

Thermodynamic Study of the Interaction of Co(II)-Schiff Base Complexes with Phosphines

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The equilibrium constants and the thermodynamic parameters for the interaction of CoL^x ($\text{L}^1 = 5\text{-OMe-salabza}$, $\text{L}^2 = \text{salabza}$, $\text{L}^3 = 5\text{-Br-salabza}$ and $\text{L}^4 = 5\text{-NO}_2\text{-salabza}$) as acceptors, with phosphines (PBu_3 , PPh_2Me) as donors in dichloromethane were studied. This was performed by using UV-Vis spectrophotometry titration for 1:1 adduct formation of the selected complexes at various temperatures ($T = 283\text{-}298\text{ K}$). The trend of the adduct formation of the Co(II) complexes with a given phosphine donor decreases as $\text{CoL}^1 > \text{CoL}^2 > \text{CoL}^3 > \text{CoL}^4$. The stability of the resulting adducts with different Co(II)-schiff base complexes found to decrease in the order $\text{PBu}_3 > \text{PPh}_2\text{Me}$.

Keywords: Cobalt, Schiff base, Equilibrium constant, Thermodynamic parameters

INTRODUCTION

The function of metal ions in natural biological systems depends on the structural arrangement of the coordination sphere and the electronic environment of the ligand [1-4]. Schiff base ligands have gained importance because of the physiological and pharmacological activities associated with them. They constitute an interesting class of chelating agents capable of coordinating metal ions given complexes which serve as models for biological systems [1,5,6].

Cobalt complexes, besides their presence in several stereochemical dispositions, are oxygen carriers and oxygen activators [7-10] which interact with molecular oxygen and ultimately oxidize the complexes of Co(II) to Co(III). The best known biological function of cobalt is its involvement in the coenzyme related to vitamin B₁₂ [1,11-15]. Thus, the chemistry of cobalt Schiff base complexes has aroused great

interest and it is shown that such ligands can stabilize cobalt complexes.

To pursue our previous work [16-21], in this paper we report the results of the thermodynamic study of the interaction of some four-coordinate Co(II)-Schiff base complexes with tributylphosphine (PBu_3) and diphenylmethylphosphine (PPh_2Me) in dichloromethane.

EXPERIMENTAL

Materials and Apparatus

All solvents and chemicals were purchased from Merck, Fluka or Aldrich and used without further purification. All of the scanning UV-Vis spectra were recorded on a Perkin-Elmer Lambda 2 spectrophotometer equipped with a LAUDA ecoline RE 104 thermostat.

Synthesis of the Complexes

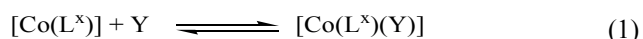
The ligands and the Co(II) complexes were prepared by

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the method described previously [22]. The general procedure for the synthesis of Co(II) complexes is as follows: to a refluxing solution of a ligand (1.0 mmol) in appropriate solvent (CHCl₃ for HL¹, HL², HL³ and CH₃OH:DMF 1:1 for HL⁴) in ambient condition, 1.0 mmol of Co(CH₃COO)₂·4H₂O was added. The mixture was refluxed for 2 h and the solvent evaporated in vacuum. The product was washed with water and cold methanol (Scheme 1).

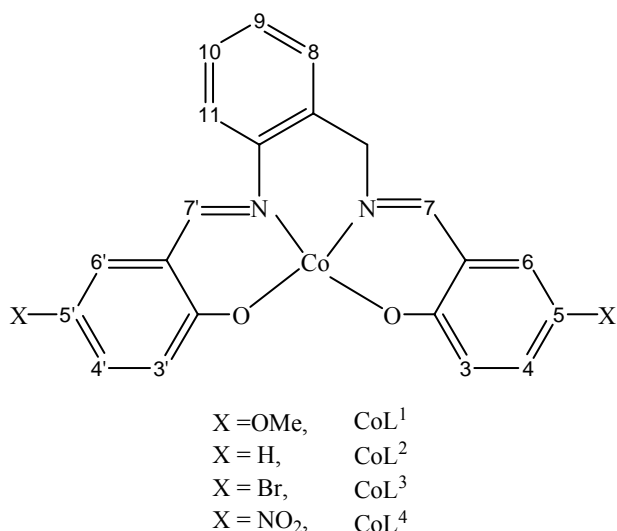
Thermodynamic Studies

The adducts were obtained from the reaction of the acceptors with the donors according to Eq. (1):



where L^x is the deprotonated form of H₂L¹, H₂L², H₂L³, H₂L⁴ and Y is PBu₃, PPh₂Me.

