Thermodynamic study of cobalt(III) Schiff base complexes in mixed EtOH/H_2O

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The $[Co(Chel)(PBu_3)]ClO_4.H_2O$(Chel = dsp, mdsp and ndsp, where dsp = N,N'-disalicylidene-1,2-phenylene diamine, mdsp = 4-methyl-N,N'-disalicylidene-1,2-phenylene diamine and ndsp = 4-nitro-N,N'-disalicylidene-1,2-phenylene diamine), were synthesised and characterised. The equilibrium constants and the thermodynamic parameters of these complexes as acceptors with PBu_3, were measured spectrophotometrically for 1 : 1 adduct formation in various mixed EtOH/H_2O and constant ionic strength (I = 0.1M $NaClO_4$) and at various temperatures T = 288–308 K. The trend of the reactivity of five coordinate Co(III) Schiff base complexes toward PBu_3 donor according to the Schiff base ligand is mdsp > dsp > ndsp. The trend of the reactivity of a given Co(III) Schiff base complexes towards PBu_3 donor according to the water/ethanol mole fractions is 0.12 > 0.36 > 0.52 > 0.64.

Keywords: cobalt Schiff base complexes, formation constants, Schiff base, thermodynamic parameters

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 kinetic aspects of chemical reactivity. For studying these effects and comparing the behaviour of these complexes with biological Co(III) complexes like vitamin B_{12} several series of Co(III) Schiff base complexes with bonded carbon and phosphines as axial ligand have been proposed as model molecules.[1-4]

In continuation of our studies on the synthesis, electronic spectra, electrochemical properties and the thermodynamics of cobalt (III) complexes containing Schiff base ligands,[5-8] we report the synthesis and spectroscopic characterisation of $[Co(mdsp)(PBu_3)]ClO_4.H_2O$, (mdsp = 4-methyl-N,N'-disalicylidene-1,2-phenylene diamine) and $[Co(ndsp)(PBu_3)]ClO_4.H_2O$(ndsp = 4-nitro-N,N'-disalicylidene-1,2-phenylene diamine). We have also measured the thermodynamics of five-coordinated $[Co(Chel)(PBu_3)]ClO_4.H_2O$ (Chel = dsp, ndsp and mdsp) complexes in equilibrium with PBu_3 as the sixth ligand in various water/ethanol mole fractions and constant ionic strength (I = 0.1M $NaClO_4$) and at various temperatures T = (288 to 308)K, with the goal of evaluating the effect of equatorial substitution(R) on electronic properties (Fig. 1).

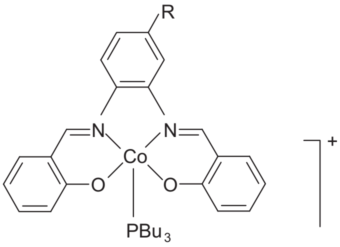

Fig. 1 The structure of $[Co(Chel)(PBu_3)]ClO_4.H_2O$, complexes. R = H(dsp), Me(mdsp) and NO_2(ndsp).

Experimental

The materials are cobaltacetatetetrahydrate(Merk, 99%), tributylphosphine(Aldrich,98%),salicylaldehyde(Merk,99%),1,2-phenylenediamine(Merk, 98%), 3,4-diaminotholuen(Merk, 99%), 4-nitro-1,2-phenylenediamine(Merk, 99%), ethanol (Merk, 96%), and sodium perchlorate monohydrate (Merk, 99%) were purchased from Merck and Aldrich.

IR spectra were recorded by a Perkin Elmer 781 IR spectophotometer. Electronic absorption spectra were recorded on a Jasco V-530 spectrometer. NMR spectra were obtained on a Bruker Avance DPX 250 MHe NMR spectrometer. Elemental analysis were performed using a Heraeus CHN-O-RAPID elemental analyser.

