

Donor Ligand, Basal Ligand and Solvent Effects on the Equilibrium Constants of Triphenylphosphinecobalt(III) Schiff Base Complexes with Phosphite Ligands

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The equilibrium constants and the thermodynamic parameters were spectrophotometrically measured for the 1:1 adduct formation of [Co(Salen)(PPh₃)]ClO₄.H₂O, and [Co(7,7'-Me₂Salen)(PPh₃)]ClO₄.H₂O as acceptors, with P(OR)₃ (R = methyl, ethyl, and i-propyl) as donors, in acetonitrile (CH₃CN) and dimethylformamide (DMF) as solvents at constant ionic strength (I = 0.1 M NaClO₄), and various temperatures (t = 10-50 °C). Our results revealed the following trends: stability of the cobalt(III) Schiff base complexes toward a given phosphite donor, [Co(7,7'-Me₂Salen)(PPh₃)]⁺ < [Co(Salen)(PPh₃)]⁺; binding of the donors (phosphites) toward a given cobalt(III) Schiff base complex, P(OEt)₃ > P(OMe)₃ > P(O-ⁱPr)₃; influence of solvent on the stability of a given cobalt(III) Schiff base complex toward a given phosphite donor, CH₃CN < DMF.

Keywords: Schiff base, Thermodynamic parameter, Equilibrium constant, Phosphine, Cobalt complex

INTRODUCTION

The nature of the effects of one ligand and their 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 chemical reactivity. For studying these effects and comparing the behavior of these complexes with biological Co(III) complexes, like vitamin B₁₂, several series of Co(III) Schiff base complexes with bonded carbon and phosphines as axial ligands were proposed as model molecules [1-7]. Extensive work using these models has been performed in the study of the equilibrium of the adduct formation of [Co(Salen)X]⁺, [X = tertiary phosphines] with NO₂⁻ showing that the equilibrium constants decrease according to the following trend: PPh₃ < PEtPh₂ < PBu₃ [8]. The formation

constants for some [Co(Salen)(PR₃)₂]⁺ were examined in acetonitrile and in 95% ethanol [9]. Previously, we determined the relationships between the steric and the electronic effects of Salen Schiff bases on the stability of pentacoordinate complexes like [Co(Salen)X]ClO₄.H₂O [10,11].

In this work, spectral and thermodynamic comparison of some cobalt(III) Schiff base complexes with various ligands is used to investigate the effects of their electronic and steric properties in two different solvents.

EXPERIMENTAL

Materials and Preparations

The compounds 2-hydroxyacetophenone, 1,2-ethylenediamine, salicylaldehyde, cobaltacetatehexa-hydrate, trialkylphosphites, sodium perchlorate, dimethylformamide (DMF), and acetonitrile (CH₃CN) were purchased from Merck, Fluka and Aldrich.

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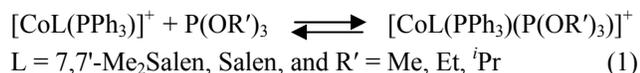
The Schiff base ligand 7,7'-Me₂Salen and Salen were prepared by the condensation of 2 mol of the appropriate 2-hydroxyacetophenone and salicylaldehyde with 1 mol of ethylenediamine in methanol as previously published [8]. The [Co(7,7'-Me₂Salen)(PPh₃)]ClO₄·H₂O and [Co(Salen)(PPh₃)]ClO₄·H₂O complexes were prepared as previously described [8,9].

Instrumental

The scanning UV-Vis spectra were recorded using a Jasco V-530 spectrophotometer.

