Bull. Chem. Soc. Jpn. Vol. 81, No. 6, 711–715 (2008)

Spectrophotometric Studies of the Thermodynamics of Molecular Interaction between Some Free Base *meso*-Tetraarylporphyrins and SbF_3

Hossein Dehghani,*[1] Maryam Bordbar,[2] Sheida Rezakhani,[1] and Mohammad Reza Mansournia[1]

[1]Department of Chemistry, Faculty of Science, University of Kashan, Kashan 87317-51167, Iran

[2]Department of Chemistry, Islamic Azad University, Ghom branch, Iran

Received September 26, 2007; E-mail: dehghani@kashanu.ac.ir

Spectrophotometric study was applied to the interaction of SbF_3 with para-, meta-, and ortho-substituted *meso*-tetraarylporphyrins ($H_2t(Xp)p$; X: H, OCH_3, CH_3, and Cl) in $CHCl_3$. The 1:1 formation constants of the resulting complexes were calculated at several temperatures by the computer fitting of absorbances of solutions versus mole ratio data with appropriate equations. Thermodynamic parameters (ΔG^0, ΔH^0, and ΔS^0) have been determined and the influence of electron donation and steric effect of the substituted aryl groups in the free base porphyrins on the stability of the complexes is discussed.

The molecular interaction of free base porphyrins (as σ-electron donors) with various acceptors has been of interest to chemists.[1–9] In most of this work, each acceptor molecule takes only an electron pair of a pyrrole nitrogen in the *meso*-tetraarylporphyrin and therefore, a 2:1 (acceptor:donor) molecular complex is formed.[3–9] Recently, we reported the reaction of free base *meso*-tetraarylporphyrins with $BiCl_3$ and $SbCl_3$ for formation of dimer molecular complexes ($[(MCl_3\{H_2t(Xp)p\})_2]$, M = Bi and Sb) that the porphyrin cores of those act as two electron pairs donors.[1,2] This paper presents the formation constants and thermodynamic parameters for the molecular complexation of *meso*-tetraarylporphyrins and its para-, meta-, and ortho-substituted derivatives (Figure 1) with SbF_3. In these molecular complexes, the porphyrins act as donors by two lone electron pairs of nitrogens to one molecule of antimony(III) fluoride. The suitable selection of SbF_3 as electron acceptor resulted in the successful preparation of 1:1 molecular complexes. The central antimony atom in SbF_3 was a big atom and had enough empty d-orbitals to accept two electron pairs of the pyrrole nitrogen atoms in the porphyrins and formed 1:1 molecular complex in contrast to usual 2:1 (acceptor:donor) molecular complexes.[3–9] The structure of these molecular complexes was similar to SAT (sitting-atop) complexes. The SAT complex is a metalloporphyrin which two pyrrole protons remain yet on the porphyrin. The metalloporphyrin formation is an important process related to the biosynthesis of heme and the SAT complex is proposed as intermediate in this reaction.[10]

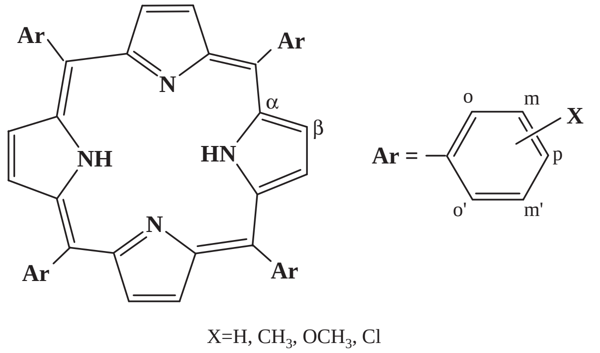

Figure 1. *meso*-Tetraarylporphyrins, $H_2t(Xp)p$.

