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Synthesis, characterization, and thermodynamics of some new unsymmetrical Co(III) Schiff base complexes derived from 2,3-diaminopyridine

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Abstract Some new Schiff bases derived from 2,3diaminopyridine and their new Co(III) complexes were synthesized and characterized. The formation constants of the Co(III) complexes vary according to the following trend: 5-MeO > 5-H > 5-Br and 5-MeO > 3-MeO > 4-MeO. For a given donor, the order of formation constants according to the axial ligand is PBu₃ > PPh₂Me. The binding trend of the donors toward a given cobalt(III) Schiff base complex is as follows: benzylamine > *n*butylamine > *sec*-butylamine > *tert*-butylamine; Im > 2-MeIm > 2-EtIm > BzIm; and PBu₃ > PPh₂Me.

Keywords Cobalt(III) · Unsymmetrical Schiff base · Thermodynamic free energy change · Formation constants

Introduction

Schiff bases involving a pyridine ring have received considerable attention in the literature because of their very important role in biological systems [1]. They may also be used as analytical reagents for metals [2, 3] and as antiinflammatory agents [4]. Schiff bases resulting from the

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condensation of *o*-hydroxyaromatic aldehydes and aminopyridines are interesting because of their thermo- and photochromic properties [5, 6], tautomeric equilibria [7, 8], potential applications in chemical analysis [2, 9], and use as therapeutic agents [3]. However, much less information is available regarding the thermodynamics of these kinds of Schiff bases.

In our previous reports, the thermodynamics of a new Co(III) Schiff base complex derivative from 2,3-diaminopyridine (2,3-DAP) with a salicylaldehyde [10] and its application as a sensor [11] were investigated. In this context, the present work focuses on the synthesis and thermodynamic properties of some other unsymmetrical cobalt(III) Schiff base complexes of 2,3-DAP with different ligand donors. The spectral and thermodynamic properties of the complexes were investigated and compared in order to determine the effects of different electronic and steric factors.

Results and discussion

Because 2,3-diaminopyridine has two different condensation sites, one might expect two mono Schiff bases to be formed by 1:1 condensation; however, only compound **1** was obtained (Scheme 1). The lower reactivity of the 2-amino group with respect to the 3-amino group may be attributed to the contribution of the resonance structure **II** [12] (Scheme 2). By mixing the mono Schiff base **1** with an appropriate aldehyde in a 1:1 ratio, the bis Schiff bases **2** were obtained. The complexes **3** were prepared according to Scheme 3. The resulting compounds are non-hygroscopic and air-stable solids. The compounds were characterized by various physicochemical techniques, viz. ¹H NMR, ¹³C NMR, IR, UV–Vis spectroscopy, and elemental analysis.

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Scheme 1





$$R = 5-Br (2a), 5-OCH_3 (2b), 4-OCH_3 (2c), 3-OCH_3 (2d)$$



Infrared spectral studies

The IR spectra of the ligands exhibit broad medium intensity bands in the 2,800–3,400 cm⁻¹ range which are assigned to the intramolecular hydrogen bonding vibration (O–H…N). These bands disappeared on complexation to cobalt(III) ions [13]. The IR spectra of the complexes exhibit absorption around 3,450 cm⁻¹ that is attributed to the presence of lattice and coordinated water [14].

The band appearing at around $1,604-1,624 \text{ cm}^{-1}$ due to azomethine was shifted to a lower frequency by approximately $1-15 \text{ cm}^{-1}$ in the complexes, indicating participation of the azomethine nitrogen in the interaction with the metal ion [15]. Coordination of azomethine the nitrogen is confirmed by the presence of new bands at 540–570 cm⁻¹ assignable to v_{M-N} for these complexes [16]. The v_{C-O} stretching frequency shifts in the complexes towards lower or higher values as a result of coordination of the oxygen to the metal ion [17–19]. A new band in the 460–470 cm⁻¹ range of the complexes is assignable to v_{M-O} [20]. The other series of weak bands between 3,100 and 2,800 cm⁻¹ are related to (C–H) modes of vibrations [21]. All the IR data suggest that the metal is bonded to the Schiff bases through the phenolic oxygen and imino nitrogen.

