Synthesis, characterization, and thermodynamics of tertiary phosphine cobalt(III) Schiff-base complexes

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Abstract: [Co(5-nitroSalen)(PBu$_3$)]ClO$_4$·H$_2$O and [Co(Salpd)(PBu$_3$)]ClO$_4$·H$_2$O were synthesized and characterized. The stability constants and the thermodynamic parameters were measured spectrophotometrically for 1:1 adduct formation of [CoL(PBu$_3$)]ClO$_4$·H$_2$O, (L = Salen, 5-nitroSalen, Salpd), and [Co(Salen)(PMe$_2$Ph)]ClO$_4$·H$_2$O as acceptors with P(OR)$_3$ (R = Me, Et, *i*-Pr) as donors, in acetonitrile solvent and in constant ionic strength (I = 0.01 M) and at various temperatures. The trend of the reactivity of cobalt(III) Schiff-base complexes with PBu$_3$ axial ligand toward a given donor is as follows: 5-nitroSalen > Salen > Salpd.

Also, the following reactivity trend of the donors toward a given cobalt(III) Schiff-base complex is in the operation: P(O-*i*-Pr)$_3$ > P(OEt)$_3$ > P(OMe)$_3$.

Key words: cobalt(III) Schiff-base complexes, thermodynamic parameters, trialkylphosphite, adduct complexes, stability constants.

Résumé : On a effectué la synthèse et on a caractérisé les complexes suivants: [Co(5-nitroSalen)(PBu$_3$)]ClO$_4$·H$_2$O et [Co(Salpd)(PBu$_3$)]ClO$_4$·H$_2$O. Faisant appel à des méthodes spectrophotométriques, on a mesuré les constantes de stabilité et les paramètres thermodynamiques pour la formation d'adduits 1:1 entre les complexes accepteurs [CoL(PBu)$_3$]ClO$_4$·H$_2$O dans lesquels L = Salen, 5-nitroSalen et Salpd et [Co(Salen)(PMe$_3$Ph)]ClO$_4$·H$_2$O et les P(OR)$_3$ (dans lesquels R = Me, Et, *i*-Pr) comme accepteurs, dans l'acétonitrile comme solvant, à force ionique constante (I = 0,01 M) et à diverses températures. La tendance de la réactivité des complexes des bases de Schiff du cobalt(III) avec le ligand PBu$_3$ axial est donnée par la séquence suivante: 5-nitroSalen > Salen > Salpd.

Du côté des donneurs vis-à-vis d'un complexe donné d'une base de Schiff du cobalt(III), la tendance est exprimée par la séquence suivante: P(O-*i*-Pr)$_3$ > P(OEt)$_3$ > P(OMe)$_3$.

Mots clés : complexes de bases de Schiff avec le cobalt(III), paramètres thermodynamiques, trialkylphosphite, adduits de complexes, constantes de stabilité.

[Traduit par la Rédaction]

Introduction

Many Co(III)–Salen tertiary phosphine complexes have been suggested as models for the vitamine B$_{12}$ coenzyme (1–3). The properties of these Salen complexes were examined with the aim to gain an insight into the chemistry of the related biological molecules. Some extensive works have been done on these models (4–8). Recently the kinetics of ligand replacement reactions of the axial H$_2$O in the *trans*-[Co(en)$_2$(H$_2$O)(Me)]$^{2+}$ complex have been studied by Hamza et al. (9). The equilibrium of the adduct formation of [Co(Salen)X]$^+$ (X = tertiary phosphines) with NO$_2^-$ has been studied. It was shown that the equilibrium constants decrease according to the following trend: PPh$_3$ < PEtPh$_2$ < PBu$_3$ (10). The formation constants for some [Co(Salen)(PR$_3$)$_2$]$^+$ were examined in acetonitrile and in ethanol 95% (11).

In this work, the new complexes [Co(5-nitroSalen)(PBu$_3$)]ClO$_4$·H$_2$O and [Co(Salpd)(PBu$_3$)]ClO$_4$·H$_2$O were synthesized and characterized. Thermodynamics of cobalt(III) Schiff-base complexes of the types [CoL(PBu$_3$)]ClO$_4$·H$_2$O, where L = Salen, 5-nitroSalen, Salpd, and [Co(Salen)(PMe$_2$Ph)]ClO$_4$·H$_2$O as acceptors with (P(OR)$_3$, R = Me, Et, *i*-Pr) as donors, in acetonitrile solvent have been examined. By comparing the spectral and the thermodynamical properties of the synthesized complexes, we aimed to investigate the effects of different electronic and steric situations.