Results and Discussion

The absorption spectra of the porphyrins and those molecular complexes with SbF_3 in chloroform were obtained. The spectra for titration of SbF_3 with $H_2t(4\text{-}OCH_3p)p$ at 25 °C are shown in Figure 2. The original peaks of $H_2t(4\text{-}OCH_3p)p$ (Soret band and Q bands) changed considerably by interaction

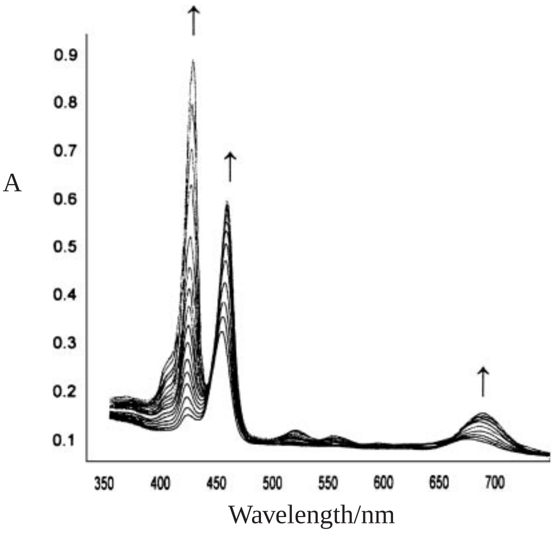

Figure 2. Typical spectral change in the course of titration of SbF_3 with $H_2t(4\text{-}OCH_3p)p$ in chloroform at 25 °C. Bands appearing at 454 and 688 nm are related to the molecular complex.

Published on the web June 11, 2008; doi:10.1246/bcsj.81.711

Table 1. UV–Vis Data for Free Base *meso*-Tetraarylporphyrins and Their Molecular Complexes with SbF_3 in $CHCl_3$ Solvent

Compound	Wavelength/nm
H_2tpp	417, 514, 549, 589, 646
$(SbF_3)H_2tpp$	445, 660
$H_2t(4\text{-}OCH_3p)p$	421, 518, 555, 594, 649
$(SbF_3)H_2t(4\text{-}OCH_3p)p$	454, 688
$H_2t(3\text{-}OCH_3p)p$	420, 517, 550, 590, 646
$(SbF_3)H_2t(3\text{-}OCH_3p)p$	451, 661
$H_2t(2\text{-}OCH_3p)p$	420, 514, 548, 590, 648
$(SbF_3)H_2t(2\text{-}OCH_3p)p$	450, 652
$H_2t(4\text{-}CH_3p)p$	419, 516, 553, 591, 649
$(SbF_3)H_2t(4\text{-}CH_3p)p$	448, 670
$H_2t(3\text{-}CH_3p)p$	419, 514, 548, 591, 646
$(SbF_3)H_2t(3\text{-}CH_3p)p$	446, 662
$H_2t(2\text{-}CH_3p)p$	415, 512, 544, 588, 644
$(SbF_3)H_2t(2\text{-}CH_3p)p$	442, 654
$H_2t(4\text{-}Clp)p$	418, 514, 550, 590, 646
$(SbF_3)H_2t(4\text{-}Clp)p$	449, 665

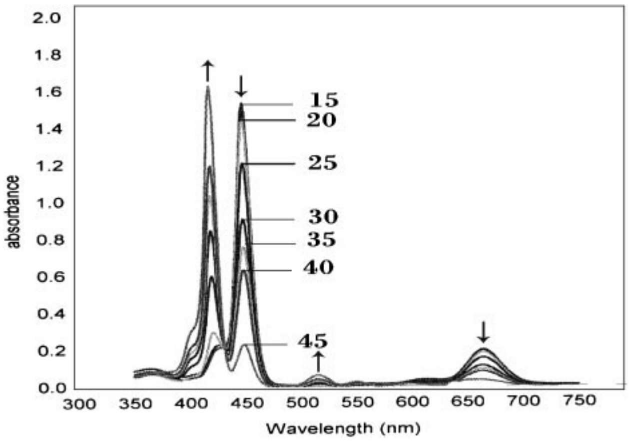

Figure 3. Thermal dissociation spectra of SbF_3–$H_2t(4\text{-}Clp)p$ molecular complex by addition of porphyrin (7×10^{-5} mol dm^{-3}) to the solution of SbF_3 (7×10^{-5} mol dm^{-3}) in chloroform in a UV–vis cell at 15 °C. The numbers in the spectra show temperatures (°C).

of the porphyrin with SbF_3 (Table 1) and in result produced an isosbestic point at 438 nm, Figure 2. Upon the interactions of the free base porphyrins with SbF_3, the purple color of the *meso*-tetraarylporphyrins changes to green. Interactions of SbF_3 with $H_2t(Xp)p$ were very sensitive to temperature (Figure 3). Increasing the temperature causes to change the green color of the molecular complex solution to the purple color of the related porphyrin.