Thermodynamic Studies

The adduct complexes were obtained from the reaction of the acceptors with the donors, according to equation (1):



A solution from each complex (6.0×10^{-5} - 1.2×10^{-4} M) with a constant ionic strength (I) of 0.1 M sodium perchlorate was prepared. Of each solution, 3 ml was transferred into the thermostated cell compartment of the UV-Vis spectrophotometer, which was kept at a constant temperature (± 0.1 °C) by circulating water. Each solution was titrated by adding aliquots of the phosphite using a Hamilton MICROLITER™ syringe. The donor concentrations were varied in the range of 0.2-1.5 fold, which was low enough to avoid substitution of PPh₃ by phosphite.

The absorption measurements were carried out in the range of 320-340 nm after the equilibrium was assessed, since this is the optimal range for detecting the difference between the formed adducts and the acceptors, while the donors show no absorption in that range.

The formation constants and molar absorptivities of the complexes were determined by measuring the absorbance in the range of 320-340 nm for a series of solutions with a varying concentration of phosphite and constant [CoL(PPh₃)]⁺ concentration by non-linear curve fitting using the Microsoft Excel Solver software. Adjustable parameters include the K_f and ε values. Refinement of the parameters continued until the sum-of-squares of the residuals between the calculated and the observed absorbances (σ) for all experimental points was

minimized. The output program, written in Microsoft Excel, is comprised of the refined parameter, the sum-of-squares of the residuals.

When P(OR)₃ as a donor (D) reacts with [CoL(PPh₃)]⁺ ions as acceptors (A) to form a 1:1 complex, K_f for equation (1) is:

$$K_f = \frac{[[\text{CoL}(\text{PPh}_3)\text{P}(\text{OR})_3]^+]}{[[\text{CoL}(\text{PPh}_3)]^+][\text{P}(\text{OR})_3]} \quad (2)$$

The mass balance equations are given by:

$$C^\circ_A = [[\text{CoL}(\text{PPh}_3)]^+] + [[\text{CoL}(\text{PPh}_3)\text{P}(\text{OR})_3]^+] \quad (3)$$

$$C^\circ_D = [\text{P}(\text{OR})_3] + [[\text{CoL}(\text{PPh}_3)\text{P}(\text{OR})_3]^+] \quad (4)$$

where C^o_A and C^o_D are the initial analytical concentrations of [CoL(PPh₃)]⁺ and P(OR)₃, respectively.

The mass balance equations for the 1:1 model can be solved in order to obtain an equation for the free ligand concentration, [D]:

$$K_f[D]^2 + (1 + K_f(C^\circ_A - C^\circ_D)) [D] - C^\circ_D = 0 \quad (5)$$

The observed absorbance of the solution is:

$$A_{\text{obs}} = \varepsilon_D [D] + \varepsilon_{AD} [AD] \quad (6)$$

where ε is the molar absorptivity of the species denoted.

The thermodynamic parameters of the studied cobalt(III) Schiff base complexes were calculated by the van't Hoff equation (7):

$$\ln K_f = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (7)$$

where K_f is the formation constant, R is the gas constant and T is the temperature in the Kelvin scale. The values of ΔH^o and ΔS^o were obtained from the slope and the intercept, respectively, using Microsoft Excel.

RESULTS AND DISCUSSION

Figure 1 shows the decreases in absorption bands in the ranges of 310-350 and 430-480 nm and increases at 370-400 and 550-650 nm for [Co(Salen)(PPh₃)]⁺ titrated with P(OEt)₃

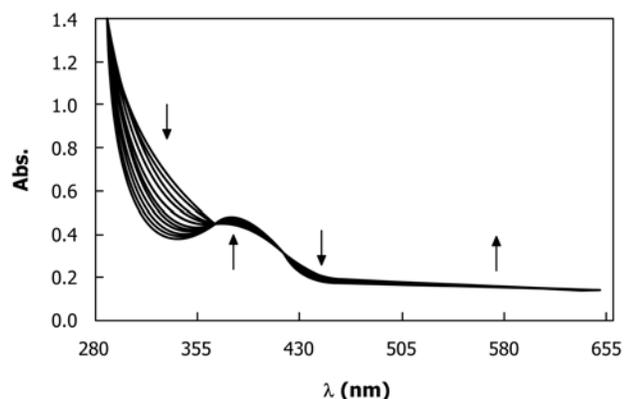


Fig. 1. Variation of electronic spectrum of $[\text{Co}(\text{Salen})(\text{PPh}_3)]^+$ with $\text{P}(\text{OEt})_3$ in CH_3CN at $20\text{ }^\circ\text{C}$.