Experimental

Materials

Salicylaldehyde, 5-nitrosalicylaldehyde, 1,2-ethylenediamine, 1,3-propanediamine, cobalt(II) acetate tetrahydrate, tributylphosphine, trialkylphosphites, tetraethylammonium perchlorate, dimethylphenylphosphine, and acetonitrile were purchased from Merck, Fluka, or Aldrich.

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Table 1. The stability constants (K, L mol^{-1}) for [Co(Salen)-(PBu_3)]$ClO_4 \cdot H_2O$ with various $P(OR)_3$ in acetonitrile solvent.

Temperature (°C)	$P(OMe)_3$	$P(OEt)_3$	$P(O\text{-}i\text{-}Pr)_3$
20	348.9 ± 0.0	1640.0 ± 0.2	2098.7 ± 0.4
25	301.5 ± 0.0	1446.4 ± 0.1	1712.1 ± 0.3
30	279.8 ± 0.0	1126.0 ± 0.2	1595.7 ± 0.2
35	250.0 ± 0.0	948.4 ± 0.1	1340.0 ± 0.1
40	236.4 ± 0.0	852.1 ± 0.1	1135.6 ± 0.0

Note: λ = 460 nm.

Table 2. The stability constants (K, L mol^{-1}) for [Co(Salen)-(PMe_2Ph)]$ClO_4 \cdot H_2O$ with various $P(OR)_3$ in acetonitrile solvent.

Temperature (°C)	$P(OMe)_3$	$P(OEt)_3$	$P(O\text{-}i\text{-}Pr)_3$
20	1611.1 ± 0.3	5580.3 ± 3.5	11 525.1 ± 7.7
25	1189.0 ± 0.1	4992.3 ± 2.1	9 924.2 ± 5.9
30	1069.3 ± 0.1	4018.3 ± 1.2	8 698.4 ± 3.2
35	889.7 ± 0.1	3198.3 ± 1.3	7 577.8 ± 3.4
40°C	724.9 ± 0.1	2378.1 ± 0.8	6 577.1 ± 2.6

Note: λ = 470 nm.

Table 3. The stability constants (K, L mol^{-1}) for [Co(5-nitroSalen)-(PBu_3)]$ClO_4 \cdot H_2O$ with various $P(OR)_3$ in acetonitrile solvent.

Temperature (°C)	$P(OMe)_3$	$P(OEt)_3$	$P(O\text{-}i\text{-}Pr)_3$
20	474.6 ± 0.0	6482.0 ± 1.3	6604.4 ± 1.6
25	398.3 ± 0.0	4701.8 ± 0.5	5707.6 ± 1.4
30	368.8 ± 0.0	2965.8 ± 0.2	4641.1 ± 1.0
35	346.6 ± 0.0	2595.3 ± 0.1	3791.5 ± 0.1
40	299.4 ± 0.1	2042.9 ± 0.4	3300.6 ± 1.3

Note: λ = 450 nm.

Table 4. The stability constants (K, L mol^{-1}) for [Co(Salpd)-(PBu_3)]$ClO_4 \cdot H_2O$ with various $P(OR)_3$ in acetonitrile solvent.

Temperature (°C)	$P(OMe)_3$	$P(OEt)_3$	$P(O\text{-}i\text{-}Pr)_3$
20	243.6 ± 0.0	1125.7 ± 0.2	875.4 ± 0.1
25	228.5 ± 0.0	920.0 ± 0.1	783.1 ± 0.1
30	204.1 ± 0.0	756.0 ± 0.0	606.1 ± 0.0
35	190.0 ± 0.0	681.2 ± 0.0	524.7 ± 0.0
40	171.0 ± 0.0	552.9 ± 0.0	438.9 ± 0.0

Note: λ = 470 nm.

Instrumentation

The UV–vis spectra were recorded by a Jusco V-530 spectrophotometer. The NMR spectra were recorded by a Bruker Avance DPX 250 MHz spectrometer, and IR spectra were recorded by a PerkinElmer 781 IR spectrophotometer.

