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#### HIGHLIGHTS

#### Synthesis and characterization of unsymmetrical cobalt(III) Schiff base complexes.

- Thermodynamic studies of their interactions with various donors.
- Investigation the effects of different electronic and steric characters of the ligand's substituent.

#### G R A P H I C A L A B S T R A C T



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#### ABSTRACT

Some new Schiff bases derived from 3,4-diaminopyridine (3,4-DAP) and their new unsymmetrical Co(III) five coordinate complexes described as  $[Co(Chel)(L)]ClO_4 \cdot H_2O$  where (Chel) is the deprotonated form of a series of unsymmetric ligands containing 3,4-diaminopyridine (3,4-DAP) and substituted salicylaldehyde moieties and a new Co(III) six coordinate Co(III) complex, were synthesized and characterized by <sup>1</sup>H NMR, IR, UV-Vis, and elemental analysis. For the new synthesized five coordinate complexes, the formation constants of the interaction of the Co(III) Schiff bases with various donors were measured spectrophotometrically. The trend of the formation constants of the five coordinate Co(III) Schiff base complexes toward a given phosphine is as follow: 5-H > 5-Br and the formation constants trend of these donors are as follow: PBu<sub>3</sub> > PPh<sub>2</sub>Me. Furthermore the adduct formation of the five coordinate [Co(3,4-Sal-pyr)(PBu<sub>3</sub>)] ClO<sub>4</sub>·H<sub>2</sub>O, with aromatic amines shows the following binding trend: Im > 2-MeIm > 2-Etm > BzIm. The trend of the formation constants of Co(III) Schiff base complexes toward a given donor according to the phosphine axial ligand is as follow: PBu<sub>3</sub> > PPh<sub>2</sub>Me.

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#### Introduction

Metal Schiff base complexes have contributed widely to the inorganic chemistry of chelate systems. Metal complexes of these organic ligands have been studied for a long time. The Schiff bases involving a pyridine ring have received considerable attention in literature [1,2]. The anti-inflammatory activity of 2-salicylideneaminopyridine and the corresponding complex with Co(II) has been reported [3].

Schiff bases derived from 3,4-diaminopyridine (3,4-DAP) have received much less attention [4,5], although many clinical studies

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of DAP suggest that this amine, known as a K<sup>+</sup> channel blocker [6–8], effectively relieves the symptoms of various neurological disorders such as the Lambert–Eaton myasthenia syndrome (LEMS) [9–11]. In order to better understand the properties of isomers of diaminopyridines, we studied the thermodynamics property of their cobalt(III) complexes. In particular, we are interested in comparing some thermodynamic features of new synthesized Schiff bases derived from 3,4-DAP with our previously investigated Schiff bases obtained from 2,3-DAP [12].

Recently we reported the thermodynamic properties of cobalt Schiff base complexes with (N,N'-bis(Salicyliden)-2,3-diaminopyridine) as ligand [12]. Sustained interest in the characteristics of the Schiff bases derived from diaminopyridines has promoted us to prepare condensation products of 3,4-DAP and various salicylaldehyde (1, 2, Fig. 1S). This report deals with their detailed characteristic, including characterization and thermodynamic properties of some new unsymmetrical cobalt(III) complexes derived from 3,4-DAP. Comparison of their properties, spectrally, and thermodynamically aimed to investigate the effects of different electronic and steric situations.

#### Experimental

#### Materials

All chemicals were used as obtained from Merck, Fluka or Aldrich. Anal. Grade solvent from Merck was used without further purification. The diamine and salicylaldehyde were distilled before use.

#### Apparatus and techniques

The infrared spectra of all ligands and their complexes were recorded in the range 4000–400 cm<sup>-1</sup> using a Shimadzu FTIR-8300 spectrophotometer applying the KBr disc technique. The UV–Vis absorption spectra were recorded using Perkin–Elmer Lambda 2 spectrophotometer at room temperature. The Elemental analysis was carried out by Thermo Finnigan-Flash-1200. The <sup>1</sup>H NMR spectra were recorded by a Bruker Avance DPX 250 MHz spectrometer.