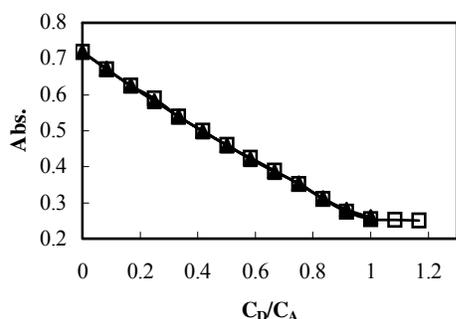


Fig. 2. The mol ratio plots of $[\text{Co}(\text{Salen})(\text{PPh}_3)]^+$, titrated with triethylphosphite in acetonitrile at $20\text{ }^\circ\text{C}$: (\square) Exp., (\blacktriangle) Cal.

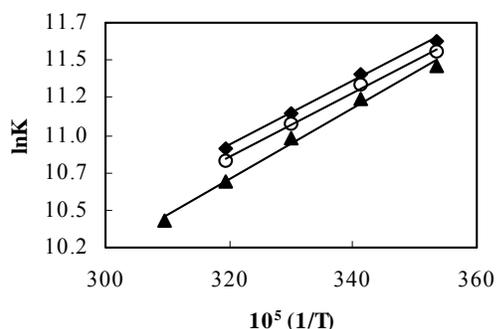


Fig. 3. The plots of $\ln K_f$ vs. $1/T$ for $[\text{Co}(7,7'\text{-Me}_2\text{Salen})(\text{PPh}_3)]\text{ClO}_4\cdot\text{H}_2\text{O}$ with $\text{P}(\text{OMe})_3$, $\text{P}(\text{OEt})_3$ and $\text{P}(\text{O-}i\text{Pr})_3$ at various temperatures in DMF: (\blacklozenge) $\text{P}(\text{OEt})_3$, (\circ) $\text{P}(\text{OMe})_3$, (\blacktriangle) $\text{P}(\text{OiPr})_3$.

in CH_3CN at $20\text{ }^\circ\text{C}$. The isosbestic points at 284, 372, 424, 510, and 655 nm for this system show that there is only one reaction in equilibrium. The same is valid for other systems.

According to the absorption curve vs. mole ratio in Fig. 2, the curves level off at a mole ratio of 1, indicating that only one phosphite is added to the substrate, and that this is a 1:1 system. Although Fig. 2 demonstrates the mole ratio plots of $[\text{Co}(\text{Salen})(\text{PPh}_3)]^+$ titrated with triethylphosphite in acetonitrile at $20\text{ }^\circ\text{C}$, the same is valid for other systems, as well.

The values of the sums-of-squares of the residuals for all systems ranged from 0.0003 to 0.004, thus displaying agreement between the experimental and calculated values of the model (Fig. 2). The formation constants of the studied cobalt(III) Schiff base complexes are shown in Tables 1 and 2. The K_f measurements were repeated at least twice with good reproducibility.

The thermodynamic parameter data are collected in Tables 1 and 2. The linear plot of $\ln K_f$ vs. $1/T$ for $[\text{Co}(7,7'\text{-Me}_2\text{Salen})(\text{PPh}_3)]\text{ClO}_4\cdot\text{H}_2\text{O}$ titrated with trialkylphosphite at various temperatures in DMF is compared to those using other phosphites in Fig. 3.