Electronic spectra

The spectra of the ligands exhibit bands at about 305-380 nm and a broad shoulder at approximately 450 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 ligand is assigned to $n \rightarrow \pi^*$ transition that involves the nonbonding electrons of the azomethine nitrogen atom. This band is shifted to a longer wavelength and is increased in intensity. This shift may be attributed to the donation of the lone pairs of the nitrogen atoms of the Schiff base to the metal ion (N \rightarrow M) [22].

All the complexes show a band in the range of 440–500 nm, which is attributed to a $d \rightarrow \pi^*$ transition that is mixed with $d \rightarrow d$ transitions. 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 [14].

Scheme 3

$$H_{2}L + Co(OAc)_{2} \cdot 4H_{2}O \xrightarrow{MeOH} [Co(L)(PX)] \xrightarrow{NaCIO_{4} \cdot H_{2}O} [Co(L)(PX)]CIO_{4} \cdot H_{2}O$$

 H_2L = 5-Br-2,3-Salpyr, 5-MeO-2,3-Salpyr, 4-MeO-2,3-Salpyr, 3-MeO-2,3-Salpyr; X = Bu_3 H_2L = 2,3-Salpyr; X = Ph_2Me

Scheme 4

[Co(Chel) (L)]⁺ + Y - [Co(Chel)(PBu₃)Y]⁺

Chel = 5-Br-2,3-Salpyr, 5-MeO-2,3-Salpyr, 4-MeO-2,3-Salpyr, 3-MeO-2,3-Salpyr; Y = n-butylamine; L= PBu ₃	(a)
Chel = 5-Br-2,3-Salpyr; Y = n-butyl-, sec-butyl-, tert-butyl-, benzylamine; L = PBu ₃	(b)
Chel = $2,3$ -Salpyr; Y = PBu ₃ , PPh ₂ Me; L = PBu ₃	(c)
Chel = 2.3-Salpyr: Y = Im. 2-EtIm. 2-Melm. BzIm: L = PPh ₂ Me	(d)

¹H and ¹³C NMR spectra

The ¹H NMR spectra of all the Schiff bases provide compelling evidence of the presence of either one or two azomethine groups. By comparing the ¹H NMR spectra of the Schiff bases and their complexes, it is noted that there is a down- or upfield shift in the frequency of the azomethine protons confirming coordination of the metal ion to these groups. In complexes, the absence of hydroxyl protons at approximately 12 ppm provides evidence for coordination through two oxygen atoms (after deprotonation of the *ortho* hydroxyl groups). The ¹H NMR spectra of the complexes showed a differentiation of almost all hydrogen atoms, because they are in different chemical environments owing to the rigid structure in which the ligand lies when it is coordinated to the metal center [23]. Three sets of signals were observed for the pyridyl groups of the Schiff bases which coordinated to metal ion (9.0–6.3 ppm). The formation of rigid structure also helps the clearer visualization of aromatic protons. These protons were observed in the range of approximately 6.9-8.5 ppm. In the spectra of complexes, two sets of resonances were observed for methine protons, which shows that they are in different chemical environments. The signals for these protons were observed at around 8.4-9.5 ppm [23] and those for the hydrogens of the methoxy groups were are at 3.7 ppm. The proton chemical shifts for the coordinated PBu₃ in the Schiff base complexes appear at 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 [10, 24, 25].

The ¹³C NMR spectra provide further support for the structural characterization of the Schiff bases. They were recorded by employing TMS as internal reference and CDCl₃ and DMSO- d_6 as solvents at ambient temperature.

The number of signals of sharp peaks represents the number of carbons of the compounds which are chemically non-equivalent. These spectra gave the correct number of carbon signals required by the suggested structures. The spectra of the complexes showed the presence of two imine and two C(O) signals for carbon atoms.

Thermodynamic studies

The formation constants were determined by UV–Vis absorption spectroscopy from the reaction of the acceptors with the donors in 96 % methanol solvent (Scheme 4).

A solution of each complex at a concentration of about 3×10^{-5} M was prepared and constant ionic strength (I = 0.1 M) was maintained by addition of sodium perchlorate. In a typical titration, 2.5 cm³ 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 against the given amine. The titration was done by adding aliquots of the amine with a Hamilton microliter syringe. The donor's concentration was varied between 1- and 3-fold in excess.

