

Thermodynamics of Cobalt(III) Schiff Base Complexes in Various Solvents

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The electronic and steric effects of some Schiff bases and the solvent on the thermodynamic parameters of the pentacoordinate Co(III) Schiff base complexes were studied. The formation constants and the thermodynamic parameters were measured spectrophotometrically for 1:1 adduct formation of the complexes as acceptors with tributylphosphine (PBU₃) as donor, in some solvents (acetonitrile, tetrahydrofuran, butanol, ethanol and N,N-dimethylformamide) in constant ionic strength (I = 0.01 M, sodium perchlorate) and at various temperatures. The trend of the reactivity of the pentacoordinate cobalt(III) Schiff base complexes toward tributylphosphine according to the solvent is as follows: acetonitrile > tetrahydrofuran > butanol > ethanol > N,N-dimethylformamide. The trend of the reactivity of pentacoordinate cobalt(III) Schiff base complexes toward the donor in a given solvent according to the equatorial Schiff base is as follows: BBE > BAE > Salen.

Keywords: Schiff base, Thermodynamics, Cobalt complex, Phosphine

INTRODUCTION

The Schiff base compounds constitute an important class of ligands which have been extensively studied in coordination chemistry. The nature of the effect of one ligand and its transmission to another ligand through the central metal ion is very important in coordination chemistry. These interactions can be observed in the thermodynamic and the kinetic aspects of the chemical reactivity.

Schiff bases are useful constructing supra molecular structures [1-3]. Schiff base complexes are also known for their significant biological activities such as photosynthesis and transport of oxygen in mammalian and other respiratory systems [4,5]. A wide variety of cobalt(II) complexes are known to bind dioxygen, more or less reversibly, and therefore frequently studied as model compounds for natural oxygen carriers and for their use in O₂ storage, as well as in organic

synthesis due to their catalytic properties under mild conditions [6]. Metal Schiff base complexes are well known catalysts, both in heterogeneous and homogeneous systems. Other applications of these complexes are reported, such as the stereoselective alkene epoxidation [7-9], the asymmetric addition of organometallic reagents to aldehydes [10] and asymmetric hetero Diels-Alder reactions [11].

We hereby report the thermodynamic studies of [Co(BAE)(PBU₃)]ClO₄.H₂O, [Co(BBE)(PBU₃)]ClO₄.H₂O and [Co(Salen)(PBU₃)]ClO₄.H₂O in five solvents with tributylphosphine(PBU₃) in constant ionic strength (I = 0.01 M) and at various temperatures with the goal of solvent effect and evaluation of the effect of equatorial ligand on electronic and steric properties (Fig. 1).

EXPERIMENTAL

Materials and Apparatus

The materials were ethylenediamine, acetylacetone,

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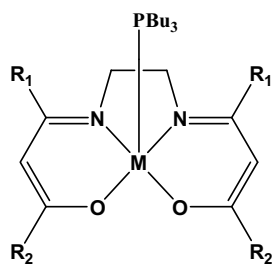


Fig. 1. The structure of $[\text{CoL}(\text{PBu}_3)]\text{ClO}_4$ complexes. $\text{R}_1 = \text{R}_2 = \text{H}$: $[\text{CoBAE}(\text{PBu}_3)]^+$ and $\text{R}_1 = \text{H}$, $\text{R}_2 = \text{Ph}$: $[\text{CoBBE}(\text{PBu}_3)]^+$.

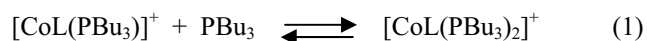
benzoylacetone, salicylaldehyde, cobalt(II) acetate, tetrahydrate, tributylphosphine, ethanol, butanol, acetonitrile, N,N-dimethylformamide, tetrahydrofuran and sodium perchlorate, all of which were obtained from Merck, Fluka and Aldrich. All of the scanning UV-Vis spectra were recorded by Jasco V-530 spectrophotometer. The NMR spectra were recorded by Bruker Avance DPX 250 MHz spectrometer; IR spectra were recorded by Perkin Elmer Infrared spectrophotometer. Elemental microanalysis (C.H.N), was performed using a Heraeus CHN-O-RAPID elemental analysis.