Synthesis of the complexes

The ligands Salen, 5-nitroSalen, and Salpd were prepared according to the literature (12). The [Co(Salen)-(PBu_3)]$ClO_4 \cdot H_2O$ and [Co(Salen)(PMe_2Ph)]$ClO_4 \cdot H_2O$ complexes were prepared by the methods described previously (10, 11).

The general procedure for the synthesis of the [Co(5-nitroSalen)(PBu_3)]$ClO_4.H_2O$ and [Co(Salpd)(PBu_3)]$ClO_4.H_2O$ is as follows: to a refluxing solution of Salpd (0.57 g, 2.01 mmol) or 5-nitroSalen (0.71 g, 2.01 mmol) in methanol (70 mL), were added $Co(OAC)_2 \cdot 4H_2O$ (0.50 g, 2.01 mmol) and tributylphosphine (0.5 mL, 2.01 mmol). The reaction mixture was refluxed for 1 h. The formed Co(II) complex was oxidized by blowing air into the solution for 2 h, and the solution was filtered. To the filtrate, an appropriate amount of sodium perchlorate (0.30 g, in 10 mL water) was added. The green crystals were formed after 24 h. The crystals were washed with some methanol, recrystallized in acetone–ethanol (95%), and dried in vacuum at 65°C.

[N,N′-*bis(salicylidene)-1,3-diaminopropanato]tri*-n-*butylphosphineCo(III) perchlorate monohydrate*

Yield: 70%. ^1H NMR ($CDCl_3$) δ: 0.76–0.81 (t, 9H, CH_3), 1.25–1.30 (m, 18H, CH_2), 2.75 (w, 2H, H_2O), 3.86–3.96, 4.22–4.28 (m, 6H, $CH_2CH_2CH_2$), 6.55–6.61 (t, 2H, ArH), 6.90–6.93 (d, 2H, ArH), 6.98–7.01 (d, 2H, ArH), 7.11–7.17 (t, 2H, ArH), 7.65 (s, 2H, CH=N). Anal. calcd. for $C_{29}H_{45}ClN_2O_7PCo$: C 52.86, H 6.88, N 4.25; found: C 53.49, H 6.69, N 4.61.

[N,N′-*bis(5-nitrosalicylidene)aza-1,2-diaminoethanato]tri*-n-*butylphosphineCo(III) perchlorate monohydrate*

Yield: 85%. ^1H NMR (DMSO-d_6) δ: 0.73–0.79 (t, 9H, CH_3), 1.21–1.26 (m, 9H, CH_2), 1.45–1.49 (m, 9H, CH_2), 2.51 (s, 2H, H_2O), 4.03 (s, 4H, CH_2CH_2), 7.15–7.19 (d, 2H, ArH), 8.15–8.20 (d, 2H, ArH), 8.51 (s, 4H, ArH, CH=N). Anal. calcd. for $C_{28}H_{41}ClN_4O_{11}PCo$: C 45.77, H 5.62, N 7.62; found: C 45.43, H 5.59, N 7.80.

Thermodynamic studies

The adduct complexes were obtained from the reaction of the acceptors with the donors, according to the eq. [1]:

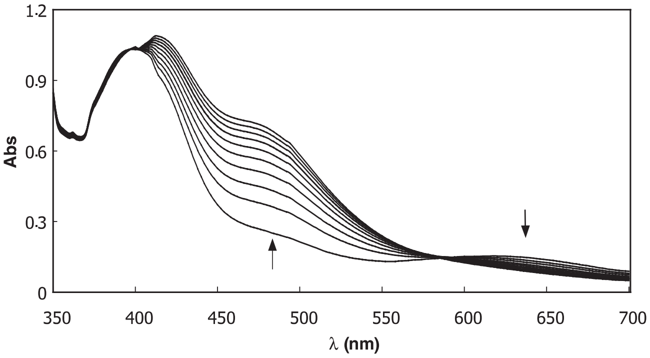
$$[1] \qquad [CoLX]^+ + P(OR)_3 \longleftrightarrow [CoLX(P(OR)_3)]^+$$

where L = Salen, Salpd, and 5-nitroSalen, X = PBu_3 and PMe_2Ph (only for Salen), R = Me, Et, and *i*-Pr.