Synthesis of the complexes

The ligands H_2dsp and H_2dst were prepared according to the literature by condensation of 1,2-phenylenediamine and 3,4-diaminotholuene with salicylaldehyde(1 : 2 mole stoichiometric ratio) in methanol (or ethanol) at room temperature and were purified by recrystallisation from hot ethyl acetate.[9-11] The H_2ndsp ligand was prepared according to the literature by dissolving of 4-nitro-1,2-phenylenediamine in salicylaldehyde(serving as both solvent and reactant) under N_2.[11] The $[Co(dsp)(PBu_3)]ClO_4.H_2O$, (dsp = N,N'-disalicylidene-1,2-phenylenediamine), was synthesised by the method dscribed previousely.[12] The novel $[Co(mdsp)(PBu_3)]ClO_4.H_2O$, and $[Co(ndsp)(PBu_3)]ClO_4.H_2O$, complexes were synthesised according to the procesure reported for synthesis of this type of complexes.[9] The crystals were washed with methanol, recrystallised in 50/50(v/v) methanol/ethanol 95% and dried in vacuum at T = 338K. Elemental analysis calculated as percent for $[Co(dst)(PBu_3)]ClO_4.H_2O$, $C_{33}H_{45}CoClN_2O_7P$ (708.65), yield: 75%: Anal. Cald (found), C 44.76 (44.73), H 5.78 (5.77), N 5.22 (5.22), and for $[Co(ndsp)(PBu_3)]ClO_4.H_2O$, $C_{32}H_{42}CoClN_3O_9P$ (738.12), yield: 73%: Anal. Cald (found), C 51.07 (51.13), H 5.73 (5.70), N 5.69 (5.5.72).

Thermodynamic studies

The adduct complexes were obtained from the reaction of the acceptors with PBu_3, according to eqn (1):

$$[Co(Chel)PBu_3]^+ + PBu_3 \leftrightarrow [Co(Chel)(PBu_3)_2]^+ \qquad (1)$$

where Chel = dsp, ndsp and mdsp, in water/ethanol mole fractions (0.12, 0.36, 0.52, 0.64).

A solution from each complex with concentration at about 10^{-5}M and constant ionic strength (I = 0.1M) by sodium perchlorate was prepared. A total of 2.5 ml was transferred into the thermostatted cell compartment of the UV-Vis instrument, which was kept at constant temperature (± 0.1K) by circulating water and was titrated by PBu_3. Adding aliquots of phosphine with a Hamilton microlitre syringe carried out the titration. The donor concentrations varied from 1-to-10 fold in excess.

The absorption measurements were carried out at various wavelengths in the 480–570 nm region where the difference in absorption between the substrate and the product was the largest after the equilibrium was matched. As an example, the variation of the electronic spectra for $[Co(dsp)(PBu_3)]^+$, titrated with PBu_3 in water/ethanolmole fraction(0.12) is shown in Fig. 2. The isosbestic points suggest that there are only two species in equilibrium. The same is valid for other systems.

Results and discussion

IR and NMR spectra

The absence of the coordinated water in the complexes studied was confirmed by the absence of the absorption band 3100 cm^{-1}.[13] The absorption band around 1600 cm^{-1} is related to azomethine group.[14,15] The ^1H NMR spectra of these complexes are consistent

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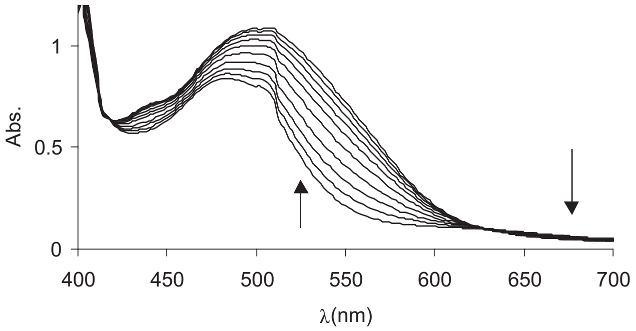

Fig. 2 Spectrophotometric titration of $[Co(dsp)(PBu_3)]^+$ with PBu_3 in water/ethanol mole fraction(0.12). (I = 0.1M $NaClO_4$, T = room temperature).

with the suggest formulation and show that the cobalt in these complexes is low spin.