The equilibrium constant measurements were carried out by spectrophotometric titration at 10, 15, 20 and 25 (±0.1) °C. In a typical measurement, 3 ml solution of [CoL^x] in dichloromethane was titrated with phosphine solution in the same solvent. The titration was carried out by adding aliquots of phosphine with Hamilton microlitre syringe. The donor concentrations were varied one-to-ten fold in excess. UV-Vis spectra were recorded in the range 200-700 nm about 5 min after each addition.



Scheme 1

RESULTS AND DISCUSSION

Sample electronic spectra for titration of [CoL³] with tributylphosphine in dichloromethane are shown in Fig. 1. As is obvious, no notable change is observed when more than ten-fold excess of phosphine was added. Furthermore, the observation of sharp isosbestic points suggests that there is only two species in equilibrium, indicating the formation of a single product in solution. Moreover, the electronic spectra of the adduct formed at the end of the titration process was the same as the electronic spectra of the separately synthesized adduct (see Fig. 2). The same procedure was followed for other systems.

The absorption measurements were carried out at various wavelengths in the spectral range 250-350 nm, where the difference in absorption between the Co(II) substrate and the product was the largest after the equilibrium was attained.

Thermodynamic Interpretations

The equilibrium constants K of various cobalt(II) Schiff base complexes with phosphines donors were calculated using Ketelaar's Eq. (2) [23]

$$(\overset{\circ}{C}_A \overset{\circ}{C}_D) / (A - A_A - A_D) = (1 / (\varepsilon_C - \varepsilon_A - \varepsilon_D)) \cdot [(1/K) + (\overset{\circ}{C}_A \overset{\circ}{C}_D)] \quad (2)$$

where $\overset{\circ}{C}_A$ and $\overset{\circ}{C}_D$ are the initial molar concentrations of the acceptor and the donor, respectively; A is the optical density of the solution including the acceptor and the donor, A_A and A_D are the absorbances of the pure acceptor $\overset{\circ}{C}_A$ and the pure donor $\overset{\circ}{C}_D$ in the solution of concentration, respectively, and ε_C , ε_A and ε_D are the respective molar absorption coefficients ($\text{M}^{-1} \text{cm}^{-1}$) of the complex, the pure acceptor and the pure donor. A plot of $(\overset{\circ}{C}_A \overset{\circ}{C}_D) / (A - A_A - A_D)$ vs. $(\overset{\circ}{C}_A \overset{\circ}{C}_D)$ should produce a straight line if only a 1:1 complex is formed; while a mixture of 1:1 and 1:2 or only 1:2 complex in a system would lead to a curve. The equilibrium constants of the studied cobalt(II) Schiff base adducts were calculated from the ratio of the slope to the intercept by least square method using Microsoft Excel 2003 computer software. The K measurements were repeated at least twice and found to be reproducible. The linear plots for [CoL¹] titrated with PPh₂Me at various temperatures in dichloromethane are shown in Fig. 3, which signify that only a