#### Preparation of the Schiff bases

A mono Schiff base (1) was prepared by mixing stoichiometric amounts of analytically pure salicylaldehyde with 3,4-diaminopyridine dissolved in ethanol and refluxing for three hours on a water bath. The separated brownish yellow crystals were recrystallized from hot ethanol [13]. Such compound as (1), commonly referred to as half-unit, is a potential precursor for the synthesis of nonsymmetrical Schiff bases comprising 3,4-DAP moieties. By mixing the half unit with appropriate aldehyde in the 1:1 ratio, using the same condensation procedure the bis-Schiff bases (2), (3) were obtained. After evaporation of the resulting solution to the half volume the separated crystals were filtered off and recrystallized from ethanol.

#### Synthesis of cobalt complexes

#### Synthesis of the five coordinate Co(III) complexes

The cobalt(III) Schiff base complexes were prepared by the methods described in the literature [14], to a refluxing solution of tetradentate ligands (1 mmol), in methanol (10 cm<sup>3</sup>) were added  $Co(OAc)_2$ ·4H<sub>2</sub>O (0.25 g, 1 mmol). After 15 min, tri-n-butylphosphine (0.2 cm<sup>3</sup>, 0.8 mmol) was added to the solution. The reaction mixture was refluxed for an hour. The Co(II) formed complex was oxidized by blowing air into the solution for 2 h, and the solution

was filtered. An appropriate amount of sodium perchlorate was added to the filtrate. The resulting brown crystals were formed after 48 h. The crystals were washed with some methanol and were purified by re-crystallization in dichloromethane/ethanol. The complex was dried in vacuum at T = 323 K for 48 h (Fig. 2S).

# Synthesis of the six coordinate Co(III) complex, [Co(3,4-Salpvr)(PBu<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub>·H<sub>2</sub>O (7)

To a methanolic solution (6 ml) of the ligand 3,4-Salpyr (0.16 g, 0.5 mmol) and tributylphosphine (0.4 ml, 1.6 mmol) was added a methanolic solution (1.5 ml) of  $Co(OAc)_2$ ·4H<sub>2</sub>O (0.136 g, 0.6 mmol). The reaction mixture was refluxed for 2 h to give a brownish red solution. A methanolic solution (7 ml) of NaClO<sub>4</sub>·H<sub>2</sub>O (0.42 g, 3 mmol) was then added and the mixture was stirred for 2 h. The resulting brown precipitate was collected by filtration and recrystallized by dichloromethane/methanol. The product (7) was dried under vacuum.

#### Thermodynamic studies

The formation constants have been determined by UV–Vis absorption spectroscopy from the reaction of the acceptors with the donors in 96% methanol solvent, according to the following equations:

$$[\operatorname{Co}(3, 4\operatorname{-Salpyr})(L)]^{+} + Y \rightleftharpoons [\operatorname{Co}(3, 4\operatorname{-Salpyr})(L)Y]^{+}$$
(1)

where L = PBu<sub>3</sub>, PPh<sub>2</sub>Me and Y = n-butylamine, PPh<sub>2</sub>Me and PBu<sub>3</sub>

 $[Co(5-Br-3, 4-Salpyr)(PBu_3)]^+ + Y \rightleftharpoons [Co(5-Br-3, 4-Salpyr)(PBu_3Y)]^+$ (2)

where 
$$Y = PPh_2Me$$
 and  $PBu_3$ 

 $[\operatorname{Co}(3,4\operatorname{-Salpyr})(\operatorname{PBu}_3)]^+ + Y \rightleftharpoons [\operatorname{Co}(3,4\operatorname{-Salpyr})(L)Y]^+$ (3)

#### where Y = Im, 2-MeIm, 2-EtIm and BzIm.

A solution from each complex with concentration at about  $3 \times 10^{-5}$  M and constant ionic strength (*I* = 0.1 M) by sodium perchlorate was prepared. In a typical titration 2.5 ml of this solution was transferred into the thermostated cell compartment of the UV–Vis instrument, which was kept at constant temperature (±0.1 K) by circulating water and was titrated by the given donor. The titration was done by adding aliquots of the donor with a Hamilton microlitre syringe. The donor's concentration was varied in 1–3 folds in excess.