The stoichiometry of the molecular complexes in chloroform was examined by the method of continuous variation (Job's method).[11–13] It is clear that 1:1 molecular complex is formed in the solution. Furthermore, the formation of the species in chloroform is supported by the mole ratio method. For example, the computer fitting of the absorbance–mole ratio data and the continuous variation plot for $[(SbF_3)H_2t(4\text{-}CH_3p)p]$ molecular complex are shown in Figure 4 and Figure 5, respectively.

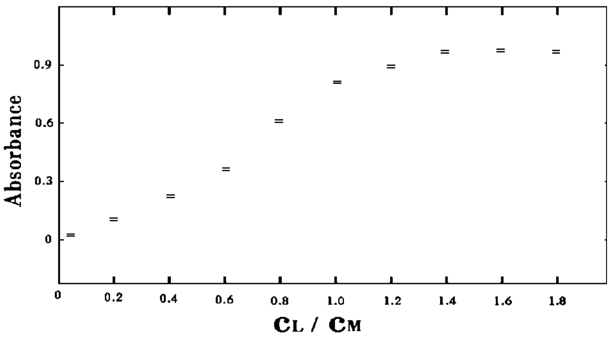

Figure 4. Computer fit of absorbance of $H_2t(4\text{-}CH_3p)p$/SbF_3 in chloroform at 670 nm and 25 °C as a function of mole ratios. (=) Experimental and calculated points are the same with the resolution of the plot.

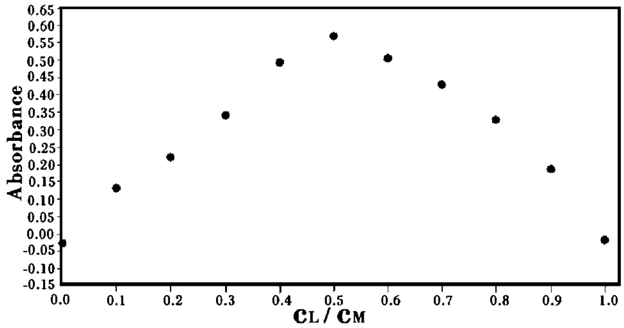

Figure 5. Continuous variation plot for $[(SbF_3)H_2t(4\text{-}CH_3p)p]$ (total concentration $= 2.8 \times 10^{-5}$ mol dm^{-3} at 25 °C and $\lambda = 671$ nm).

It is useful to consider the enthalpy and entropy contributions to these reactions, in order to have a better understanding of the thermodynamics of molecular complexation between porphyrins and SbF_3 in chloroform solution. The enthalpies and entropies of the molecular complexation reactions were determined by measuring the formation constants of the 1:1 molecular complexes as a function of temperature. All the $\log K$ values evaluated from the computer fitting of the corresponding absorbance–mole ratio data are listed in Table 2. van't Hoff plots of $\ln K$ vs. $1/T$ for all of the molecular complexes in chloroform were linear (Figure 6). ΔH^0 and ΔS^0 values were determined in the usual manner from the slopes and intercepts of the plots, respectively (Table 3).

The investigation of Table 3 shows that the nature of substitutions (X) on the aryl rings of the *meso*-tetraarylporphyrins significantly influence the interaction of the porphyrins with SbF_3. In all of the five temperatures we had the following order for formation constants (Table 2): $[(SbF_3)H_2t(4\text{-}OCH_3p)p] > [(SbF_3)H_2t(4\text{-}CH_3p)p] > [(SbF_3)H_2tpp] > [(SbF_3)H_2t(4\text{-}Clp)p] > [(SbF_3)H_2t(3\text{-}OCH_3p)p] > [(SbF_3)H_2t(3\text{-}CH_3p)p] > [(SbF_3)H_2t(2\text{-}OCH_3p)p] > [(SbF_3)H_2t(2\text{-}CH_3p)p]$. This trend is in accordance with the better electron donation (π-resonance is more significant than σ-induction effects) and lower steric effects (para > meta > ortho) for the porphyrins. For example, the ability of ortho-substituted derivatives of *meso*-tetraarylporphyrins is lower than those of meta-substituted ones. This is related to more steric hindrance for the ortho-substituted derivatives and in result lower tendency for participation of

Table 2. The Formation Constants K ($\mathrm{mol\,dm^{-3}}$) for Molecular Complexes between *meso*-Tetraarylporphyrins and SbF_3 in $CHCl_3$ Solvent