Electronic spectra

The UV-Vis spectum of dsp in methanol consists of a relatively intense band centred at 337 nm assigned to $\pi \rightarrow \pi^*$ transition and a second band at 362 nm corresponding to $n \rightarrow \pi^*$ excitation.[16] After complexation with Co(III) several transitions appear below 400 nm still involving principally interligand $\pi \rightarrow \pi^*$ excitation. Moreover, an intense $d \rightarrow \pi^*$ charge transfer band appears in the 450–550 nm region in the spectra of the complexes studied here. This transition was also seen in $[Co(dsp)(amine)_2]ClO_4$ complexes.[17] The λ_{max} for this transition in the complexes studied here is changed according to the substitution group on the Schiff base in trend of NO_2 (λ_{max} = 500nm) > H (λ_{max} = 480nm) > CH_3 (λ_{max} = 475nm). The $d \rightarrow \pi^*$ charge transfers depended on the charge density in the Schiff base. The electron-withdrawing NO_2 group reduces the density of charge over the Schiff base and the metal to ligand charge transfer ($d \rightarrow \pi^*$) happened at lower energy. This effect is reversed by an electrondonating group such as methyl. On the other hand, in the thermodynamic studies of the five coordinated complexes with PBu_3 and formation of hexacoordinated complexes, this band shifts to lower energy (high λ_{max}) because of the increasing charge density over the metal ion and the $d \rightarrow \pi^*$ charge transfer was easier.

Thermodynamic interpretations

The equilibrium constants of the various cobalt (III) Schiff-base complexes studied here were calculated by using the Ketelaar's equation.[6] The linear plots for $[Co(dsp)(PBu_3)]ClO_4.H_2O$ titrated with PBu_3 at various temperatures in water/ethanol mole fraction(0.36) are shown in Fig. 3, which signify that only a 1 : 1 complex is formed. Similar plots are obtained for other systems. The equilibrium constants data are collected in Tables 1–3.

The thermodynamic parameters of the studied complexes were approximated by using of the well-known van't Hoff equation.[6] The thermodynamic parameters data are collected in Tables 4–6. The linear plots of lnK *vs* 1/T for $[Co(Chel)(PBu_3)]ClO_4.H_2O$ at various temperatures in water/ethanol mole fraction(0.12) is shown in Fig. 4. Similar plots are obtained for other systems.

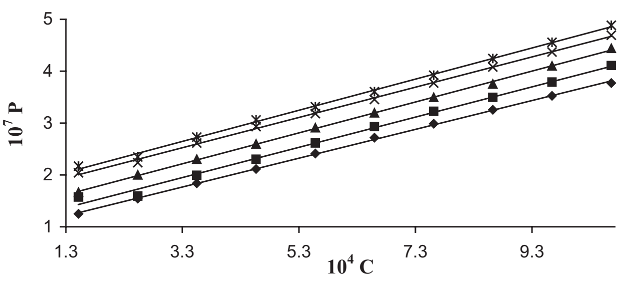

Fig. 3 Plots of variable P against C for $[Co(dsp)(PBu_3)]^+$ with PBu_3 in water/ethanol mole fraction(0.36), where

$P = \frac{C_A^o C_D^o}{A - A_A^o - A_D^o}$ and $C = (C_A^o + C_D^o)$. T = ◆ 288 K, ■ 293 K, ▲ 298 K, × 303 K, ⋇ 308 K.

Table 1 The equilibrium constants $10^{-3}\times K/(l\ mol^{-1})$, for $[Co(dsp)(PBu_3)]^+$ with PBu_3, in various water/ethanol mole fractions.

