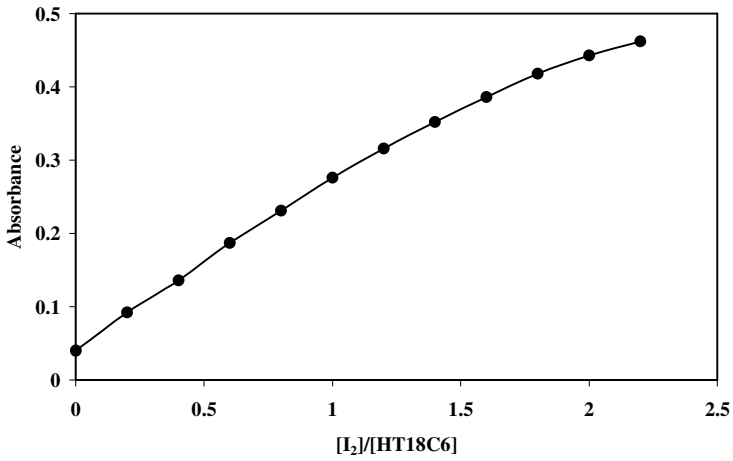


Figure 4. Plot of absorption vs. $[I_2]/[HT18C6]$ at 310 nm and 25 °C.

The formation constant of the resulting complex was evaluated from the absorbance-mole ratio data by using a non-linear least square curve-fitting program (curve-fitting toolbox in MATLAB). The program is based on the iteration adjustment of calculated absorbances to the observed values. The observed absorbance of complex is given by equation 2. The mass balance equations can be written as 3 and 4 and the formation constant of the complex as 5. Substitution of equations 3 and 4 into 5 and rearrangement yields equation 6.

$$A = \epsilon b [DA] \quad (2)$$

$$C_D = [D] + [DA] \quad (3)$$

$$C_A = [A] + [DA] \quad (4)$$

$$K_f = [DA] / [D] [A] \quad (5)$$

$$K_f [DA]^2 - (C_A K_f + C_D K_f + 1) [DA] + K_f C_D C_A = 0 \quad (6)$$

In the equations 1-6, A is absorbance of complex at 310 nm and [DA], [D] and [A] are the molar concentrations of complex, HT18C6 and I_2, respectively. With use of an approximation value for K_f, the free DA concentrations [DA] were calculated by solution of second order equation. Then, with using the data of DA concentrations as X data and data of observed absorbances as Y data, the least square fit technique is used for fitting the data. The output of this fitting is the coefficients of line fit. The coefficient of X value is ε. The obtained coefficient was used for calculation data of calculated absorbances with using of parabolic fit. To find the least squares error, the sum of squares of the differences between the parabolic fit and the experimental data must be evaluated. Refinement of parameters (K_f value) was continued until the sum of squares of the residuals between calculated and observed values of the absorbance for all experimental points was minimized [33, 34]. The computer fit of absorbance-mole ratio data are shown in Figure 5. Fair agreement between the calculated and observed data further confirms the 1:1 stoichiometry. The log K_f and ε values obtained by this method are 2.43±0.17 and 1564.8, respectively. The moderate value of log K_f indicated that the reaction of I_2 and HT18C6 is not complete and is in accordance with the absorption spectra of HT18C6-I_2 mixtures (Figure 1).

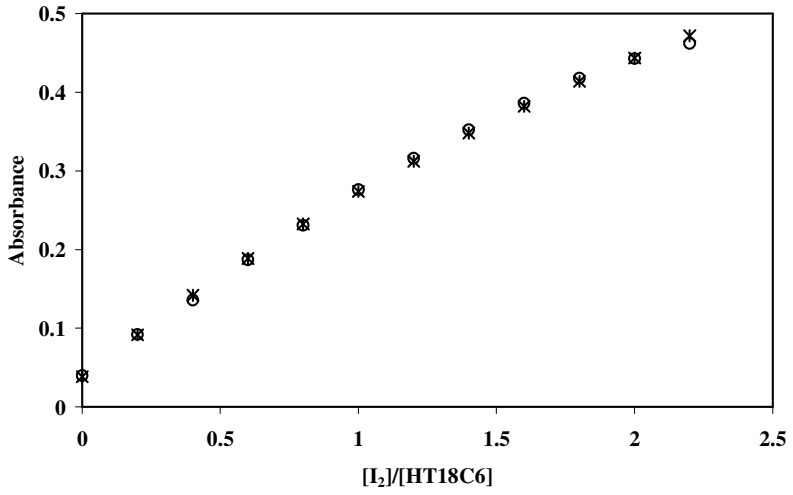


Figure 5. Computer fitting of absorbance vs. mole ratio data at 310 nm and 25 °C; (x) experimental and (o) calculated points.