Complex		Temperature/°C				
		5	10	15	20	25
$(SbF_3)H_2$tpp	log K	7.05 (±0.01)	6.97 (±0.01)	6.91 (±0.01)	6.85 (±0.01)	6.79 (±0.01)
$(SbF_3)H_2t(4\text{-}OCH_3p)p$	log K	7.23 (±0.01)	7.13 (±0.01)	7.06 (±0.01)	6.97 (±0.01)	6.90 (±0.01)
$(SbF_3)H_2t(3\text{-}OCH_3p)p$	log K	6.92 (±0.01)	6.87 (±0.01)	6.82 (±0.01)	6.76 (±0.01)	6.72 (±0.01)
$(SbF_3)H_2t(2\text{-}OCH_3p)p$	log K	6.64 (±0.01)	6.60 (±0.02)	6.55 (±0.05)	6.51 (±0.08)	6.48 (±0.01)
$(SbF_3)H_2t(4\text{-}CH_3p)p$	log K	7.13 (±0.01)	7.04 (±0.01)	6.96 (±0.01)	6.90 (±0.01)	6.84 (±0.01)
$(SbF_3)H_2t(3\text{-}CH_3p)p$	log K	6.84 (±0.01)	6.80 (±0.01)	6.76 (±0.01)	6.70 (±0.01)	6.66 (±0.01)
$(SbF_3)H_2t(2\text{-}CH_3p)p$	log K	6.52 (±0.01)	6.49 (±0.01)	6.45 (±0.01)	6.41 (±0.01)	6.38 (±0.01)
$(SbF_3)H_2t(4\text{-}Clp)p$	log K	7.00 (±0.01)	6.95 (±0.01)	6.88 (±0.01)	6.82 (±0.01)	6.77 (±0.01)

Table 3. The Thermodynamic Parameters for $[(SbF_3)H_2t(Xp)p]$ Molecular Complexes in $CHCl_3$ Solvent

Complex	$\Delta H^0/\mathrm{kJ\,mol^{-1}}$	$\Delta S^0/\mathrm{J\,mol^{-1}\,K^{-1}}$	$\Delta G^0_{300K}/\mathrm{kJ\,mol^{-1}}$ a)
$(SbF_3)H_2$tpp	−20.22 (±0.66)	62.14 (±0.04)	−38.77 (±0.65)
$(SbF_3)H_2t(4\text{-}OCH_3p)p$	−26.30 (±0.27)	43.79 (±0.95)	−39.40 (±0.02)
$(SbF_3)H_2t(3\text{-}OCH_3p)p$	−16.40 (±0.44)	73.50 (±1.54)	−38.45 (±0.02)
$(SbF_3)H_2t(2\text{-}OCH_3p)p$	−13.07 (±0.19)	80.09 (±0.67)	−37.1 (±0.01)
$(SbF_3)H_2t(4\text{-}CH_3p)p$	−23.00 (±0.44)	53.62 (±1.52)	−39.05 (±0.02)
$(SbF_3)H_2t(3\text{-}CH_3p)p$	−14.89 (±0.94)	77.54 (±3.26)	−38.15 (±0.04)
$(SbF_3)H_2t(2\text{-}CH_3p)p$	−11.19 (±0.46)	84.61 (±1.60)	−36.57 (±0.02)
$(SbF_3)H_2t(4\text{-}Clp)p$	−18.77 (±0.77)	66.54 (±2.66)	−38.73 (±0.03)

a) The uncertainty values are calculated on the basis of $\sigma(\Delta G^0) = 1\sigma(\Delta H^0) - T\sigma(\Delta S^0)$.[14]

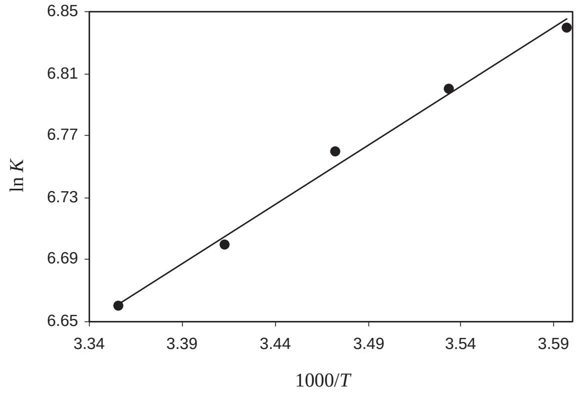

Figure 6. van't Hoff plot of ln K vs. $1000/T$ for $[(SbF_3)H_2t(3\text{-}CH_3p)p]$.