T/K	0.12	0.36	0.52	064
288	14.3±2.3	9.3±1.0	8.7±1	6.3±0.7
293	10.6±1.1	8.1±0.6	7.0±0.5	5.4±0.4
298	8.1±0.4	6.2±0.6	5.3±0.7	3.9±0.2
303	7.0±0.3	5.2±0.4	4.9±0.4	3.2±0.9
308	5.2±0.2	4.6±0.2	3.9±0.2	2.6±0.1

Table 2 The equilibrium constants $10^{-3}\times K/(l\ mol^{-1})$, for $[Co(mdsp)(PBu_3)]^+$ with PBu_3, in various water/ethanol mole fractions

T/K	0.12	0.36	0.52	0.64
288	29.5±4.5	15±3.0	13.5±1.4	10.4±1.7
293	20.5±3.4	12.0±1.4	10.4±0.9	8.1±1.2
298	16.2±1.9	10.4±1.0	8.9±0.9	5.8±0.8
303	10.7±1.0	8.1±0.6	7.7±0.6	4.5±0.4
308	6.9±0.4	5.8±0.5	5.0±0.3	3.1±0.3

Table 3 The equilibrium constants $10^{-3}\times K/(l\ mol^{-1})$, for $[Co(ndsp)(PBu_3)]^+$ with PBu_3, in various water/ethanol mole fractions

T/K	0.12	0.36	0.52
288	6.1±0.2	4.1±0.2	3.4±0.3
293	5.3±0.2	3.4±0.1	3.1±0.3
298	4.2±0.3	2.9±0.9	2.5±0.2
303	3.1±0.3	2.5±0.7	2.1±0.1
308	2.5±0.7	2.1±0.1	1.9±0.6

Table 4 The thermodynamic parameter values ΔH°, ΔS° and ΔG° for for $[Co(dsp)(PBu_3)]^+$ with PBu_3, in various water/ethanol mole fractions

$EtOH/H_2O$	$\Delta H^\circ/kJ\ mol^{-1}$	$\Delta S^\circ/J\ K^{-1}\ mol^{-1}$	$\Delta G^\circ/kJ\ mol^{-1a}$
0.12	-41±2	-71±7	-23±1
0.36	-26±7	-17±3	-22±4
0.52	-28±3	-24±8	-21±3
0.64	-32±2	-38±3	-20±2

[a] T = 303K.

Table 5 The thermodynamic parameter values ΔH°, ΔS° and ΔG° for for $[Co(mdsp)(PBu_3)]^+$ with PBu_3, in various water/ethanol mole fractions

$EtOH/H_2O$	$\Delta H^\circ/(kJ\ mol^{-1})$	$\Delta S^\circ/(J\ K^{-1}\ mol^{-1})$	$\Delta G^\circ/(kJ\ mol^{-1})^a$
0.12	-52±5	-95±12	-24±2
0.36	-36±3	-35±10	-23±1
0.52	-34±3	-39±11	-22±2
0.64	-40±3	-63±10	-21±2

[a] T = 303K.

Table 6 The thermodynamic parameter values ΔH°, ΔS° and ΔG° for for $[Co(ndsp)(PBu_3)]^+$ with PBu_3, in various water/ethanol mole fractions.

$EtOH/H_2O$	$\Delta H^\circ/(kJ\ mol^{-1})$	$\Delta S^\circ/(J\ K^{-1}\ mol^{-1})$	$\Delta G^\circ/(kJ\ mol^{-1})^a$
0.12	-34±3	-46±8	-21±2
0.36	-24±4	-15±3	-20±2
0.52	-23±2	-13±6	-19±2

[a] T = 303K.

The electronic effect of the equatorial Schiff base ligands

In continuation of our studies on cobalt(III) Schiff base complexes, we studied here the electronic effect of substitutional groups bonded to Schiff base ligands complexed to Co(III) ion. For this purpose, studies on $[Co(Chel)(PBu_3)]^+$ where Chel = dsp, ndsp and mdsp with PBu_3 as donor in water/ethanol mole fractions were carried out.