A solution from each complex with a concentration at about 1×10^{-4} M and a constant ionic strength (I = 0.01 M) by tetraethylammonium perchlorate was prepared. From this solution, 2.5 mL was transferred into the thermostated cell compartment of the UV–vis instrument which was kept at constant temperature (±0.1°C) by circulating water and was titrated by the phosphite. The titration was done by adding aliquots of the phosphite with a Hamilton syringe (μL). The donors' concentrations were varied one- to threefold in excess.

The absorption measurements were carried out at a fixed wavelength where the difference in absorption between the substrate and the product was the largest after the equilibrium was assessed. These fixed wavelengths for the systems are listed in Tables 1–4. The adduct formed shows an absorption different from the acceptor, while the donors show no absorption at those wavelengths.

Fig. 1. Spectrophotometric titration of $[Co(Salen)(PMe_2Ph)]^+$ with $P(O\text{-}i\text{-}Pr)_3$ in acetonitrile (I = 0.01 M Et_4NClO_4, T = 30°C).



Results and discussion

The characterization of the complexes

The new complexes $[Co(5\text{-}nitroSalen)(PBu_3)]ClO_4{\cdot}H_2O$ and $[Co(Salpd)(PBu_3)]ClO_4{\cdot}H_2O$ were identified by elemental analysis, IR, NMR, and electronic spectra. The other complexes were identified only by IR, NMR, and electronic spectra.

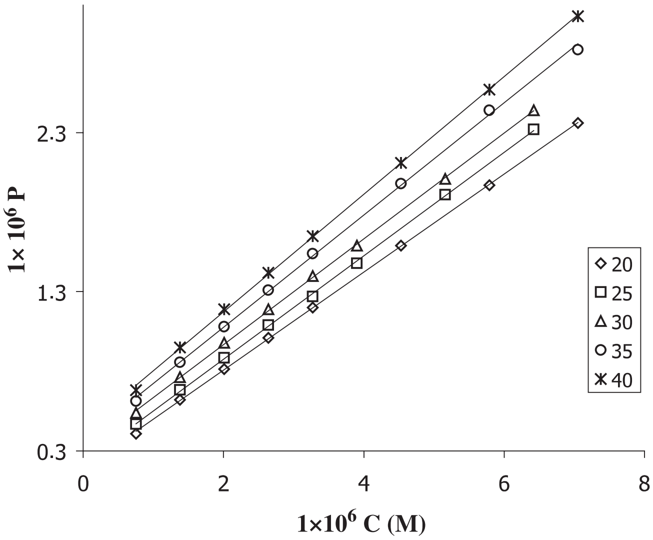
Spectral characterization

IR spectra: The absence of the coordinated water in all the studied complexes was confirmed by the absence of the absorption band around 3100 cm^{-1} (10). The absorption band around 1625–1640 cm^{-1} is related to the azomethane group, and the aromatic double bonds appeared at 1600–1605 cm^{-1} (13).

Electronic spectra: The electronic spectra, of all the studied complexes, show an absorption at 600–700 nm in non-coordinated solvent, that indicate the five-coordinated structure for them. All complexes show an intensive absorption band at 370–400 nm. This band did not reallychange in all the reactions studied. The absorption band at 600–700 nm vanished and the six-coordinated product species showed an absorption band at 400–500 nm (10). All measurements for the thermodynamic studies were carried out in this range. As an example, the variation of the electronic spectra for $[Co(Salen)(PMe_2Ph)]^+$, titrated with the $P(O\text{-}i\text{-}Pr)_3$, is shown in Fig. 1. The isosbestic points for this system show that there is only one reaction in equilibrium. The same is valid for other systems.

The ^1H NMR spectra: The ^1H NMR spectral data have been presented in the *Experimental* section. The NMR spectra of these complexes are consistent with the suggest formulation and show that the cobalt in these complexes is low-spin. The interesting point in the NMR of these complexes is the aromatic proton signals that are resolved in four groups in the ^1H NMR. For example, in $[Co(Salpd)(PBu_3)]^+$ these signals arranged from δ = 6.55 to 7.17 in the form of triplet, doublet, doublet, and triplet, that are related to the protons in the positions of 5, 3, 6, and 4 to the azomethane group, respectively. In the complex of $[Co(5\text{-}nitroSalen)(PBu_3)]^+$, because of the NO_2 group, the aromatic proton signals shifted to the low field in such a way that the proton in the position 6 to the azomethane overlaps with the azomethane proton at δ = 8.51.