The absorption measurements were carried out at various wavelengths where the difference in absorption was the maximum



**Fig. 1.** The variation of the electronic spectra of  $[Co(3,4-Salpyr)(PBu_3)]ClO_4 H_2O$  titrated by PBu<sub>3</sub> at *T* = 293 K in 96% methanol.

after the equilibrium was assessed. The formed adduct shows an absorption different from the acceptor, while the donors show no absorption at those wavelengths. As an example the variation of the electronic spectra for  $[Co(3,4-Salpyr)(PBu_3)]ClO_4$ ·H<sub>2</sub>O, titrated with PBu<sub>3</sub> at *T* = 293 K in 96% methanol 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.

#### **Results and discussion**

It is interesting to note that 3,4-DAP is converted to Schiff bases with difficulty in contrast to 2,3-DAP. This is supported by the fact that 3,4-DAP, unlike 2,3-DAP, is unreactive to 3-(4'-nitrophenyl)-3-oxo-propanal [15]; several attempts to obtain the Schiff bases, using different experimental procedures, failed.

In the asymmetric unit of compound **1**, there are two identical molecules (labeled **1A** and **1B**). The single X-ray diffraction analysis shows that the condensation reaction takes place in the amino group at 3-position of the pyridine ring (isomer **1A**) [16].

By mixing the half unite (1) with appropriate aldehyde in the 1:1 ratio, the bis Schiff bases were obtained. The complexes were prepared according to the following equations:

$$H_{2}L + Co(OAc)_{2} \cdot 4H_{2}O \xrightarrow[PX]{\text{Methanol}} [Co(L)(PX_{3})]^{+} \xrightarrow[AiclO_{4}+H_{2}O]{AiclO_{4}+H_{2}O} [Co(L)(PX)]ClO_{4} \cdot H_{2}O \xrightarrow[PX]{AiclO_{4}+H_{2}O} [Co(L)(PX)]ClO_{4} \cdot H_{2}O \xrightarrow[PX]{AiclO_{4}+H_{2}O} [Co(L)(PX_{3})]^{+} \xrightarrow[AiclO_{4}+H_{2}O]{AiclO_{4}+H_{2}O} [Co(L)(PX_{3})]^{+} \xrightarrow[PX]{AiclO_{4}+H_{2}O} [Co(L)(PX_{3})$$

where  $H_2L = 3,4$ -Salpyr $H_2$ , 5-Br-3,4-Salpyr $H_2$  and X = Bu<sub>3</sub>, PPh<sub>2</sub>Me.

The resulting compounds are non-hygroscopic and air stable solids. Some physical properties, such as, decomposition temperatures, colors and percentage of yields as well as the analytical data of these compounds are given in Table 1. The compounds so obtained were characterized by various physico-chemical techniques, viz. <sup>1</sup>H NMR, IR, UV–Vis spectroscopy and elemental analysis.

#### Infrared spectral studies

The IR spectra provide valuable information regarding the nature of functional groups attached to the metal atom. The ligands and the metal complexes were characterized mainly using the azomethine band. The main infrared bands and their assignments are listed in Table 2. The IR spectra of the ligands exhibit broad medium intensity bands in the range 3402-3456 cm<sup>-1</sup> which are assigned to the intra molecular hydrogen bonding vibration  $(O-H \cdots N)$  (see Table 2). These bands were disappeared via complexation to the metal ions [17]. The band appearing at  $\sim$ 1616 cm<sup>-1</sup> due to azomethine was shifted to a lower frequency by  $\sim 1-15 \text{ cm}^{-1}$  in the complexes, indicating participation of azomethine nitrogen in the interaction with the metal ion [18]. Coordination of azomethine nitrogen is affirmed with the presence of new bands at 450–480  $cm^{-1}$  region assignable to  $\nu_{M-N}$  for these complexes [19]. The  $v_{C-0}$  stretching frequency shifts in the complexes towards lower or higher values as a result of coordination

Table 1

Analytical and physical data of the ligands and their Co(III) complexes.

of the oxygen to the metal ion [20,21]. A new band in the 400–460 cm<sup>-1</sup> range of the complexes is assignable to  $v_{M-O}$  [22]. The other series of weak bands between 3100 and 2800 cm<sup>-1</sup> are related to (C–H) modes of vibrations [23]. At ~1093 cm<sup>-1</sup> very strong bands are ascribed to the stretching vibration of  $ClO_4^-$ .