In order to have a better understanding of the thermodynamics of the complexation reaction of iodine with macrocycle, it is useful to consider enthalpy and entropy contributions to these reactions. The enthalpy and entropy in chloroform solution were determined by measuring the formation constant as a function of temperature [35]. Formation constants, as well as ε values at various temperatures were obtained by computer fitting of the absorbance vs. mole ratio data. The plot of absorbance vs. $[I_2]/[HT18C6]$ data at 7, 13, 19, and 25 ^oC is shown in Figure 6. Plot of log K_f vs. 1/T was linear (Figure 7). The enthalpy (ΔH^o) and entropy (ΔS^o) of complexation was determined in the usual manner from the slope and intercept of plot and obtained -110.3 kJ/mol and -323.7 J/mol·K, respectively. The log K_f and ε values in different temperatures are included in Table 1. The data in Table 1 indicate that the molecular complex between I_2 and HT18C6 is enthalpy stabilized and entropy destabilized. Similar behavior was previously observed for some macrocycle complexes with iodine [19, 21]. The enthalpy stabilization can be attributed to the effective overlapping of molecular orbital of donor and acceptor partner in the process of charge-transfer complexation. On the other hand the entropy destabilization can be related to the difference between the entropy of the free and complexed HT18C6. In fact, the cavity size of HT18C6 is about 2 Å [36], which is considerably less than van der Waals diameter of iodine [37]. Thus the probability of the insertion of iodine in the cavity of macrocycle is completely discarded. On the other side, the effective overlapping of donor orbital with the σ^* antibonding molecular orbital of iodine involves the special orientation of sulfur atoms toward iodine. This acts as a driving force for a special conformation of HT18C6 in the complex. If the freedom of the recent conformation differs significantly from the unreacted one, the complexations would be along with considerable entropy decreasing. If not, a little entropy change would be observed. It seems that upon complexation the conformation freedom of donor is highly lost which resulted in the observation of negative ΔS^o.

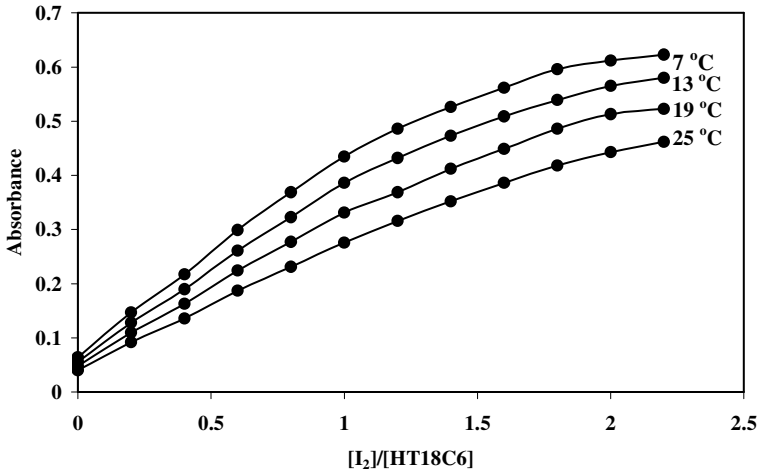


Figure 6. Plots of absorbance vs. $[I_2]/[HT18C6]$ at different temperatures and 310 nm.