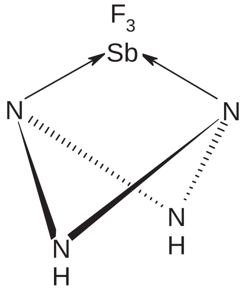

Figure 7. A saddle distortion of porphyrin core due to donating of two electron pairs of pyrrole nitrogens to an antimony atom of SbF_3. Two nitrogen atoms of pyrroles in one side of porphyrin plane act as the electron donors to antimony atom of SbF_3.

those aryl rings in the resonance of the porphyrin core. The porphyrin of $H_2t(4\text{-}Clp)p$ is a weaker donor than H_2tpp and this related to the electron withdrawing of the chloro group. Further, methoxy substituent acts as a π-donor group and the para position has lowest steric hindrance and consequently $H_2t(4\text{-}OCH_3p)p$ is the strongest donor in the trend.

These molecular complexes had negative values of ΔH^0 and ΔG^0 that indicate the strong interaction in our reaction system. The negative values of ΔH^0 and the positive value of ΔS^0 are because the formation of adduct was favorable.

UV–vis correspondences between spectral data of molecular complexes of σ- or π-acceptors with *meso*-tetraarylporphyrins (σ-electron donors) and $[(SbF_3)H_2t(Xp)p]$ lead to the proposition of similar structure for the porphyrin core in all of the species, with non-coplanar pyrrole rings tilted alternatively up and down.[1–9,15,16] This conformation causes the lone pairs of two pyrrole nitrogens to act as the electron donors to one molecule of SbF_3, that locate above or below the mean plane of the porphyrin so two hydrogen atoms of pyrroles (NHs) are located on the other side of the porphyrin plane (Figure 7). The porphyrin core of the proposed structure for $[(SbF_3)H_2t(Xp)p]$ was similar to those of dimer molecular complexes of *meso*-tetraarylporphyrins with $BiCl_3$.[1] But this study showed that $[(SbF_3)H_2t(Xp)p]$ molecular complexes had a monomer structure and the donor:acceptor mole ratio for those was 1:1 whereas $[(BiCl_3\{H_2t(Xp)p\})_2]$ molecular complexes had a mole ratio of 2:2 (donor:acceptor) and were as dimer. Furthermore, $BiCl_3$ was a weaker acceptor than SbF_3 and in result showed no interaction with ortho-substituted *meso*-tetraarylporphyrins.[1]

^{1}H NMR spectra results showed that upon the molecular complexation of $H_2t(Xp)p$ with SbF_3, the aryl ring signals

Table 4. ^{1}H NMR Spectral Data (δ) for Molecular Complexes of Different *meso*-Tetraarylporphyrins and SbF_3

Compounds	N–H	H_β	H_o	$H_{o'}$	H_m	$H_{m'}$	H_p	X
$[(SbF_3)H_2tpp]$	−2.88	8.80	8.62		8.03		8.03	—
$[(SbF_3)H_2t(4\text{-}Clp)p]$	−2.85	8.78	8.53		8.05		—	—
$[(SbF_3)H_2t(4\text{-}CH_3p)p]$	−2.52	8.72	8.56		7.85		—	2.91
$[(SbF_3)H_2t(3\text{-}CH_3p)p]$	−2.78	8.77	8.42		—	7.91	7.73	2.83
$[(SbF_3)H_2t(2\text{-}CH_3p)p]$	−3.21	8.68	—	8.30–8.32	7.74		7.86	2.06–2.16
$[(SbF_3)H_2t(4\text{-}OCH_3p)p]$	−2.45	8.66	8.54		7.56		—	4.17
$[(SbF_3)H_2t(3\text{-}OCH_3p)p]$	−2.98	8.84	8.17		—	7.92	7.54	4.17
$[(SbF_3)H_2t(2\text{-}OCH_3p)p]$	−2.98	8.72	—	8.23	7.90		7.45	3.55–3.77

are shifted downfield and the β-hydrogens upfield. These shifts were similar to the observed shifts for the molecular complexation of *meso*-tetraarylporphyrins with σ- or π-acceptors, and were related to the tilting of the porphine core in the *meso*-tetraarylporphyrins.[1–9,15,16] Further, the NH chemical shifts for the studied molecular complexes were similar to those of the porphyrins with BF_3 as electron acceptor.[5] The ^{1}H NMR data for the molecular complexes is presented in Table 4.