Acceptor Property of Cobalt(III) Schiff Base Complexes

The equatorial Schiff base ligands and the strong σ -donors, like phosphines in the axial position, can affect the stability of five- or six-coordinated cobalt(III) Schiff base complexes. The phosphine axial ligand trans effect on the thermodynamics of the five-coordinated Co(III) Schiff base complexes has been studied well [8-12]. The steric and electronic effects of Schiff bases and the axial ligands on equilibrium constants were investigated in our laboratory, previously [10-12]. In an effort to study the effects of the other Schiff bases complexes, this work on $[\text{Co}(7,7'\text{-Me}_2\text{Salen})(\text{PPh}_3)]^+$, and $[\text{Co}(\text{Salen})(\text{PPh}_3)]^+$ with phosphites as donors in acetonitrile and DMF were carried out.

Effect of Equatorial Ligands

The formation constants in acetonitrile for $[\text{Co}(7,7'\text{-Me}_2\text{Salen})(\text{PPh}_3)]^+$ are larger than $[\text{Co}(\text{Salen})(\text{PPh}_3)]^+$ with all phosphites as donors. It was observed that the addition of two methyl groups to Salen reduces the stability of the solvated

Table 1. Formation Constants^a, and Thermodynamic Parameter Values^{b,c,d} for [Co(Salen)(PPh₃)]ClO₄·H₂O and [Co(7,7'-Me₂Salen)(PPh₃)]ClO₄ with Various P(OR)₃ at Various Temperatures in CH₃CN

T (°C)	P(OEt) ₃		P(OM) ₃		P(O- ⁱ Pr) ₃	
	Salen	Me ₂ Salen	Salen	Me ₂ Salen	Salen	Me ₂ Salen
10	10.5	12.0	10.0	11.2	9.6	10.4
20	9.0	9.8	8.6	9.3	8.1	8.7
30	7.0	7.5	6.6	7.1	6.2	6.8
40	5.5	6.0	5.1	5.6	4.7	5.1
50			4.1	4.5	3.6	3.9
ΔH ^{ob}	-16.1 (1.5)	-17.2 (0.9)	-17.3 (1.1)	-17.7 (0.7)	-18.8 (1.2)	-18.9 (1.3)
ΔS ^{oc}	39.5 (5.0)	36.5 (2.9)	35.0 (3.6)	34.4 (2.4)	29.4 (4.1)	29.8 (4.3)
ΔG ^{od}	-27.7 (2.0)	-27.9 (1.2)	-27.6 (1.5)	-27.8 (1.0)	-27.7 (1.7)	-27.6 (1.8)

^a10⁻⁴ × K_f (M⁻¹). ^bΔH^o (kJ mol⁻¹). ^cΔS^o (J mol⁻¹ K⁻¹). ^dΔG^o (kJ mol⁻¹), calculated by ΔG^o = ΔH^o - TΔS^o, at 20 °C.

Table 2. Formation Constants^a and Thermodynamic Parameter Values^{b,c,d} [Co(Salen)(PPh₃)]ClO₄·H₂O and [Co(7,7'-Me₂Salen)(PPh₃)]ClO₄·H₂O with Various P(OR)₃ at Various Temperatures in DMF

T (°C)	P(OEt) ₃		P(OM) ₃		P(O- ⁱ Pr) ₃	
	Salen	Me ₂ Salen	Salen	Me ₂ Salen	Salen	Me ₂ Salen
10	9.9	10.8	9.0	9.9	8.3	9.0
20	7.9	8.6	7.4	8.0	6.8	7.2
30	6.1	6.6	5.6	6.1	5.0	5.6
40	4.7	5.2	4.2	4.8	3.8	4.2
50					2.8	3.2
ΔH ^{ob}	-18.4 (0.8)	-17.9 (0.7)	-18.9 (1.3)	-17.9 (0.8)	-21.1 (1.3)	-19.8 (1.0)
ΔS ^{oc}	30.9 (2.8)	33.3 (2.4)	28.5 (4.4)	32.4 (7.8)	20.0 (4.3)	25.2 (3.1)
ΔG ^{od}	-27.4 (1.2)	-27.6 (1.0)	-27.2 (1.8)	-27.4 (1.2)	-27.0 (1.8)	-27.2 (1.3)