Fig. 2. The linear plot for $[Co(Salen)(PBu_3)]^+$ with $P(OEt)_3$ system at various temperatures (T = 20–40°C). $P = \frac{C_A^\circ C_D^\circ}{A - A_A^\circ - A_D^\circ}$, $C = (C_A^\circ C_D^\circ)$.



Thermodynamic interpretations

The equilibrium constants of the various cobalt(III) Schiff base complexes studied were calculated by using Ketelaar et al.'s (14) equation

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

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 and the donor; A_A° and A_D° are the optical densities of the pure acceptor and the pure donor in the 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 stability constant of the formed complex and the cell optical path length is 1 cm. A plot of $(C_A^\circ C_D^\circ/(A - A_A^\circ - A_D^\circ))$ vs. $(C_A^\circ + C_D^\circ)$ should produce a straight line if only the 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 stability constants of the studied cobalt(III) Schiff base complexes were calculated from the ratio of the slope to the intercept by the least-squares method using Excel 5 computer software. The K measurements were repeated at least twice and were reproducible. The linear plots for $[Co(Salen)(PBu_3)]^+$ with $P(OEt)_3$ at various temperatures are shown in Fig. 2, which signifies that only 1:1 complex is formed. Similar plots are obtained for other systems.

The thermodynamic parameters of the studied cobalt(III) Schiff base complexes were calculated by use of the well-known van't Hoff eq. [3]:

$$[3] \qquad \ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

Table 5. The thermodynamic parameter values ΔH°, ΔS°, and ΔG° for $[Co(Salen)(PBu_3)]ClO_4 \cdot H_2O$ with various $P(OR)_3$ in acetonitrile solvent.

$P(OR)_3$	ΔH° (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1})	ΔG° (kJ mol^{-1})^a
$P(OMe)_3$	–14.8 ± 1.1	–1.9 ± 3.7	–14.2 ± 2.2
$P(OEt)_3$	–25.6 ± 1.2	–25.9 ± 4.0	–17.7 ± 2.4
$P(O\text{-}i\text{-}Pr)_3$	–22.6 ± 1.3	–13.7 ± 4.4	–18.6 ± 2.6

[a] At 30°C.

Table 6. The thermodynamic parameter values ΔH°, ΔS°, and ΔG° for $[Co(Salen)(PMe_2Ph)]ClO_4 \cdot H_2O$ with various $P(OR)_3$ in acetonitrile solvent.

$P(OR)_3$	ΔH° (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1})	ΔG° (kJ mol^{-1})^a
$P(OMe)_3$	–28.8 ± 2.3	–37.3 ± 7.6	–17.6 ± 4.6
$P(OEt)_3$	–34.3 ± 0.3	–44.2 ± 0.9	–20.9 ± 0.6
$P(OIpr)_3$	–21.3 ± 0.4	+5.5 ± 1.2	–22.8 ± 0.8

[a] At 30°C.

where K is the stability 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 from the linear plots of ln K vs. 1/T. The values of ΔH° and ΔS° were obtained from the slope and the intercept, respectively, by using the Excel computer program.

The stability constants and the thermodynamic parameters data are collected in Tables 1–8. The stability constants are given for the formation of 1:1 adducts only.

The acceptor property of cobalt(III) Schiff base complexes

It was suggested (15) that when Co(III) ion is chelated in a macrocycle having delocalized electronic structure, the complex loses its transition character and might become 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. It can be concluded that in the ground state, the thermodynamic effects and even the kinetic *trans*-effects are mainly due to the charge donation to the cobalt atom via the σ-bond (2). Therefore the equatorial Schiff base ligands and the strong σ-donors like phosphines in the axial position can affect the stability of six- or five-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 well-studied (10, 11), but the *cis*-effect appears to be far less evident in this literature. We tried to find the steric and the electronic effects of some Schiff bases on the thermodynamic parameters of five-coordinated Co(III) Schiff base complexes. The steric effect of the axial phosphine ligands and the entering ligands were also studied. The thermodynamic aspect of the influence of the equatorial Schiff bases' ligands can be clearly seen from Tables 1, 3, and 4, and show the trend of Salpd < Salen < 5-nitroSalen, irrespective of the nature of the axial ligand. These results are in agreement with the trend of nucleophilicity of the cobalt atom in the Schiff base complexes toward the electrophiles.