All the IR data suggest that the metal is bonded to the Schiff base through the phenolic oxygen and the imino nitrogen.

#### Electronic spectra

The electronic spectra of the Schiff bases and their complexes are summarized in Table 3. The spectra of the ligands exhibit bands at about 330 nm and a broad shoulder at 460 nm. The first peak is attributed to  $\pi \rightarrow \pi^*$  transitions. This band was not significantly affected by chelation. The second band in the spectra of the ligands is assigned to  $n \rightarrow \pi^*$  transition. This band is disappeared via complexation and a new band attribured to the donation of the lone pairs of the nitrogen atoms of the Schiff base to the metal ion  $(N \rightarrow M)$  appear [24]. Camparing this with  $n \rightarrow \pi^*$  transition, this band was shifted to a longer wavelength along with increasing in its intensity.

All the complexes show a band in the range of 440–500 nm, which is attributed to  $d \rightarrow \pi^*$  transition that is mixed with  $d \rightarrow d$  transition. The study of the electronic spectra to identify the  $d \rightarrow d$  transitions in the presence of a ligand field has encountered difficulties because several bands fall in the near-infrared region with a low intensity while a large part of the visible region is obscured by intense charge transfer and intraligand ( $\pi \rightarrow \pi^*$ ) transitions [25].

#### <sup>1</sup>H NMR spectra

The <sup>1</sup>H NMR spectra of all the Schiff bases (data shown in Table 4) provide compelling evidence of the presence of either one or two azomethine groups. By comparing the <sup>1</sup>H NMR spectra of the Schiff bases and their complexes, it is noted that there is a down- or upfield shift in the frequency of azomethine protons confirming coordination of the metal ion to these groups. In complexes, the absence of hydroxyl protons in  $\sim$ 12 ppm provides evidence for coordination through two oxygen atoms (after deprotonation of the ortho hydroxyl groups). The <sup>1</sup>H NMR spectra of the complexes showed a differentiation of almost all hydrogen atoms, since they are in different chemical environments due to the rigid structure in which the ligand lies when it is coordinated to the metal center [26]. Three sets of signals were observed for the pyridyl groups of the Schiff bases which coordinated to the metal ion (9.1–6.5 ppm). The formation of rigid structure also supports the clearer visualization of aromatic protons. These protons were observed in the range of  $\sim$ 6.4–8.2 ppm and CH<sub>3</sub> proton was seen at 1.5 ppm. In the spectra of complexes, two sets of resonances were observed for methine proton, which

Compounds	Color	Yields (%)	m.p. (°C)	Anal. found (Calcd)%		
				С	Н	Ν
Half unit 0.25 (H <sub>2</sub> O)	Yellow	62	140	65.82(66.19)	4.99(5.32)	19.02(19.30)
3,4-SalpyrH <sub>2</sub>	Oranges	52	145	69.70(69.93)	4.99(4.94)	12.50(12.88)
	yellow					
(3,4-5-Br-SalpyrH <sub>2</sub> )·0.5(H <sub>2</sub> O)	Yellow	50	120	56.03(56.31)	4.08(3.73)	9.95(10.37)
[Co(3,4-Salpyr) (PBu <sub>3</sub> )]ClO <sub>4</sub> ·(H <sub>2</sub> O)	Brown	51	>250	53.79(53.65)	6.30(6.10)	6.30(6.05)
[Co(5-Br-3,4-Salpyr)(PBu <sub>3</sub> )]ClO <sub>4</sub> ·(H <sub>2</sub> O)	Brown	64	>250	47.79(48.17)	5.30(5.35)	5.33(5.44)
$[Co(3,4-Salpyr)(PPh_2Me)]ClO_4(H_2O)$	Brown	67	>250	55.23(55.55)	3.8(4.08)	6.10(6.07)
$[Co(3,4-Salpyr)(PBu_3)_2]ClO_4 \cdot (H_2O)$	Brown	61	>250	60.45(60.63)	8.15(7.99)	5.00(4.93)

Table 2
IR spectral data of the Schiff bases and their Co(III) complexes (cm <sup>-1</sup> )

Compounds	U <sub>(NH2)</sub>	U <sub>(OH)</sub>	$\upsilon_{(C=N)}$	$\upsilon_{(C=C)}$	υ <sub>(C-O)</sub>	$\upsilon_{(M-N)}$	υ <sub>(M-O)</sub>	$\upsilon_{ClO4}$
1	3463 3290	2750	1616	1589	1276			
2		3456	1610	1554	1274			
3		3427	1612	1558	1272			
4		3427	1608	1573	1188	623	405	1093
5		3444	1604	1573	1176	536	464	1093
6		3436	1606	1573	1190	501	457	1095
7		3342	1602	1548	1149	536	472	1093

#### Table 3

UV-Vis data of the compounds in methanol.