FT-IR (400–4000 cm^{-1}) spectra of the free base $H_2t(4\text{-}Xp)p$ show an N–H stretching band at 3320 cm^{-1}[17] that upon molecular complexation with SbF_3 does not change. Consequently there was no intramolecular or intermolecular hydrogen bonding for the N–H of $H_2t(4\text{-}Xp)p$ in $[(SbF_3)H_2t(4\text{-}Xp)p]$ molecular complex.[1]

Conclusion

The formation constants for the molecular complexes increased with the enhancement of electron donation and the steric hindrance diminution of aryl rings in the porphyrins. The ΔG^0 for the molecular complexes were negative values. This indicated that the formation of adduct between the porphyrin and SbF_3 is favorable. In the molecular complexes, the lone pairs of two pyrrole nitrogens acted as electron donors to one molecule of SbF_3. In the proposed structure two hydrogen atoms of pyrrole (N–H) are located on one side of the porphyrin plane and there is no hydrogen bonding in the molecular complex.

Experimental

For the synthesis and purification of porphyrin and its derivatives, distilled pyrrole (Merck), benzaldehyde and para-, meta-, and ortho-substituted benzaldehydes (Merck), propionic acid and chloroform (Merck) were used. Chloroform solvent for UV–vis measurements was distilled over K_2CO_3 before use. Antimony(III) fluoride was obtained from Merck, and used as received. Porphyrin and para-, meta-, and ortho-substituted porphyrins were prepared and purified by usual methods.[18–20]

Molecular complexes of the porphyrins with SbF_3 in chloroform solvent were prepared. Firstly, the solutions of H_2tpp (7×10^{-5} mol dm^{-3}) and SbF_3 (7×10^{-5} mol dm^{-3}) were provided separately. Then, on the basis of mole ratio method,[21] different amounts of the porphyrin solution were added to fixed amounts of SbF_3 solution and all of the solutions brought to the specified volume and 12 solutions with different C_L/C_M mole ratios were obtained. The absorbance of the solutions was measured and the plots of absorbance vs. C_L/C_M were obtained. UV–vis spectra of the solutions were taken for 5 different temperatures (5, 10, 15, 20, and 25 °C). The formation constants of 1:1 molecular complexes (ML) produced as a result of the interactions between *meso*-tetraphenylporphyrin or its derivatives (L) and SbF_3 (M) in solution were calculated by fitting the absorbance as a function of porphyrin/SbF_3 mole ratios. The mass balance equation for formation of ML, was solved in order to obtain an equation for free acceptor concentration [M]. The resulting equation is:

$$K[M]^2 + (1 + K(C_L - C_M)[M] - C_M = 0, \qquad (1)$$

where K is the formation constant for the 1:1 complex, C_L and C_M are the analytical concentrations of porphyrin and SbF_3, respectively. It has been shown that the observed absorbance of solution is also given by:

$$A_{obs} = \varepsilon_L[L] + \varepsilon_{ML}[ML], \qquad (2)$$

where ε_L and ε_{ML} are the respective molar absorptivity of the free and complexed porphyrin.

The non-linear least-squares curve-fitting program KINFIT,[22] based on Powell's technique,[23] and was used to evaluate the formation constants of the resulting complexes. The free SbF_3 concentrations, [M], were calculated by means of a Newton–Raphson procedure by using the estimated values K and ε at the current iteration step of the program. Then, by using the calculated value of [M] and all estimated parameters, the absorbance was calculated from eq 2. Refinement of the parameters was continued until the sum-of-squares of the residuals between calculated and observed values of absorbance for all experimental points were minimized.

Equilibrium constants can be expressed in terms of the Gibbs free energy change for the reaction:[24,25]

$$K_f = \exp(-\Delta G^0/RT) = \exp(-\Delta H^0/RT + \Delta S^0/R), \qquad (3)$$

where ΔH^0 is the enthalpy change and ΔS^0 is the entropy change for the reaction, and R is the universal gas constant.