Synthesis of the Ligands and Complexes

The ligands bis(acetylacetonethylendiimine) (BAE), salicylaldehydeethylendiimine (Salen) and (BBE), bis(benzoylacetoneethylendiimine) were prepared according to the literature [12,13]. The $[\text{CoBAE}(\text{PBu}_3)]\text{ClO}_4 \cdot \text{H}_2\text{O}$, $[\text{CoSalen}(\text{PBu}_3)]\text{ClO}_4 \cdot \text{H}_2\text{O}$, $[\text{CoBBE}(\text{PBu}_3)]\text{ClO}_4 \cdot \text{H}_2\text{O}$ were prepared by methods described previously [12,14].

Thermodynamic Studies

The formation constants of the 1:1 adducts were determined by UV-Vis absorption spectrophotometry from the reaction of the acceptors with the donor, according to equation (1):



where L = BAE, BBE and Salen. The formation constants, K, were determined by spectrophotometric titration of the monophosphine complexes with tributylphosphine in five solvents, *i.e.* acetonitrile, tetrahydrofuran (THF), butanol,

ethanol and N,N-dimethylformamide (DMF).

A solution from each complex with concentration at about 10^{-4} M and constant ionic strength ($I = 0.01$ M by sodium perchlorate) was prepared. A total of 2.5 ml was transferred to the thermostated cell compartment of UV-Vis instrument, kept at constant temperature (± 0.1 °C), by circulating water and titrated by tributylphosphine. The titration was carried out by adding aliquots of tributylphosphine with a Hamilton microlitre syringe. The donor concentrations were varied one-to-ten fold in excess.

Electronic Spectra

The electronic spectra of all the studied complexes show an absorption band at 600-700 nm in noncoordinated solvents that indicate the five coordinated structure for them. All complexes show an intensive absorption band at 350-370 nm ($\pi \rightarrow \pi^*$). During the reactions, a new absorption band (440-500 nm, $d \rightarrow \pi^*$) appeared and the absorption band at 600-700 nm vanished. The isosbestic point was observed at 615 nm (Fig. 2). The isosbestic point shows that there is one equilibrium system in the adduct formation. All measurements for the thermodynamic studies were carried out in 450-500 nm (Table 1).

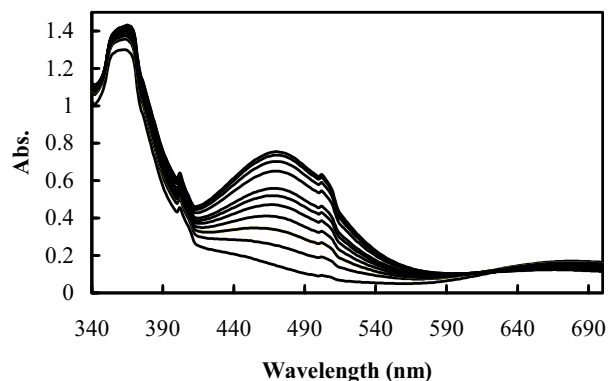


Fig. 2. The spectral titration curve of $[\text{Co}(\text{BAE})(\text{PBu}_3)]\text{ClO}_4$ with PBu_3 in THF.

RESULTS AND DISCUSSION

The formation constants of the various Co(III) Schiff base complexes were calculated by Ketelaar's Eq. (2) [16].

Table 1. The Fixed Wavelengths in Various Systems

Complexes	Wavelengths selected (λ , nm)
[Co(BAE)(PBU ₃) ⁺	475, 470, 465, 460, 455, 450
[Co(BBE)(PBU ₃) ⁺	500, 495, 490, 485, 480, 475
Co(Salen)(PBU ₃) ⁺	500, 495, 490, 485, 480, 475

$$\frac{C_A^{\circ}C_D^{\circ}}{A-A_A^{\circ}-A_D^{\circ}} = \frac{1}{(\varepsilon_C-\varepsilon_A-\varepsilon_D)} \times \left[\frac{1}{K} + (C_A^{\circ}+C_D^{\circ}) \right] \quad (2)$$