Compounds	$\lambda$ max (nm)
2	334, 465(sh) <sup>a</sup>
3	330, 460(sh) <sup>a</sup>
4	308, 379, 490
5	319, 381, 503
6	307, 380, 487
7	306, 385, 500

<sup>a</sup> sh = shoulder.

shows they are in different chemical environments. The signals for these protons were observed in the ~8.2–9.6 ppm range [26]. The protons chemical shifts for the coordinated PBu<sub>3</sub> in the Schiff base complexes appear at  $\delta$  = 0.7 up to 1.3 ppm. These results are in agreement with the previous results observed for metal complexes of phosphine as axial ligand [27,28].

# The study of the donor ligand, axial and equatorial ligand on the formation constants of tributyl phosphinecobalt(III) Schiff base complexes derived from 3,4-DAP

The formation constants of the various cobalt(III) Schiff-base complexes titrated with various donors were calculated by using, Ketelaar's equation [12,27,29]. The linear plots of *P* against *C*, where *P* is defined as  $P = (C_A^c C_D^c) / (A - A_A^c - A_D^c)$  and *C* as  $C = (C_A^c + C_D^c)$  for [Co(3,4-Salpyr)(PBu<sub>3</sub>)]ClO<sub>4</sub>·H<sub>2</sub>O titrated with PBu<sub>3</sub> at various temperatures in 96% methanol are shown in Fig. 2, which signify that only a 1:1 complex is formed.

Similar plots are obtained for other systems. The adduct formation constants are collected in Tables 5–8.

## Table 4 $^{1}$ H NMR spectral data of the Schiff bases and the complexes in DMSO d<sub>6</sub> ( $\delta$ , ppm)

Thermodynamic properties of the cobalt(III) Schiff base complexes with donors

Aromatic amines as donors. In our earlier work of this series, the base strength of the cyclic amines on the adduct formation constants of some symmetrical pentacoordinated Co(III) Schiff base complexes were studied [12]. In the present article, the effect of these amines have been examined on the formation constants of the unsymmetrical Co(III) Schiff base complexes derived from 3,4-DAP according to Eq. (3) (Table 5).

As one can see, the formation constants for these bases with  $[Co(3,4-Salpyr)(PBu_3)]^+$  are decreased with increasing the steric hindrance of the donor bases and it is in contrast with trend of the basic constants,  $K_b$ , of these amines [12,30] (see Table 5).

*Phosphines as donors.* The adduct formation of some pentacoordinated cobalt(III) Schiff base complexes were studied according to Eqs. (1) and (2) with two phosphines as donors. The steric and the electronic effects of the entering ligands toward the Schiff base complexes and the entering ligands were studied. These data are collected in Table 6.

The electronic effects of phosphines have been expressed by  $\sigma^*$  values of Taft (Taft constants).  $\sigma^*$  value for PBu<sub>3</sub> is -0.390 and for PPh<sub>2</sub>Me was not reported in literature (but for PPh<sub>2</sub>Et is +1.10 and for PPhMe<sub>2</sub> is +0.60) [12,31,32]. Also, the phenyl withdrawing groups decrease the basic properties of PPh<sub>2</sub>Me with respect to PBu<sub>3</sub>. The formation constants increased according to the following trend:PBu<sub>3</sub> > PPh<sub>2</sub>Me.