UV–vis measurements were carried out in a GBC Cintra 6 UV–vis spectrometer equipped with a Lauda Ecoline RE204 thermostat. The ^{1}H NMR spectrum was recorded on a Bruker 400 Ultrashield spectrometer in $CDCl_3$. The residual $CHCl_3$ in the conventional 99.8% atom $CDCl_3$ gives a signal at δ 7.26, which was used for calibration of the chemical shift scale. FT-IR spectrum was recorded on a Magna 550 Nicolet spectrometer using KBr pellets.

This work was supported by Kashan University Research Council.

References

1 H. Dehghani, A. R. Ansari Sardrood, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 518.

2 H. Dehghani, A. R. Ansari Sardrood, *Polyhedron* **2007**, *26*, 4263.

3 H. Dehghani, F. Fathi, *Dyes Pigm.* **2008**, *77*, 323.

4 D. Mohajer, S. Rayati, *New J. Chem.* **2003**, *27*, 242.

5 D. Mohajer, S. Zakavi, S. Rayati, M. Zahedi, N. Safari, H. R. Khavasi, S. Shahbazian, *New J. Chem.* **2004**, *28*, 1600.

6 M. Asadi, A. Zabardasti, J. Ghasemi, *Polyhedron* **2002**, *21*, 683.

7 M. Asadi, A. Zabardasti, V. Karimvand, J. Ghasemi, *Polyhedron* **2002**, *21*, 1255.

8 M. Asadi, A. Zabardasti, J. Ghasemi, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1137.

9 A. Zabardasti, M. Mirzaeian, *Chem. Lett.* **2006**, *35*, 1348.

10 a) E. B. Fleischer, J. H. Wang, *J. Am. Chem. Soc.* **1960**, *82*, 3498. b) J. P. Macquet, T. Theophanides, *Can. J. Chem.* **1973**, *51*, 219. c) K. Letts, R. A. Mackay, *Inorg. Chem.* **1975**, *14*, 2990. d) M. Inamo, N. Kamiya, Y. Inada, M. Nomura, S. Funahashi, *Inorg. Chem.* **2001**, *40*, 5636. e) Y. Inada, Y. Nakano, M. Inamo, M. Nomura, S. Funahashi, *Inorg. Chem.* **2000**, *39*, 4793. f) Y. Inada, Y. Sugimoto, Y. Nakano, Y. Itoh, S. Funahashi, *Inorg. Chem.* **1998**, *37*, 5519. g) M. Inamo, T. Kohagura, I. Kaljur, I. Leito, *Inorg. Chim. Acta* **2002**, *340*, 87. h) Y. Hsiao, U. Ryde, *Inorg. Chim. Acta* **2006**, *359*, 1081. i) Z. Valicsek, O. Horvath, *J. Photochem. Photobiol., A* **2007**, *186*, 1.

11 P. Job, *Ann. Chim.* **1928**, *9*, 113.

12 M. Shamsipur, A. Avanes, M. K. Rofouei, H. Sharghi, G. Aghapour, *Talanta* **2000**, *52*, 637.

13 R. Winkler, *Struct. Bonding* **1972**, *10*, 1.

14 G. Binsch, H. Kesster, *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 411.

15 D. Mohajer, H. Dehghani, *J. Chem. Soc., Perkin Trans. 2* **2000**, 199.

16 D. Mohajer, H. Dehghani, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1477.

17 H. H. Limbach, J. Henning, J. Stulz, *J. Chem. Phys.* **1983**, *78*, 5432.

18 A. M. d'A. Rocha Gonsalves, J. M. T. B. Varejao, M. M. Pereira, *J. Heterocycl. Chem.* **1991**, *28*, 635.

19 A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour, L. Korsakoff, *J. Org. Chem.* **1967**, *32*, 476.

20 G. H. Barnett, M. F. Hudson, K. M. Smith, *Tetrahedron Lett.* **1973**, *14*, 2887.

21 J. D. Ingle, S. R. Crouch, *Spectrochemical Analysis*, **1988**.

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

23 M. R. Johnson, I. O. Sutherland, R. F. Newton, *J. Chem. Soc., Perkin Trans. 1* **1979**, 357.

24 M. L. Honkela, T. Ouni, A. O. I. Krause, *Ind. Eng. Chem. Res.* **2004**, *43*, 4060.

25 M. S. Masoud, H. H. Hammud, H. Beidas, *Thermochim. Acta* **2002**, *381*, 119.