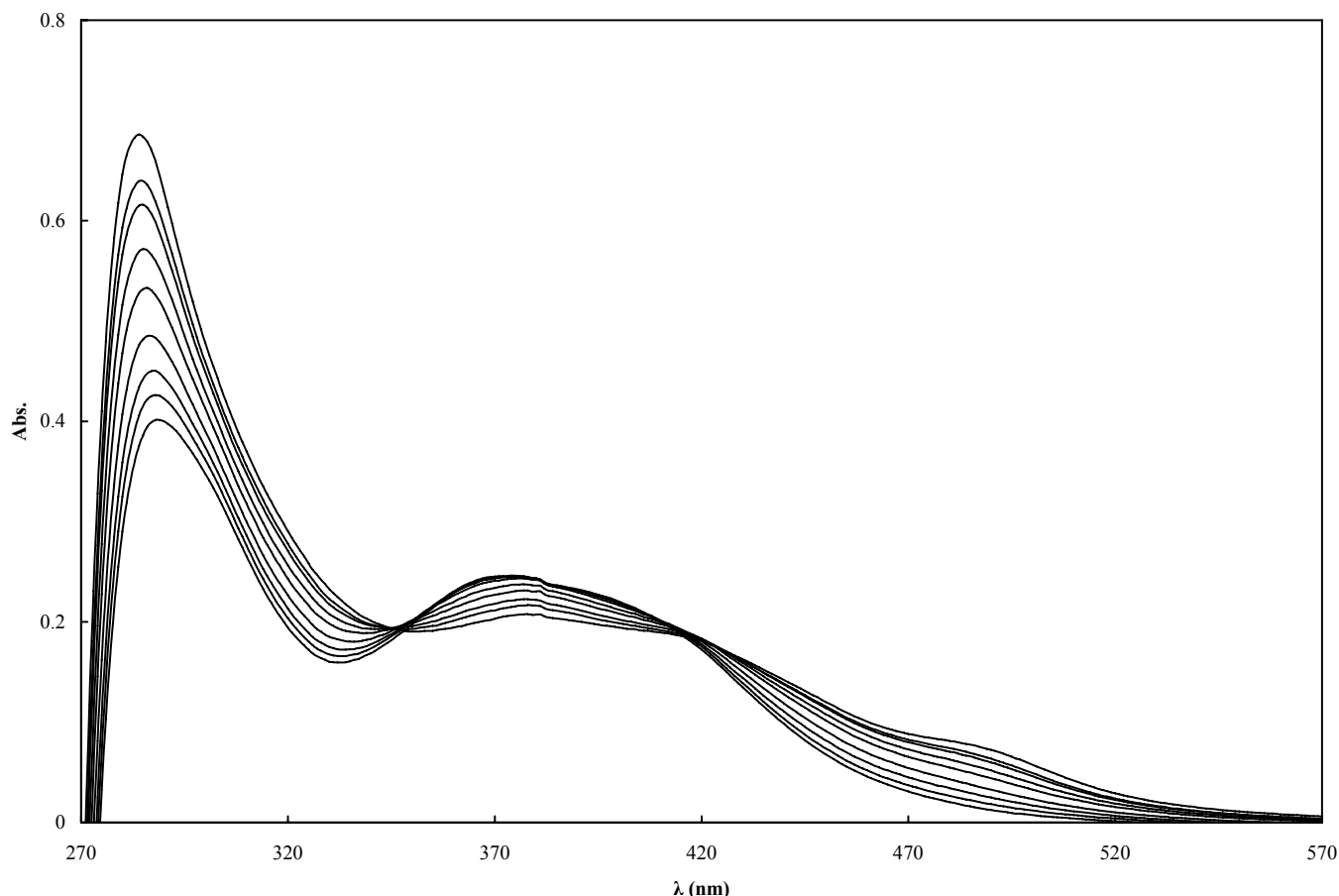


Fig. 1. Variation of electronic spectrum of $[\text{CoL}^3]$ with PBU_3 in CH_2Cl_2 at 10°C .

1:1 adduct is formed. Similar plots are obtained for other systems.

The thermodynamic parameters of the studied complexes with phosphines were obtained using the well-known van't Hoff Eq. (3)

$$\ln K = (-\Delta H^\circ/RT) + (\Delta S^\circ/R) \quad (3)$$

where K is the equilibrium constant, R is the gas constant and T is the temperature in Kelvin. The values of ΔH° and ΔS° were obtained from the slope and the intercept of the linear plots of $\ln K$ against $1/T$ (Fig. 4), respectively. The equilibrium constants and thermodynamic parameters data are presented in Tables 1 and 2.

We have already reported the synthesis and spectroscopic

characterization of $[\text{CoL}^x]$ Schiff base complexes [22]. There was no evidence of the interaction of these compounds with phosphine donors in the solution and their tendency to form the adducts. The goal of this study was to find the effect of the electronic and the steric parameters of the donors and the acceptors on the equilibrium constants and the thermodynamic parameters of the interaction of the $[\text{CoL}^x]$ complexes as acceptors with PBU_3 and PPh_2Me as donors. The results given in Table 1 show that the equilibrium constants and the interaction between the donors and the acceptors are related to the type of Schiff base, phosphine and the temperature.