where C_A° and C_D° are the initial concentrations of the acceptor and the donor, respectively; A is the optical density of the solution including the acceptor, the donor and the adduct complex, A_A° and A_D° are the optical densities of the pure acceptor and the pure donor in the pure solution of concentration C_A° and C_D° ; ε_C , ε_A and ε_D are the molar extinction coefficients of the complex, the acceptor and the donor, respectively. K is the formation constant of the complex formed and cell optical path is 1 cm. A plot of $P = C_A^{\circ}C_D^{\circ}/(A-A_A^{\circ}-A_D^{\circ})$ vs. $C = (C_A^{\circ}+C_D^{\circ})$ should produce a straight line if only 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 [19]. The isobestic point and the mole ratio curve show only 1:1 complex formed (Fig. 3).

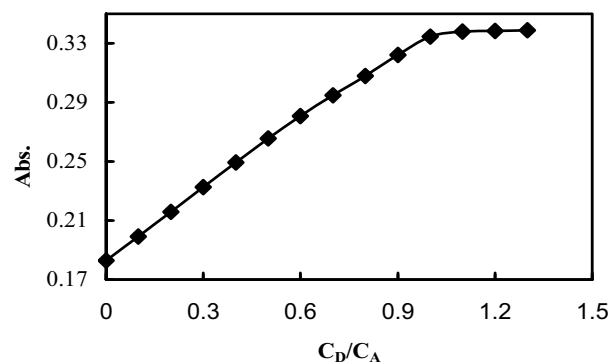
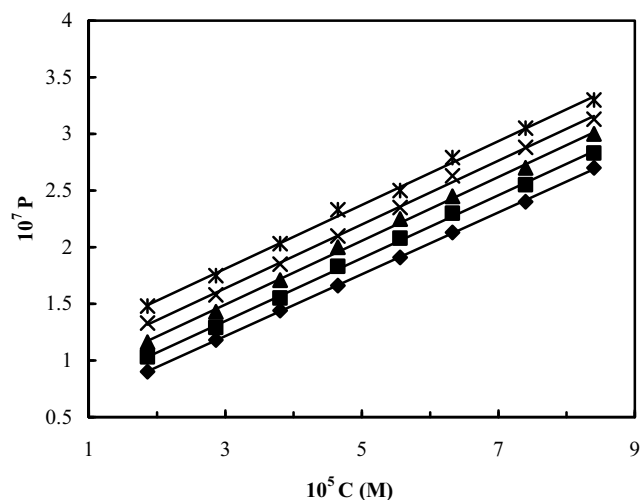
The formation constants of the studied cobalt(III) Schiff base complexes were calculated from the ratio of the slope to the intercept. The K value for multifixed wavelengths systems was carried out from mean of K values calculated for each wavelength (Table 1).

The linear plot of P vs. C for [Co(BBE)(PBU₃)ClO₄] with tributylphosphine at various temperatures is shown in Fig. 4.

The thermodynamic parameters of the studied cobalt(III) Schiff base complexes were calculated by the use of the well-known, van't Hoff equation:

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

where K is the formation constant, R is the gas constant and T is the temperature in Kelvin scale. Thermodynamic parameters of the studied cobalt(III) Schiff base complexes were obtained


Fig. 3. Mole ratio of [Co(BAE)(PBU₃)] with PBU₃ in acetonitrile.

Fig. 4. Plots of P vs. C for [Co(BBE)(PBU₃)ClO₄] with PBU₃ at various temperatures ($t = 20-40$ °C) in THF. $P = C_A^{\circ}C_D^{\circ}/(A-A_A^{\circ}-A_D^{\circ})$ and $C = (C_A^{\circ}+C_D^{\circ})$: (◆) $t = 20$, (■) $t = 25$, (▲) $t = 30$, (×) $t = 35$ and (*) $t = 40$.

from the linear plots of $\ln K$ vs. $1/T$. The linear plot for [Co(BBE)(PBU₃)⁺ with tributylphosphine at various temperatures in THF is shown in Fig. 5.