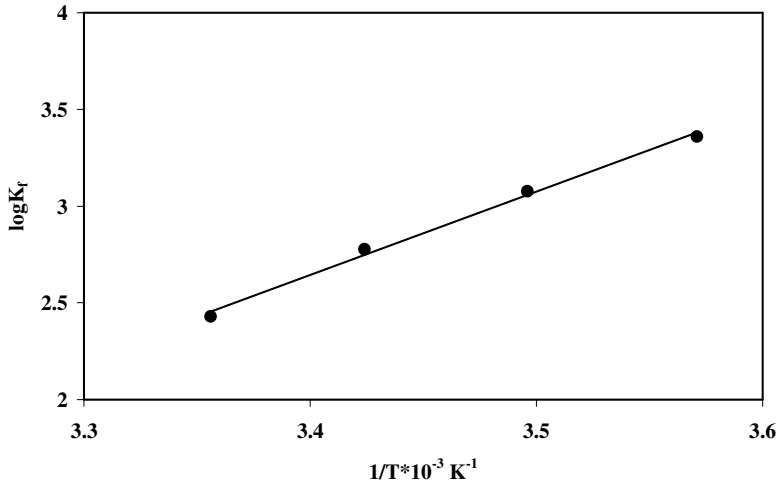


Figure 7. Vant Hoff plot for charge-transfer complex of I_2 and HT18C6 in chloroform solution.

It is interesting to note that the stoichiometries, stabilities and final adducts of 18C6-I_2 and HA18C6-I_2 interactions differ significantly with those of HT18C6-I_2 [24, 38]. The information's given in Table 2 clearly indicate that HA18C6 and 18C6 do have 1:2 (Crown:I_2). Meanwhile HT18C6 has a 1:1 stoichiometry. On the other hand, through the interaction of HA18C6-I_2 or 18C6-I_2, I_3^- is formed, however, HT18C6 and I_2 do not produce such adduct. Also, the stability of HT18C6-I_2 complex is more than 18C6-I_2 and less than HA18C6-I_2 complex. The highest stability of HA18C6 can be attributed to the soft-soft interactions between nitrogen and iodine [39]. On the other hand the higher donocity of sulfur than that of oxygen causes that HT18C6-I_2 complex to be stronger than 18C6-I_2 one. Finally the formation of 18C6$I^+I_3^-$ or HA18C6$I^+I_3^-$ can be assigned to the more suitable fitting of I^+ in the cavities of 18C6 and HA18C6. It seems that the rigid structure of HT18C6 hinders the convenient fitting of I^+ inside the cavity of this donor. Thus, through the interaction of HT18C6 and I_2, the triiodide ion will not form.

Table 1. Formation constants and ε values of HT18C6-I_2 complex at different temperatures.

T, K	Log K_f	ε
280	3.36 ± 0.18	843.0
286	3.08 ± 0.14	953.2
292	2.78 ± 0.12	1149.2
298	2.43 ± 0.17	1564.8

Table 2. The chemical equations and stability constants of HT18C6, HA18C6 and 18C6.

Crown ether	Chemical equation	Log K_f
[a]HT18C6	HT18C6 + I_2 ⇆ HT18C6·I_2	2.43 ± 0.01
[b]18C6	18C6 + 2I_2 ⇆ 18C6I^+·I_3^-	0.12 ± 0.01
[c]HA18C6	HA18C6 + 2I_2 ⇆ HA18C6 I^+·I_3^-	9.30 ± 0.10

a: This work, b: ref. [34], c: ref. [38].