Electronic Effect of Equatorial Schiff Base Ligands

It has been suggested [24] that when cobalt ion is chelated in a macrocycle having delocalized electronic structure, the

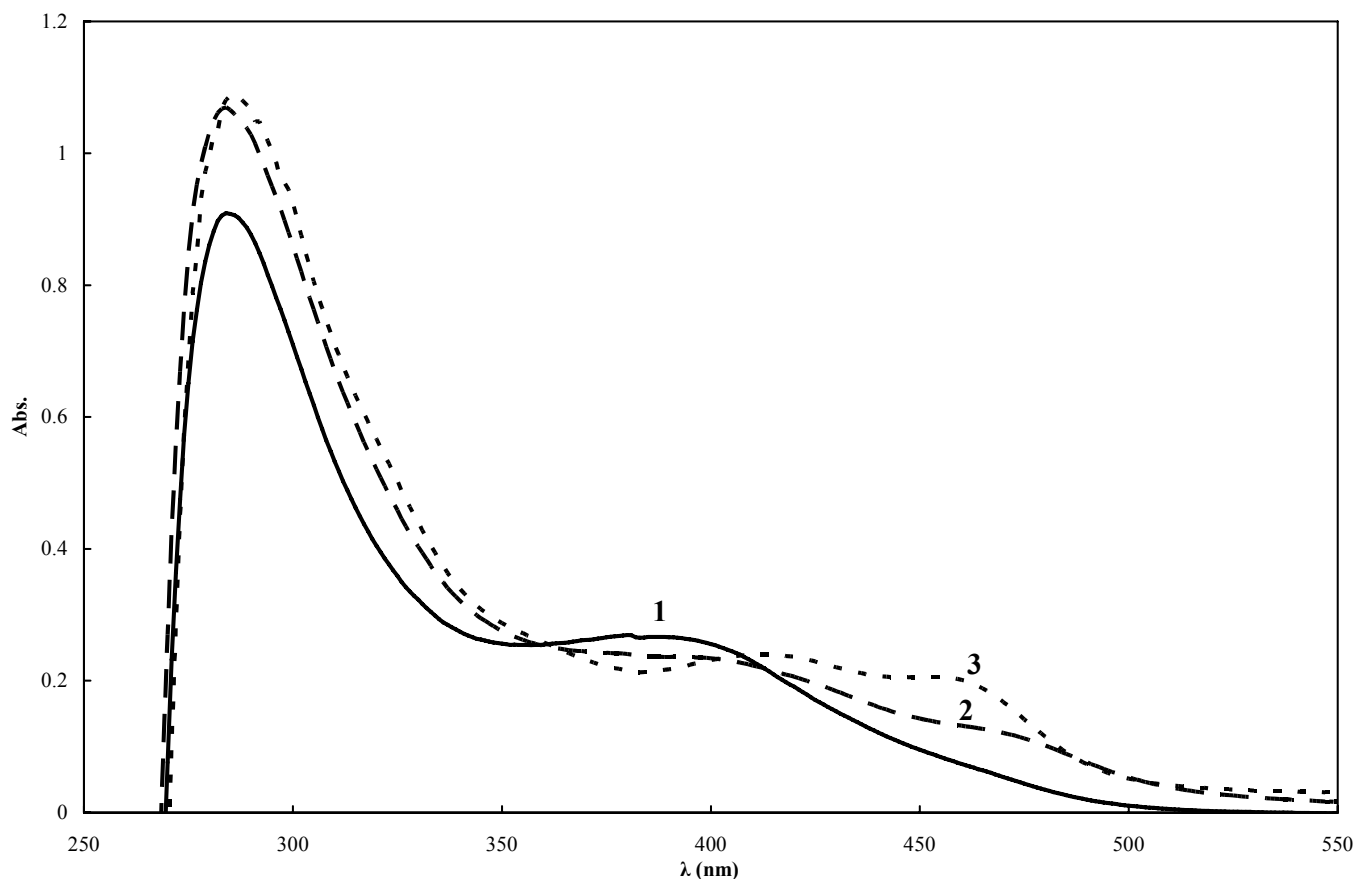


Fig. 2. The electronic spectra of $[\text{CoL}^2]$ (1), the end point of titration of complex with PBU_3 (2), separately synthesized $[\text{CoL}^2\text{PBU}_3]$ adduct (3) in dichloromethane.