The values of ΔH° and ΔS° were obtained from the slope and the intercept, respectively, by using Excel computer program. The values of ΔG° of complex formations were obtained from Eq. (4):

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (4)$$

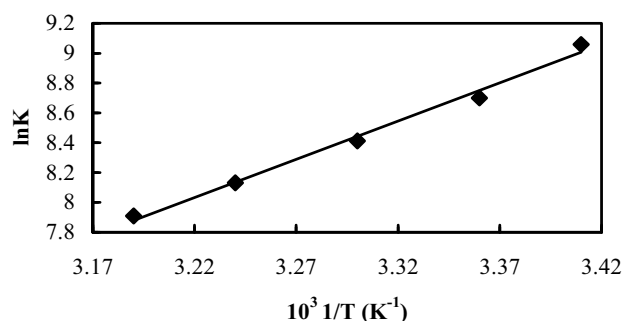


Fig. 5. Plot of $\ln K$ vs. $1/T$ for $[\text{Co}(\text{BBE})(\text{PBu}_3)]^+$ with PBu_3 in THF.

The formation constants and the thermodynamic parameters are presented in Tables 2-7.

The Acceptor Properties of Cobalt(III) Schiff Base Complexes

It is assumed that when Co(III) ion is chelated in a macrocycle having delocalized electronic structure, the complex loses its transition character and might be kinetically labile [17]. The extent to which this happens is most likely to be dependent on the structure of the planar chelating system acting as acceptor of the donated charge. The existence of

Table 2. The Formation Constants, $10^{-3} \text{ K (M}^{-1}\text{)}$, for $[\text{Co}(\text{BAE})(\text{PBu}_3)]\text{ClO}_4$ with PBu_3 in Various Solvents

T (K)	Acetonitrile	THF	Butanol	Ethanol	DMF
293	11.4 ± 0.7	4.9 ± 0.2	2.0 ± 0.1	2.0 ± 0.1	0.38 ± 0.01
298	8.1 ± 0.5	3.6 ± 0.1	1.7 ± 0.1	1.7 ± 0.1	0.33 ± 0.01
303	5.0 ± 0.5	2.7 ± 0.1	1.3 ± 0.1	1.2 ± 0.1	0.26 ± 0.01
308	3.9 ± 0.2	2.2 ± 0.1	1.2 ± 0.1	0.9 ± 0.1	0.21 ± 0.01
313	2.5 ± 0.1	1.5 ± 0.1	1.1 ± 0.1	0.8 ± 0.1	0.17 ± 0.01

Table 3. The Formation Constants, $10^{-3} \text{ K (M}^{-1}\text{)}$, for $[\text{Co}(\text{BBE})(\text{PBu}_3)]\text{ClO}_4$ with PBu_3 in Various Solvents

T (K)	Acetonitrile	THF	Butanol	Ethanol	DMF
293	23.4 ± 1.0	8.6 ± 0.4	6.0 ± 0.2	5.8 ± 0.2	1.6 ± 0.1
298	15.3 ± 0.7	6.0 ± 0.2	5.0 ± 0.2	4.9 ± 0.1	1.4 ± 0.1
303	12.6 ± 0.5	4.5 ± 0.1	4.1 ± 0.2	3.5 ± 0.2	1.1 ± 0.1
308	10.0 ± 0.2	3.4 ± 0.1	3.4 ± 0.2	2.7 ± 0.1	1.0 ± 0.1
313	7.8 ± 0.4	2.7 ± 0.1	2.6 ± 0.1	1.9 ± 0.1	0.9 ± 0.1

Table 4. The Formation Constants, $10^{-3} \text{ K (M}^{-1}\text{)}$, for $[\text{Co}(\text{Salen})(\text{PBu}_3)]\text{ClO}_4$ with PBu_3 in Various Solvents

T (K)	Acetonitrile	THF	Butanol	Ethanol	DMF
293	6.6 ± 0.3	2.6 ± 0.1	1.6 ± 0.1	1.5 ± 0.1	0.31 ± 0.01
298	5.3 ± 0.2	2.2 ± 0.1	1.3 ± 0.1	1.2 ± 0.1	0.26 ± 0.01
303	3.9 ± 0.1	1.7 ± 0.1	1.1 ± 0.1	1.1 ± 0.1	0.21 ± 0.01
308	3.1 ± 0.1	1.4 ± 0.1	1.0 ± 0.1	0.9 ± 0.1	0.17 ± 0.01
313	2.6 ± 0.1	1.2 ± 0.1	0.9 ± 0.1	0.8 ± 0.1	0.14 ± 0.01