In the cases of the complexes studied here, the order of formation constant for the complexes $[Co(Chel)(PBu_3)]^+$ with PBu_3 is as follow: mdsp > dsp > ndsp (Table 1). This is in contrast to the electronic

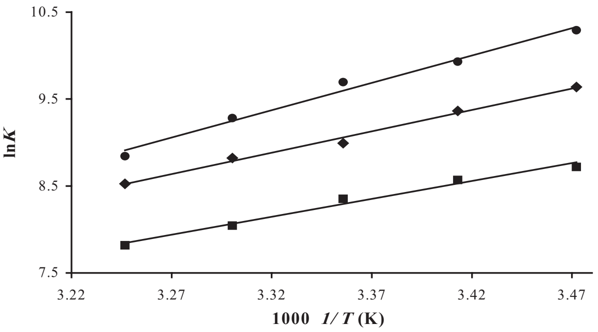

Fig. 4 Plot of ln*K* versus 1/*T* for $[Co(Chel)(PBu_3)]^+$ with PBu_3 in water/ethanol mole fraction(0.12), Chel = ● mdsp, ◆ dsp, ■ ndsp.

spectra in that the charge donation from Co(III) ion to Schiff base's π* molecular orbitals is increased by electron-withdrawing groups on the Schiff base ligands. The NO_2 group makes the Schiff base a poor donor ligand (and a good acceptor ligand), so it is needed by the sixth ligand for stabilising the five-coordinated complexes. The $[Co(ndsp)(PBu_3)]^+$ has the least formation constant toward PBu_3, but the mdsp has the highest, also the CH_3 is a donating group. According to the literature, if in the six-coordinate complexes, a water molecule or a solvent molecule occupies the sixth position, the interaction is very weak.[6,13] It seems that, for this type of five-coordinated complexes, there is a tendency to interaction with the H_2O molecule to formation six-coordinate complex according to eqn (3).

$$[Co(Chel)(PBu_3)]^+ + H_2O \leftrightarrow [Co(Chel)(PBu_3)(OH_2)]^+ \quad (3)$$

The reaction is shifted to the right by decreasing the electron donating power of Schiff base, in the trend of, ndsp > dsp > mdsp. For ndsp, the important species is $[Co(Chel)(PBu_3)(OH_2)]^+$ in the solution but for mdsp complex, is $[Co(mdsp)(PBu_3)]^+$. For mdsp, the five coordinate complex, form **1** (Scheme 1), is predominent and can combine with PBu_3 easly in an equilibrium reaction. On the other hand, form **2** is predominant for ndsp that reacts slowly with PBu_3. Unfortunately the equilibrium between the five-coordinate **1** and the six-coordinate **2** cannot be detected by the spectra. In other words, the electronic spectra of **1** and **2** are similar,and **1** shows little change when it reacts with water.

Effect of solvent

In previous work, the effects of the solvent were studied. It was shown that the five-coordinated form of $[Co(Chel)(PBu_3)]^+$, complexes is the predominant species and more stable in polar solvents and solvents with higher donor number.[6,7] These results and the idea of coordinated water molecule in $[Co(Chel)(PBu_3)(OH_2)]^+$complexes prompted us to research the effect of water concentration on the stability of five-coordinated $[Co(Chel)(PBu_3)]^+$ complexes. By increasing the H_2O mole fraction, the hexa-coordinated form of $[Co(Chel)(PBu_3)(OH_2)]^+$ (form 2) is increased and the formation constants are decreased (Tables 1–3). There is a good linear relationship between water mole fractions(X_{H2O}) and equilibrium constants (or ΔG°). The linear plots of lnK *vs* X_{H2O} for $[Co(Chel)(PBu_3)]^+$ complexes are shown in Fig. 5. The stability constants are decreased by increasing H_2O mole fractions linearly. On the other hand, for the ndsp complex the measurement of the formation constants in water/ethanol mole fraction(0.64) was difficult. It seems that the $[Co(Chel)(PBu_3)(OH_2)]^+$ is the predominant form that is stable and does not react with PBu_3.