The electronic effect of the equatorial Schiff base ligands

The electron-withdrawing property of the substituent groups on the Schiff base can influence the ability of the acceptor property of the complexes. The presence of an NO_2 withdrawing group causes 5-nitroSalen to become a weaker Schiff base than the unsubstituted Salen. Therefore, the cobalt atom in the $[Co(5\text{-}nitroSalen)(PBu_3)]^+$ complex has more acceptor property than $[Co(Salen)(PBu_3)]^+$ and forms more stable complexes with donors (Tables 1 and 3).

Table 7. The thermodynamic parameter values ΔH°, ΔS°, and ΔG° for $[Co(Salpd)(PBu_3)]ClO_4 \cdot H_2O$ with various $P(OR)_3$ in acetonitrile solvent.

$P(OR)_3$	ΔH° (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1})	ΔG° (kJ mol^{-1})^a
$P(OMe)_3$	–13.7 ± 0.7	–1.0 ± 2.3	–13.4 ± 1.4
$P(OEt)_3$	–26.3 ± 1.3	–31.3 ± 4.3	–16.7 ± 2.6
$P(OIpr)_3$	–26.5 ± 1.6	–34.1 ± 5.4	–16.1 ± 3.2

[a] At 30°C.

Table 8. The thermodynamic parameter values ΔH°, ΔS°, and ΔG° for $[Co(5\text{-}nitroSalen)(PBu_3)]ClO_4 \cdot H_2O$ with various $P(OR)_3$ in acetonitrile solvent.

$P(OR)_3$	ΔH° (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1})	ΔG° (kJ mol^{-1})^a
$P(OMe)_3$	–16.8 ± 1.1	–6.1 ± 3.6	–14.9 ± 2.2
$P(OEt)_3$	–44.6 ± 1.8	–79.5 ± 6.0	–20.1 ± 3.6
$P(OIpr)_3$	–27.3 ± 1.2	–19.9 ± 3.9	–21.3 ± 2.4

[a] At 30°C.

The steric effect of the equatorial Schiff base ligands

By increasing the steric interactions of the Schiff base, the five-coordinate complex becomes more stable and the formation constant of this type decreases with an increase in steric interactions. Therefore, the five-coordinated $[Co(Salpd)(PBu_3)]^+$ complex has less acceptor ability than $[Co(salen)(PBu_3)]^+$ (Tables 1 and 4).

The effect of the axial ligand

The steric effect of the axial ligand is more important than the equatorial (10, 11). The stability constants for the PMe_2Ph axial ligand with lower steric interactions are more larger than PBu_3 (Tables 1 and 2). The difference between the nucleophilicity of the phosphites in the $[Co(Salen)(PMe_2Ph)]^+$ is better seen because of the decrease in steric interactions (Table 2).

Effect of the donors

In this work, we have examined three donors, $P(OMe)_3$, $P(OEt)_3$, and $P(O\text{-}i\text{-}Pr)_3$. The phosphite complexes are often similar to the phosphines but the phosphites tend to be more basic and less sterically hindered (16).

In addition to the electronic property, the phosphites have an important steric factor that is demonstrated by the Tolmane cone angle. The cone angles (degrees) for these phosphites are 107, 109, and 130°, for $P(OMe)_3$, $P(OEt)_3$, and $P(O\text{-}i\text{-}Pr)_3$, respectively (17). The steric interaction is increased with an increase in cone angle.

In the Salen and 5-nitroSalen complexes, the stability constants were increased by increasing Tolmane cone angles of the phosphites, which is in contrast to what is expected;, therefore, it seems that the electronic effect of the phosphites is more important than the steric effect toward the given acceptor (Tables 1–3), and there is an increasing tendency for the adduct formation in the order $P(OMe)_3 < P(Oet)_3 < P(O\text{-}i\text{-}Pr)_3$. By increasing the steric interactions in the Salpd complex, the stability constant is decreased when the Tolmane cone angle increased (Table 4) and this order changes to $P(OMe)_3 < P(O\text{-}i\text{-}Pr)_3 < P(OEt)_3$.