Thermodynamics of Cobalt(III) Schiff Base Complexes

Table 5. The Thermodynamic Parameter Values (ΔH° , ΔS° and ΔG°) for $[\text{Co}(\text{BAE})(\text{PBU}_3)]\text{ClO}_4$ with Tributylphosphine in Various Solvents

PBU ₃	$-\Delta H^\circ$ (kJ mol ⁻¹)	$-\Delta S^\circ$ (J mol ⁻¹)	$-\Delta G^\circ$ (kJ mol ⁻¹) ^a
Acetonitrile	56.9 ± 4.2	116.6 ± 3.5	22.3 ± 2.3
THF	43.5 ± 3.9	77.7 ± 3.9	20.3 ± 2.3
Butanol	25.2 ± 1.4	22.7 ± 5.8	18.9 ± 1.7
Ethanol	36.1 ± 2.5	60.2 ± 3.3	18.2 ± 1.9
DMF	31.8 ± 2.9	58.6 ± 6.6	14.3 ± 2.2

^aat 25 °C.

Table 6. The Thermodynamic Parameter Values (ΔH° , ΔS° and ΔG°) for $[\text{Co}(\text{BBE})(\text{PBU}_3)]\text{ClO}_4$ with Tributylphosphine in Various Solvents

PBU ₃	$-\Delta H^\circ$ (kJ mol ⁻¹)	$-\Delta S^\circ$ (J mol ⁻¹)	$-\Delta G^\circ$ (kJ mol ⁻¹) ^a
Acetonitrile	39.2 ± 4.5	50.6 ± 6.8	24.1 ± 2.7
THF	44.2 ± 1.5	75.8 ± 5.0	21.6 ± 1.7
Butanol	31.7 ± 2.0	35.7 ± 5.8	21.0 ± 1.9
Ethanol	43.6 ± 2.9	76.2 ± 7.5	20.8 ± 2.3
DMF	22.4 ± 2.2	15.0 ± 2.2	17.9 ± 1.7

^aat 25 °C.

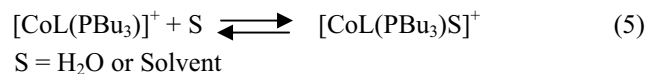
stable, apparently pentacoordinated species $[\text{Co}(\text{chel})\text{PR}_3]^+$, suggests that the influence of the sixth ligand on the z-axis is not essential in the stabilization of the cobalt phosphine ligand. Therefore, the equatorial Schiff base ligands and the strong σ -donors like phosphines in the axial position can affect the stability of hexa- or pentacoordinate cobalt(III) Schiff base complexes. Such an effect on stability of Schiff base complexes clarifies the reaction of some complexes with phosphine in different solvents (Eq. 1).

The Effect of Equatorial Schiff Base Ligands

The equatorial ligands play important role in stability and reactivity of their complexes. This reactivity is affected by the electronic and the steric of the ligands.

The Salen ligand is more withdrawing than BAE and BBE, and the presence of phenyl withdrawing group causes the BBE become a weaker Schiff base than BAE. Therefore, according to electronic effect, the trend of reactivity of cobalt complexes toward PBU₃ must be as follows: Salen > BBE > BAE. The results show that the trend of reactivity of cobalt complexes

toward PBU₃ is not compatible with the electronic effect only. The reactivity of cobalt complexes concerning the electronic effect is: BBE > BAE > Salen. It seems that other factors affect the reactivity of cobalt complexes. The solvent effect and the steric factors are also important concerning the reactivity of the complexes. The stability or the reactivity of the complexes with different coordination numbers are usually related to solvents. It seems that water or a solvent molecule can occupy the sixth position of the five-coordinated complex (Eq. 5).