$$\underset{\mathbf{1}}{[Co(Chel)(PBu_3)]^+} + H_2O \leftrightarrow \underset{\mathbf{2}}{[Co(Chel)(PBu_3)(OH_2)]^+}$$

$$\updownarrow PBu_3$$

$$\underset{\mathbf{3}}{[[Co(Chel)(PBu_3)_2]^+}$$

Scheme 1

Thermodynamic parameters

The ΔH° value and its sign, is dependent on the heat of formation of the complex and the solvation effect.[18] For complexes studied here, The ΔH° values are negative and appropriate to the formation constants because of bond formation in all reactions. The solvation effect on the heat of formation was investigated by using mixed H_2O/EtOH. The five-coordinate complex is smaller and more polar than the six-coordinate so it is better solvated in solvents with high donor number. By increasing the H_2O mole fraction, the hydrated form of five-coordinated complexes is increased. This form of complex has a positive sign on heat of formation in reaction with PBu_3.

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 enthalpy changes of PBu_3 towards these complexes are related to the equilibrium constants for these systems and with enhancing the tendency of complex formation, the enthalpy changes becomes more negative. The results show that by increasing the water mole fractions, the formation constants were decreased, so the enthalpy changes become less negative. On the other hand, by increasing the water mole fractions, the solvated form of five-coordinated complexes ($[Co(Chel)(PBu_3)(OH_2)]^+$) is increased. When this form of complex reactes with PBu_3, the cobalt bond(Co–OH_2) breaks which has a positive effect on enthalpy values. In water/ethanol mole fraction (0.12) the water molecules form the azeotrope with ethanol and the free water molecules are very small, but in the other systems by increasing the water mole fractions the free water molecules were increased that can react with the five-coordinated complex.

The ΔS° value and its sign is also 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.[18] Δn for the reactions involving $[Co(Chel)(PBu_3)]^+$ with PBu_3 is –1 and the entropy change is decreased. According to the second factor, the entropy change is increased, but the net entropy change for all reactions is negative, and it shows that the first factor is more important. The entropy values in the water/ethanol mole fraction(0.12) is more negative than the others. At first, decreasing the formation constants leads to less negative values of entropies. On the other hand, the solvated form of $[Co(Chel)(PBu_3)(OH_2)]^+$ complexes is increased by increasing the water mole fraction. When this complex reacts with PBu_3, the H_2O is released that has some values with positive sign on net entropies.

Conclusion

By considering the formation constants and the ΔG° of formation for pentacoordinate Co(III) Schiff base complexes as acceptors and PBu_3 as donor, the following conclusions have been drawn:

The formation constant changes according to the following trend for Schiff base ligands: mdsp > dsp > ndsp

The formation constant for a given Schiff base ligand changes according to the following trend for water/ethanol mole fractions: 0.12 > 0.36 > 0.52 > 0.64.

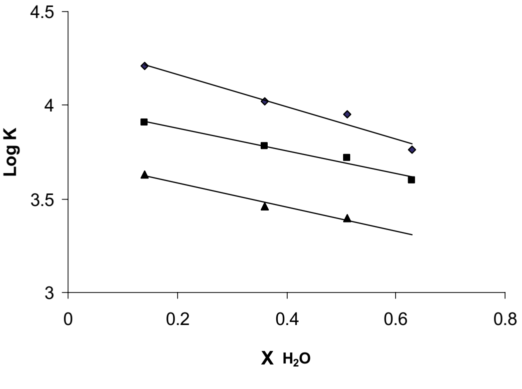

Fig. 5 Plot of log*K* versus water mole fraction for $[Co(Chel)(PBu_3)]^+$ with PBu_3 in water/ethanol mole fractions(X_{H2O} = 0.12, 0.36, 0.52, 0.64), at 298K. Chel = ◆ mdsp, ■ dsp, ▲ ndsp.

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