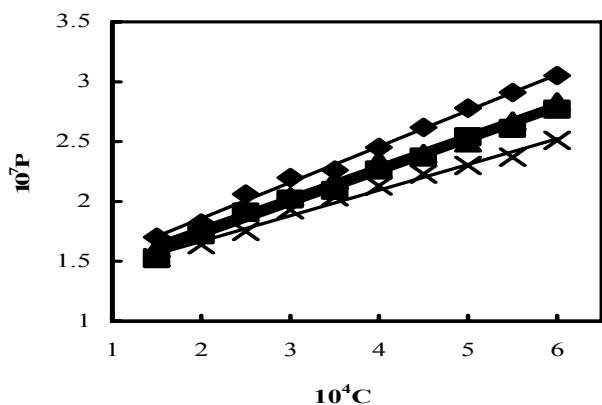


Fig. 3. Typical plots of P against C for $[\text{CoL}^1]$ with PPh_2Me at various temperatures ($T = 283\text{-}298$) K in dichloromethane. $P = C_A^\circ \times C_D^\circ / (A - A_A^\circ - A_D^\circ)$ and $C = (C_A^\circ + C_D^\circ)$: (♦) 283, (■) 288, (▲) 293 and (×) 298.

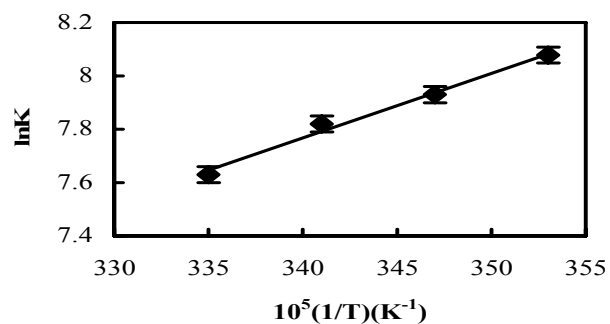


Fig. 4. Plots of $\ln K$ vs. $1/T$ (K^{-1}) for $[\text{CoL}^1]$ with PPh_2Me .

complex obtained might be kinetically labile. The extent to which this happens is likely to be strongly dependent on the structure of the planar chelating system acting as acceptor of the donated charge. The steric and the electronic effects of the

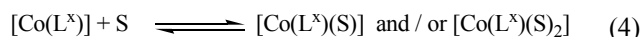
Table 1. The Equilibrium Constants for Co(II) Complexes with PBU₃ and PPh₂Me in CH₂Cl₂ at Different Temperatures

	T (K)	Co(L ¹)	Co(L ²)	Co(L ³)	Co(L ⁴)
PBU ₃	283	7579.1 ± 7.2 × 10 ²	5305.9 ± 3.4 × 10 ²	3779.3 ± 1.1 × 10 ³	2977.3 ± 1.4 × 10 ²
	288	6836.6 ± 7.4 × 10 ²	4177.4 ± 3.9 × 10 ²	2466.2 ± 9.0 × 10 ²	2396.6 ± 2.1 × 10 ²
	293	6094.1 ± 7.1 × 10 ²	3390.3 ± 5.4 × 10 ²	1809.1 ± 1.5 × 10 ³	1777.7 ± 1.3 × 10 ²
	298	5576.6 ± 3.4 × 10 ²	2838.9 ± 5.4 × 10 ²	1714.4 ± 2.3 × 10 ³	1607.6 ± 6.1 × 10 ²
PPh ₂ Me	283	3222.8 ± 3.7 × 10 ²	2442.2 ± 4.5 × 10 ²	1844.7 ± 9.1 × 10 ¹	1725.6 ± 9.6 × 10 ¹
	288	2775.6 ± 2.5 × 10 ²	1990.1 ± 1.7 × 10 ²	1543.8 ± 6.9 × 10 ¹	1493.0 ± 3.6 × 10 ²
	293	2480.7 ± 1.8 × 10 ²	1409.2 ± 7.0 × 10 ¹	1208.5 ± 7.6 × 10 ¹	1188.5 ± 2.6 × 10 ²
	298	2066.5 ± 1.7 × 10 ²	1243.7 ± 7.1 × 10 ¹	1052.9 ± 2.3 × 10 ²	991.8 ± 6.9 × 10 ²

Schiff base and the axial ligands on the equilibrium constants were investigated in our laboratory, previously [16-21].

In the present work, the order of the adduct formation constant with a given phosphine was formed to follow the trend: [CoL¹] > [CoL²] > [CoL³] > [CoL⁴].