The lower stability constant of the trimethylphosphite may be attributed to a “keto–enol” type of rearrangement to produce a phosphoryl linkage (18), but the triethylphosphite do not show this property (19).

Thermodynamic parameters

The heat of formation

The $\Delta H°$ value and its sign, is dependent on two factors: one of these factors, is the solvation effect and the other one is the heat of formation of the complex (20). The solvation effect for five- and six-coordinated complexes is not that different due to the same charge, although it seems that the five-coordinated complex is better solvated. The solvation effect for the donors is related to the interaction of solvent with the phosphites and this contribution for $\Delta H°$ can be positive after the equilibrium. In all cases, $\Delta H°$ values are negative, and it shows that the complex-formation contribution of $\Delta H°$ values is more important (Tables 5–8). For example, the heat of formations of $P(OMe)_3$ toward the acceptors are related to the stability constants for these systems (Tables 5–8).

Concerning the electronic effect contribution, the $\Delta H°$ values for $[Co(5\text{-}nitroSalen)(PBu_3)]^+$ are more negative than the $[Co(Salen)(PBu_3)]^+$, and it shows that the complex formation in 5-nitroSalen is more important (Tables 5 and 8).

Concerning the steric effect of the equatorial Schiff base ligand on heat of formation, the $\Delta H°$ values for $[Co(Salpd)(PBu_3)]^+$ are nearly the same as $[Co(Salen)(PBu_3)]^+$. It can be due to the second factor, and there is some positive value from the solvation effect for $[Co(Salen)(PBu_3)]^+$, especially with $P(OEt)_3$ and $P(O\text{-}i\text{-}Pr)_3$ (Tables 5 and 7). The steric effect of the axial ligand is important and the enthalpy change values show this effect (Tables 5 and 6).

For a given acceptor, the solvation effect is different for the donors. $\Delta H°$ values for the triisopropylphosphite are less negative than triethylphosphite and these are in contrast to the stability constants. For example, the heat of formation for $[Co(Salen)(PMe_2Ph)]^+$ is smaller than the others, although the complex formation is the greatest. This is repeated for $[Co(Salen)(PBu_3)]^+$ and $[Co(5\text{-}nitroSalen)(PBu_3)]^+$, and it seems that this donor is better solvated, and it reduces the overall enthalpy (Tables 1–8). The importance of this factor is better seen in the entropy.

The entropy

The $\Delta S°$ value and its sign, is also dependent on two factors: one of these factors is the difference in the number of the particles of the initial substances and the product complexes. The second factor is the liberation of the solvent molecules from the solvation shells (20). Concerning the first factor, the entropy change is decreased while the second factor is increased, but the net entropy change in most cases is negative, and it shows that the first factor is more important. The entropy change for trimethyl- and triethylphosphite properly decreases with increasing stability constant and indicates that the first factor is more important (Tables 5–8). For example, the entropy changes of $P(OMe)_3$ toward the acceptors are related to the stability constants for these systems and with increasing complex formation, the entropy change is decreased. The more negative entropy change for $P(OMe)_3$ in Table 6 is related to the higher stability constant for this system. The entropy change for triisopropylphosphite is governed by the second factor i.e., the libration of the solvent molecules, and it is less negative and is sometimes positive, although the stability constants are larger than the others. For example, the entropy change for $[Co(Salen)(PMe_2Ph)]^+$ complex with $P(O\text{-}i\text{-}Pr)_3$ is positive (Table 6), although the complex formation is the highest.

Conclusion

In this work, efforts were made to provide a quantitative measure of Schiff base effect on the acceptor property of Co(III) in some cobalt(III) Schiff base complexes, such as $[Co(Salen)(PBu_3)]^+$, $[Co(Salen)(PMe_2ph)]^+$, $[Co(5\text{-}nitroSalen)(PBu_3)]^+$, and $[Co(Salpd)(PBu_3)]^+$, through adduct formation with $P(OMe)_3$, $P(OEt)_3$, and $P(O\text{-}i\text{-}Pr)_3$ in acetonitrile. The stability constants and the thermodynamic parameters obtained have showed the following trend of acceptor property of theSchiff-base complexes: 5-nitroSalen > Salen > Salpd.

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