The phosphine ligands have an important steric factor that it can decrease the trend of five-coordinated complex toward the donor bases. This factor is shown by Tolman's cone angle. The cone angle for PPh<sub>2</sub>Me and PBu<sub>3</sub> are  $136^{\circ}$  and  $132^{\circ}$ , respectively [33]. The steric effect increased with increase in the cone angle. So by

Compounds	H-C=N	Pyridine-H	Ar—H	OH	PBu <sub>3</sub>	NH <sub>2</sub>	$-CH_3$
1	8.8(1H, H <sup>7</sup> )	7.0(1H, H <sup>5</sup> ) 7.6(1H, H <sup>6</sup> ) 7.8(1H, H <sup>2</sup> )	6.6-7.4(4H)	12.1(H <sup>1</sup> )		5.8(2H)	
2	8.1(1H, H <sup>14</sup> ) 8.6(1H, H <sup>7</sup> )	6.6–7.6(2H) 8.1(1H, H <sup>2</sup> )	6.6-7.6(8H)	12.5(1H, H <sup>2</sup> ) 12.6(1H, H <sup>1</sup> )			
3	8.9(1H, H <sup>14</sup> ) 9.0(1H, H <sup>7</sup> )	6.9–7.9(1H, H <sup>5</sup> ) 8.5(1H, H <sup>6</sup> ) 8.6(1H, H <sup>2</sup> )	6.9-7.9(7H)	12.1(1H, H <sup>2</sup> ) 12.5(1H, H <sup>1</sup> )			
4	9.1(1H, H <sup>14</sup> ) 9.6(1H, H <sup>7</sup> )	8.3(1H, H <sup>5</sup> ) 8.6(1H, H <sup>6</sup> ) 9.1(1H, H <sup>2</sup> )	6.7-7.6(8H)		0.7-0.8(9H, CH <sub>3</sub> ) 1.2-1.3(18H, CH <sub>2</sub> )		
5	9.1(1H, H <sup>14</sup> ) 9.5(1H, H <sup>7</sup> )	7.6-8.6(2H) 9.1(1H, H <sup>2</sup> )	6.7-8.2(7H)		0.7–0.8(9H, CH <sub>3</sub> ) 1.2–1.3(18H, CH <sub>2</sub> )		
6	8.5(1H, H <sup>14</sup> ) 8.8(1H, H <sup>7</sup> )	6.6–7.4(1H, H <sup>5</sup> ) 8.0(1H, H <sup>6</sup> ) 8.5(1H, H <sup>2</sup> )	6.6-7.4(18H)				1.4
7	8.7(1H, H <sup>14</sup> ) 9.0(1H, H <sup>7</sup> )	6.4–7.4 (2H) 7.5(1H, H <sup>2</sup> )	6.4-7.4(8H)		0.6–0.8(18H, CH <sub>3</sub> ) 1.2–1.3(36H, CH <sub>2</sub> )		

increasing the cone angle in PPh<sub>2</sub>Me, the formation constant is decreased. The formation constants increased according to the following trend:  $PBu_3 > PPh_2Me$  So, the steric and the electronic properties affect the formation constant of the complexes.



**Fig. 2.** Typical plots of *P* against *C* for [Co(3,4-Salpyr)(PBu<sub>3</sub>)]ClO<sub>4</sub>·H<sub>2</sub>O titrated with PBu<sub>3</sub> at various temperatures (*T* = 283 to 313 K) in 96% methanol, *I* = 0.1 M.  $P = (C_A^c C_D^c) / (A - A_A^c - A_D^c)$  and *C* as  $C = (C_A^c + C_D^c)$ .

#### Table 5

The formation constants,  $(10^{-1})/K/(dm^3 mol)^{-1}$ , for the interaction between  $[Co(3,4-Salpyr)(PBu_3)]^*$  with Im and its derivatives in 96% methanol.

Donors	$(10^{-1})/K/(dm^3 mol)^{-1}$
Im	118.7 ± 3.0
2-MeIm	11.2 ± 1.1
2-EtIm	$8.0 \pm 1.0$
BzIm	$4.9 \pm 0.8$

<sup>a</sup> T = 293 K.

#### Table 6

The formation constants,  $10^{-1}/K/(dm^3 \text{ mol})^{-1}$ , for the interaction between Co(III) complexes with PBu<sub>3</sub> and PPh<sub>2</sub>Me in 96% methanol.