These K values for electron releasing methoxy Schiff bases (L¹) were more than those for the electron withdrawing bromo (L³) and nitro (L⁴) Schiff bases (Table 1). As for the stabilization of four-coordinated Co(II) complexes, the donation power of Schiff base is important; therefore the cobalt atom in [CoL⁴] has more acceptor properties than the cobalt atom in [CoL³], [CoL²] and [CoL¹]. Accordingly, [CoL⁴] forms more stable adduct with the solvent molecule (Eq. 4), so its tendency to react with the phosphine donor decreases. Therefore, the replacement of the solvent molecule in the fifth position by the phosphine donor is more difficult in [CoL⁴] compared to the [CoL¹], and its adduct formation constants with phosphines are lower.



Effect of the Nature of Donors

In this work, we have examined two donors: PBU₃ and PPh₂Me. Phosphine ligands have an important steric factor that is shown by Tolman's cone angle. The "cone angle" is

defined as the apex angle of the cone, centred at the metal atom, just enclosing the van der Waals radii of the ligand atoms whose the cone angles for PPh₂Me and PBU₃ are 136° and 132°, respectively [25]. The steric effect increases with an increase in cone angle. So by increasing the cone angle in PPh₂Me, the formation constant is decreased.

The electronic effects of the phosphines have been expressed by σ* values of Taft (Taft constants). σ* value for PBU₃ is -0.390 but for PPh₂Me this value is not reported in literature (note that for PPh₂Et σ* value is +1.10 and for PPhMe₂ it is +0.60) [26-28]. Also, the phenyl withdrawing groups decrease the basic properties of PPh₂Me compared to PBU₃. The equilibrium constants for a given complex increased according to the following trend of phosphines: PBU₃ > PPh₂Me. Therefore, both the steric and the electronic properties affect the equilibrium constant of the adducts formation.

Effect of Temperature on Adduct Formation

The equilibrium constants were carried out at various temperatures. Because of bond formation, by increasing the temperature, the formation constants were decreased.

In general, the ΔH° value and its sign is dependent on the solvation effect and the heat of adduct formation [28]. According to the results (Table 2), the enthalpy values for all

Table 2. The Thermodynamic Parameters for Different Co(II) Complexes with PBU₃ and PPh₂Me

		Co(L ¹)	Co(L ²)	Co(L ³)	Co(L ⁴)
PBU ₃	ΔH° (kJ mol ⁻¹)	-40.1 ± 4.1	-29.3 ± 1.1	-46.2 ± 3.3	-30.2 ± 3.6
	ΔS° (J K ⁻¹ mol ⁻¹)	-62.7 ± 1.4	-32.2 ± 3.6	-93.9 ± 7.5	-41.3 ± 2.3
	ΔG° (kJ mol ⁻¹) ^a	-21.4 ± 0.6	-19.7 ± 1.5	-18.2 ± 4.8	-17.9 ± 5.2
PPh ₂ Me	ΔH° (kJ mol ⁻¹)	-38.6 ± 1.4	-33.3 ± 3.8	-27.1 ± 1.8	-26.5 ± 1.7
	ΔS° (J K ⁻¹ mol ⁻¹)	-65.7 ± 1.4	-52.7 ± 3.2	-33.0 ± 6.3	-31.5 ± 5.8
	ΔG° (kJ mol ⁻¹) ^a	-19.0 ± 2.1	-17.6 ± 5.5	-17.2 ± 2.6	-17.1 ± 2.4

ΔG° is calculated from $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ and T = 298 K.

Co(II) complexes are negative because of bond formation in all reactions. The solvation effect for four- and five-coordinated complexes are not very different due to similar charges, but it seems that the five-coordinated complex is better solvated because of the polarity. The five-coordinated complex is more polarized than the four-coordinated complex and it is better solvated. The solvation contribution for ΔH° can be negative after the equilibrium. In all cases, ΔH° values are negative (Table 2).

The value of the ΔS° and its sign are dependent on the difference in the number of the particles of the initial substances and the product complexes, and the liberation of the solvent molecules from the solvation shells [29]. The n for all studied systems is -1. Concerning this factor, the entropy decreases and its sign is negative. With respect to the second factor, the more involvement of the solvent molecules in five-coordinated complex leads to more negative ΔS° . The net entropy change for all reactions is negative and this emphasizes the importance of both of the factors (see Table 2).

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