REFERENCES

1. Slifkin, A.M. *Charge Transfer Interaction of Biomolecules*, Academic Press: New York; **1971**.
2. Pullman, B. *Molecular Association in Biology*, Academic Press: New York; **1968**.
3. Pedersen, C.J. *J. Am. Chem. Soc.* **1967**, 89, 7017.
4. Izatt, R.M; Bradshaw, J.J.; Pawlak, K; Bruening, R.L. *Chem. Rev.* **1991**, 91, 1721.
5. Shchori, E.; Jaqur-Grodzinski, H.; Lus, Z; Shporer, M. *J. Am. Chem. Soc.* **1971**, 93, 7133.
6. Hopkins, H.P.; Jahagirdar, D.V.; Windler, F.J. *J. Phys. Chem.* **1978**, 82, 1254.
7. Andrews, L.J.; Keefer, R.M. *J. Org. Chem.* **1987**, 52, 2690.
8. Rao, N.S.; Rao, G.B.; Ziessow, D. *Spectrochim. Acta A* **1990**, 46, 1107.
9. Cooper, S.R. *Acc. Chem. Res.* **1988**, 21, 141.
10. Setzer, W.N.; Tang, Y.; Grant, G.J.; Vanderver, D.G. *Inorg. Chem.* **1991**, 30, 3652.
11. Alberto, R.; Net, W.; Smith, A.; Kaden, T.A.; Neuburger, M.; Zehnder, M.; Frey, A.; Abram, U.; Schubiger, P.A. *Inorg. Chem.* **1996**, 35, 3420.
12. Sellmann, D.; Haaussinger, D.; Knock, F.; Moll, M. *J. Am. Chem. Soc.* **1996**, 118, 5368.
13. Yatsimirskii, K.B.; Pavlishchuk, V.V. *J. Coord. Chem.* **1996**, 37, 341.
14. Saito, K.; Murakami, S.; Muromatsu, A.; Sekido, E. *Polyhedron* **1993**, 12, 1587.
15. Moyer, B.A.; Delamu, L.H.; Case, G.N.; Bajo, S.; Baes, C.F. *J. Sep. Sci. Technol.* **1995**, 30, 1047.
16. Yamini, Y.; Alizadeh, N.; Shamsipur, M. *Anal. Chim. Acta* **1997**, 355, 69.
17. Kamata, S.; Yamasaki, K.; Higo, M.; Bhale, A.; Fukunaga, Y. *Analyst* **1988**, 113, 43.
18. Siswanta, D.; Nagat, K.; Yamada, H.; Kumakura, K.K.; Hisamoto, H.; Shichi, Y.; Toshima, K.; Suzuki, K. *Anal. Chem.* **1996**, 68, 4166.
19. Izatt, R.M.; Bradshaw, J.S.; Pawlak, K.; Bruening, R.L.; Tarbet, B.J. *Chem. Rev.* **1992,** 92, 1261.
20. Nour, E.M.; Shahada, L.A.; Alkaabi, Sh. S. *Bull. Soc. Chim. Fr.* **1989**, 126, 727.
21. Shamsipur, M.; Mashhadizadeh, M.H. *J. Inclusion Phenomena Macrocyclic Chem.* **2000**, 38, 277.
22. Semnani, A.; Shamsipur, M. *J. Inclusion Phenomena Mole. Recog. Chem.* **1995**, 22, 99.
23. Semnani, A.; Shamsipur, M. *J. Chem. Soc. Dalton Trans.* **1996**, 2215.
24. Semnani, A.; Shamsipur, M. *Polish J. Chem.* **1997**, 71, 134.
25. Semnani, A.; Shareghi, B.; Pouretedal, H.R. *Iran. J. Chem. Chem. Eng.* **2004**, 23, 1.
26. Semnani, A.; Pouretedal, H.R.; Firooz, A.R. *Asian J. Chem.* **2006**, 18, 385.
27. Semnani, A.; Pouretedal, H.R. *Bull. Chem. Soc. Ethiop.* **2006**, 20, 183.
28. Semnani, A.; Pouretedal, H.R.; Keshavarz, M.H. *Bull. Korean Chem. Soc.* **2006**, 27, 886.
29. Mulliken, R.S. *Molecular Complexes*, Wiley-Interscience: New York; **1969**.
30. Beck, M.T.; Nagypal, I. *Chemistry of Complex Equilibria*, John Wiley and Sons: New York; **1990**.
31. Job, P. *Ann. Chim. (Paris)* **1928**, 9, 113.
32. Skoog, D.A.; West, D.; Holler, J.F. *Fundamentals of Analytical Chemistry*, Saunder College Publishing: New York; **1988**.
33. Gans, P. *Data Fitting in the Chemical Sciences by the Method of Least Squares*, John Wiley and Sons: England; **1992**.
34. Quhn, M.; Guckenheimer, J.; Land, B.R.; Harris, R.; Warrick, A. *J. Neurophysiology* **2005**, 94, 2883.
35. Mortimer, C.E. *Chemistry*, 7th ed., Wadsworth Publishing Company: New York; **1986**.
36. Shamsipur, M.; Semnani, A.; Mokhtarifard, A. *Iranian J. Sci. Techn.* **1994**, 18, 193.
37. Huheey, I.E. *Inorganic Chemistry*, Harper and Row Polishers: New York; **1983**.
38. Hasani, M.; Shamsipur, M. *J. Inclusion Phenomena Macrocyclic Chem.* **2004**, 48, 135.
39. Pearson, R.G. *Struct. Bonding (Berlin)* **1993**, 2, 80.