	283 K	293 K	303 K	313 K
PPh <sub>2</sub> Me [Co(5-Br-3,4-Salpyr)(PBu <sub>3</sub> )] <sup>*</sup> [Co(3,4-Salpyr)(PBu <sub>3</sub> )] <sup>*</sup> [Co(3,4-Salpyr)(PPh <sub>2</sub> Me)] <sup>*</sup>	58.3 ± 7.7 65.0 ± 6.5 60.7 ± 8.7	42.7 ± 5.8 58.1 ± 7.0 44.0 ± 1.0	33.0 ± 1.3 35.3 ± 5.3 31.1 ± 2.3	26.8 ± 1.0 30.1 ± 4.7 28.4 ± 1.2
PBu <sub>3</sub> [Co(5-Br-3,4-Salpyr)(PBu <sub>3</sub> )] <sup>+</sup> [Co(3,4-Salpyr)(PBu <sub>3</sub> )] <sup>+</sup> [Co(3,4-Salpyr)(PPh <sub>2</sub> Me)] <sup>+</sup>	64.4 ± 1.4 73.9 ± 9.3 68.0 ± 5.2	52.0 ± 8.6 67.6 ± 1.0 55.6 ± 1.5	33.9 ± 1.4 58.9 ± 4.8 34.7 ± 1.0	30.0 ± 5.2 49.9 ± 7.1 31.2 ± 1.1

#### Table 7

The formation constants  $(10^{-3})/K/(dm^3 mol)^{-1}$ , for the interaction between Co(III) Schiff base complexes with n-butyl amine in 96% methanol.

Compounds	$(10^{-3})/K/(dm^3 mol)^{-1}$
[Co(3,4-Salpyr)(PBu <sub>3</sub> )] <sup>+</sup>	$2.9 \pm 0.2$
[Co(3,4-Salpyr)(PPh <sub>2</sub> Me)] <sup>+</sup>	$2.0 \pm 0.2$

 $^{a}T = 293$  K.

#### The electronic effect of the equatorial Schiff base ligands

The equatorial ligands play important role in the stability and the reactivity of their complexes. Herein, the role of 2 equatorial ligands was shown on the stability of the five-coordinated complexes. In the cases of the complexes studied here, the formation constants for  $[Co(3,4-Salpyr)(PBu_3)]^+$  in methanol are larger than the other complexes with a given donor (Table 6).

It is observed that in 3,4-Salpyr the stability of the solvated fivecoordinated complex has decreased and the formation constants of the six-coordinated adduct has been increased. It seems that in the five-coordinated complexes, a water or a solvent molecule occupies the sixth position (Eq. (4)) which would decrease the tendency of the complexes toward the interaction with the donors.

$$[Co(Chel)(PBu_3)]^+ + S \rightleftharpoons [Co(Chel)(PBu_3)S]^+$$
(4)

#### where $S = H_2O$ or solvent molecule.

Concerning the stabilization of the five-coordinate complex, the donation power of the Schiff base is important. Therefore the cobalt atom in  $[Co(5-Br-3,4-Salpyr)(PBu_3)]^*$  complex has more acceptor property than the other type of the complexes and forms more stable complex with H<sub>2</sub>O or solvent molecule (Eq. (4)). Therefore its tendency for the reaction with donors decreases, hence its formation constant, K, with donors is lower and it is in agreement with our previous work [12].

#### The effect of the axial ligands

Concerning the stabilization of the five-coordinate complex, the donation power of the Schiff base is important. By decreasing the  $\sigma^*$  in PPh<sub>2</sub>Me, the cobalt atom in  $[Co(3,4-Salpyr)(PPh_2Me)]^*$  complex has more acceptor property than the other type of the complexes and forms more stable complex with H<sub>2</sub>O or solvent molecule (Eq. (4)). Therefore its tendency for the reaction with donors decreases and its formation constant, K, with donors is lower [12]. So, the formation constants increased according to the following trend: PBu<sub>3</sub> > PPh<sub>2</sub>Me.