If in the six-coordinated complex a water molecule or a polar solvent molecule occupies the sixth position, the interaction with the incoming donor is very weak [15]. Therefore, the solvated form (Eq. 5) of the Salen complex is larger relative to BBE and BAE because the Salen is planar, hence the steric factor is lower. Thus, the formation constant for Salen is

Table 8. The Formation Constants for [Co(BBE)PBu₃]ClO₄ with PBu₃ and the Donor Number of Solvents

Solvents	CH ₃ CN	THF	BuOH	EtOH	DMF
D.N	14.1	20.0	29.0	32.0	26.1
10 ⁻³ K	15.1 ± 0.7	6.0 ± 0.2	5.2 ± 0.2	5.0 ± 0.2	1.4 ± 0.1

reduced relative to BBE and BAE. The steric of BBE is larger than BAE, and thus, the solvated form is lower and the formation constant is larger.

Solvent Effect

The formation constants in solvents are dependent on two factors: one of these factors is the donor number, the other one is the polarity of the solvents.

In this work, we determined the formation constants of three complexes [Co(BAE)PBu₃]⁺, [Co(BBE)PBu₃]⁺ and [Co(Salen)PBu₃]⁺ with tributylphosphine in five solvents *i.e.* acetonitrile, THF, butanol, ethanol and DMF. The solvent donor numbers are shown in Table 8 [18].

Ethanol (32) > butanol (29) > DMF (26.1) > THF (20.0) > acetonitrile (14.1).

It seems that the formation constants are decreased with increasing of the donor number of solvents (Table 8), because the solvents with higher donor number are better coordinated to the five-coordinated complexes (Eq. 5). Therefore, they hardly depart the complex to make room for the incoming tributylphosphine. Results in DMF don't obey the donor number trend. All the formation constants in DMF are less than those in other solvents. This is due to its high polarity. From the qualitative studies, the pentacoordinate complexes are more stable in polar solvents. For example, in chloroform the donor-acceptor solution containing hexacoordinate complex is red, but in DMF is green (pentacoordinate complexes of this type are green and the hexacoordinate complexes are red). Therefore, it seems that the formation constant in highly polar solvent is less than that with low polar or non-polar solvents.

In DMF, since the polarity is high relative to the other solvents, the pentacoordinated complex is more stable and the formation constant is decreased.

Presumably, two factors affect the formation constants. Therefore, in comparing the formation constants, the two

factors must be considered together. It seems that the predominate factor is the donor number of the solvents, except for DMF, whose polarity factor is more important.

Thermodynamic Parameters

The ΔH° value and its sign, is dependent on the heat of formation of the complex and the solvent effect [19].

In all cases, it is found that the ΔH° values are negative. This shows that the complex-formation contribution of ΔH° values is more important. The ΔH° value for [Co(Salen)(PBu₃)]⁺ and [Co(BBE)(PBu₃)]⁺ in acetonitrile is more negative than for other solvents, which shows that the complex formation for these complexes in acetonitrile is more important. On the other hand, the ΔH° for [Co(BAE)(PBu₃)]⁺ in THF is more negative than for other solvents.

The ΔS° values and its sign is also dependent on the difference in the number of particles of the initial substance and the product complexes and the liberation of the solvent molecule from solvation shells [19]. Δn for the reactions involving [Co(Chel)(PBu₃)]⁺ with PBu₃ is -1 and the entropy changes is decreased. According to the second factor, the entropy changes is increased, but the net entropy changes for all reactions is negative which indicates that the first factor is more important.

CONCLUSIONS

By considering the formation constants, K, and the ΔG° of formation for pentacoordinate Co(III) Schiff base complexes as acceptors and tributylphosphine as donor the following conclusions could be drawn:

1. Reactions are exothermic, because with increasing temperature, K is decreased *i.e.* $\Delta H^\circ < 0$.
2. The formation constants of Co(III)Schiff base complexes with tributylphosphine as a donor changes according to the following trend in five solvents for all systems: acetonitrile >

THF > butanol > ethanol > DMF.

3. The formation constant in a given solvent changes according to the following trend for the equatorial Schiff bases: BBE > BAE > Salen.

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