^a10⁻⁴ × K_f (M⁻¹). ^bΔH^o (kJ mol⁻¹). ^cΔS^o (J mol⁻¹ K⁻¹). ^dΔG^o (kJ mol⁻¹), calculated by ΔG^o = ΔH^o - TΔS^o, at 20 °C.

five-coordinated complex and increases the formation constants of the six-coordinated adduct. In the six-coordinate adduct, when a water or solvent molecule occupies the sixth position, the interaction is very weak [8], resulting in the larger solvated form of the Salen complex, and a lower formation constant compared to Me₂Salen, despite the higher steric factor of Me₂Salen *vs.* that of Salen. This trend is seen for Me₂Salen and Salen of cobalt(III) complexes with P(Bu₃)

and PMe₂Ph as axial ligands, as well [9,10].

Effect of Phosphite Donors

In this work, we have examined three donors: P(OMe)₃, P(OEt)₃, and P(O-ⁱPr)₃. The phosphite complexes are often similar to the phosphines but the phosphites tend to be more basic and less sterically hindered [13]. In addition to the electronic property, the phosphites have an important steric

factor, as demonstrated by the Tolman cone angle. The cone angles for these phosphites are 107°, 109°, and 130° for P(OMe)₃, P(OEt)₃, and P(O-^{*i*}Pr)₃, respectively [14]. The steric factor increases with an increase in the cone angle. The trend of formation constants of the studied complexes in both solvents is: P(OEt)₃ > P(OMe)₃ > P(O-^{*i*}Pr)₃. This trend shows that the steric factor is more important than the electronic factor for each donor toward a given acceptor. When the steric hindrance of the entering ligand is increased, the formation constant is lower for all systems (see Tables 1 and 2). For P(OMe)₃ and P(OEt)₃, the steric factor is the same, so the electronic factor is the determining factor, and the formation constants for P(OEt)₃ are larger. Another reason for this trend is that the trimethylphosphite may be attributed to a “keto-enol” type of rearrangement to produce a phosphoryl linkage [15]. However, the triethylphosphites do not have this property [16].

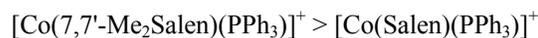
Effect of Solvent

The results in Tables 1 and 2 show that the formation constants are dependent on the solvent and the trend is related to the donor number of the solvents. The Gutmann donor number for acetonitrile is 14.1 and 26.6 for DMF [17]. The formation constants for DMF are smaller than acetonitrile, therefore the formation constant decreases with increasing solvent donor numbers. The five-coordinated complex was found to be more stable in a solvent with higher donor number. In other words, a solvent with high donor number can coordinate to a five-coordinated complex and stabilizes it toward a higher coordination number. Therefore the trend of the influence of the solvent on the reactivity of the studied complexes toward a given phosphite donor is: Acetonitrile > DMF.

CONCLUSIONS

In this work, efforts were made to provide a quantitative measure of the Schiff-base effect on the acceptor property of Co(III) in certain cobalt(III) Schiff-base complexes, such as [Co(7,7'-Me₂Salen)(PPh₃)]ClO₄·H₂O, [Co(Salen)(PPh₃)]ClO₄·H₂O, through adduct formation with P(OMe)₃, P(OEt)₃, and P(O-^{*i*}Pr)₃ in acetonitrile and DMF. The formation constants and the thermodynamic parameters obtained show the

following trend of the acceptor properties of the Schiff-base complexes:



The formation constants for all phosphites with the complexes have the following trend:



The trend of the solvent effect on the reactivity of the studied complexes was: CH₃CN > DMF

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