#### Effect of the temperature on the formation constants

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

#### Table 8

The thermodynamic parameter values  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  values for the interaction between Co(III) Schiff base complexes with various phosphines in 96% methanol.<sup>a</sup>

Compounds	$\Delta G^{\circ a}/(\text{kJ mol}^{-1})$	$\Delta H^{\circ}/(\text{kJ mol}^{-1})$	$\Delta S^{\circ}/(\text{kJ mol}^{-1})$
PPh <sub>2</sub> Me [Co(5-Br-3.4-Salpyr)(PBu <sub>2</sub> )] <sup>+</sup>	-14.6 ± 1.1	$-19.1 \pm 0.7$	-14.7 ± 2.7
$[Co(3,4-Salpyr)(PBu_3)]^+$ $[Co(3,4-Salpyr)(PPh_2Me)]^+$	$-15.0 \pm 5.6$ $-14.7 \pm 3.8$	$-20.6 \pm 3.9$ $-19.4 \pm 2.7$	$-18.6 \pm 13.1$ $-15.7 \pm 9.1$
PBu <sub>3</sub> [Co(5-Br-3,4-Salpyr)(PBu <sub>3</sub> )] <sup>+</sup> [Co(3,4-Salpyr)(PBu <sub>3</sub> )] <sup>+</sup> [Co(3,4-Salpyr)(PPh <sub>2</sub> Me)] <sup>+</sup>	$-15.0 \pm 3.9$ $-16.0 \pm 1.5$ $-15.0 \pm 4.8$	$\begin{array}{c} -20.0 \pm 2.7 \\ -9.6 \pm 1.1 \\ -20.7 \pm 1.1 \end{array}$	$-17.0 \pm 9.4$ 21.0 ± 3.7 $-18.8 \pm 11.3$

<sup>a</sup>  $\Delta G^{\circ}$  values are calculated from  $\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$  at T = 293 K.

Table 9
$\Delta G^{\circ}$ (kJ mol <sup>-1</sup> ) values for the interaction between Co(III) Schiff base complexes with various phosphines in 96% methanol.

Compounds	283 K	293 K	303 K	313 K
PBu <sub>3</sub>				
$[Co(3,4-Salpyr)(PBu_3)]^+$	$-15.5 \pm 0.2$	$-15.8 \pm 0.9$	$-16.0 \pm 1.0$	$-16.2 \pm 0.2$
[Co(3,4-Salpyr)(PPh <sub>2</sub> Me)] <sup>+</sup>	$-15.3 \pm 0.5$	$-15.4 \pm 0.3$	$-14.7 \pm 0.8$	$-14.9 \pm 0.5$
[Co(5-Br-3,4-Salpyr)(PBu <sub>3</sub> )] <sup>+</sup>	$-15.2 \pm 0.6$	$-15.2 \pm 0.6$	$-14.7 \pm 0.7$	$-14.8 \pm 0.1$
PPh <sub>2</sub> Me				
[Co(3,4-Salpyr)(PBu <sub>3</sub> )] <sup>+</sup>	$-15.2 \pm 0.7$	$-15.5 \pm 0.8$	$-14.8 \pm 0.4$	$-14.8 \pm 0.6$
[Co(3,4-Salpyr)(PPh <sub>2</sub> Me)] <sup>+</sup>	$-15.1 \pm .08$	$-14.8 \pm 0.4$	$-14.4 \pm 0.8$	$-14.7 \pm 0.7$
$[Co(5-Br-3,4-Salpyr)(PBu_3)]^+$	$-15.0 \pm 0.5$	$-14.7 \pm 0.6$	$-14.6 \pm 0.6$	$-14.5 \pm 0.5$

#### Thermodynamic free energy change

The free energy change  $\Delta G^{\circ}$  values of the studied cobalt(III) Schiff base complexes titrated with various donors were calculated from  $\Delta G^{\circ} = -RT \ln K_f$  at various temperatures (see Table 9). The linear plot of [Co(3,4-Salpyr)(PBu<sub>3</sub>)]ClO<sub>4</sub>·H<sub>2</sub>O titrated with PBu<sub>3</sub> at various temperatures in 96% methanol is shown in Fig. 3S.

#### 4. Conclusions

The synthesis and characterization of some new Schiff bases derived from 3,4-DAP and their new five and six coordinated Co(III) complexes were performed. The thermodynamic formation constants, K, the thermodynamic free energy change values for the above adducts of the mentioned complexes with various donors were determined spectrophotometrically. The results show that the formation constants depend on electronic and steric effects of the donors and the axial ligands.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2013.09.098.

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