The absorption measurements were carried out at various wavelengths where the difference in absorption was the maximum after the equilibrium was assessed. The formed adduct shows an absorption different from the acceptor, whereas the donors show no absorption at those wavelengths. As an example, the variation of the electronic spectra for [Co(2,3-Salpyr)(PBu₃)]ClO₄·H₂O titrated with PBu₃ at T = 293 K in 96 % methanol is shown in Fig. 1. The isosbestic points of this system show that there is only one reaction in equilibrium. The same is valid for other systems.



Fig. 1 Variation of the electronic spectra of [Co(2,3-Salpyr)(PBu₃)] ClO₄·H₂O titrated with PBu₃ at 293 K in 96 % methanol



Fig. 2 Typical plots of *P* against *C* for [Co(5-Br-2,3-Salpyr)(PBu₃)]ClO₄·H₂O titrated with *n*-butylamine at various temperatures (283–313 K) in 96 % methanol, I = 0.1 M. $P = (C^{\circ}_{A}C^{\circ}_{D})/(A - A^{\circ}_{A} - A^{\circ}_{D})$ and $C = (C^{\circ}_{A} + C^{\circ}_{D})$

Effects of donor, axial and equatorial ligands, and temperature on the formation constants of the tributylphosphinecobalt(III) Schiff base

The formation constants of the various cobalt(III) Schiff base complexes were calculated by using Ketelaar's equation [10, 24, 26]. The linear plots of *P* against *C*, where $P = (C^{\circ}_{A}C^{\circ}_{D})/(A - A^{\circ}_{A} - A^{\circ}_{D})$ and $C = (C^{\circ}_{A} + C^{\circ}_{D})$, for [Co(2,3-Salpyr)(PBu₃)]ClO₄·H₂O titrated with PBu₃ at various temperatures in 96 % methanol are shown in Fig. 2, which signify that only a 1:1 complex is formed. Similar plots were obtained for other systems. The adduct formation constants are collected in Tables 1, 2, 3, 4, and 5.

Acceptor properties of Co(III) Schiff base complexes

Aliphatic amines as donors

The comparison of the reactivity of amine compounds toward metal complexes has primarily focused on pK_a

Table 1	Formation constants,	10^{-3}	³ / <i>K</i> /dm ³	mol^{-1} ,	for th	e interaction
[Co(5-Br	-2,3-Salpyr)(PBu ₃)] ⁺	with	various	amines	in 96	% methanol

<i>T/</i> K	Benzyl	<i>n</i> -Butyl	sec-Butyl	<i>tert</i> -Butyl
283	5.2 ± 1.1	4.1 ± 0.5	3.8 ± 0.2	1.4 ± 0.1
293	4.5 ± 0.7	3.6 ± 0.4	3.5 ± 0.3	1.0 ± 0.1
303	3.0 ± 0.1	2.9 ± 0.3	2.7 ± 0.4	0.7 ± 0.0
313	2.2 ± 0.4	1.9 ± 0.1	1.6 ± 0.3	0.6 ± 0.0

Table 2 Formation constants, $10^{-1}/K/dm^3 \text{ mol}^{-1}$, for the interaction $[Co(2,3-Salpyr)(PPh_2Me)]^+$ with Im and its derivatives in 96 % methanol

T/K	Im	2-MeIm	2-EtIm	BzIm
283	257.0 ± 19.0	16.7 ± 1.0	13.2 ± 1.0	10.4 ± 0.6
293	226.7 ± 10.0	13.2 ± 1.6	12.3 ± 1.0	8.6 ± 0.1
303	182.8 ± 7.0	12.7 ± 0.9	7.2 ± 1.7	6.8 ± 0.2
313	123.8 ± 4.0	5.4 ± 0.4	1.8 ± 0.6	4.3 ± 0.1

Table 3 Formation constants, $10^{-2}/K/dm^3 \text{ mol}^{-1}$, for the interaction [Co(2,3-Salpyr)(PBu₃)]⁺ with phosphines in 96 % methanol at 293 K

PBu ₃	7.2 ± 0.3
PPh ₂ Me	2.3 ± 0.2

trends [27, 28]. Four amines, *n*-butyl-, *sec*-butyl-, *tert*butyl-, and benzylamine, were chosen to measure the relative binding constants for a range of sterically and electronically varied amines. Here, we attempt to separate these two parameters and use cone angles to place amine and phosphine ligands on a common steric scale. The amines have an important steric factor that is shown by Trogler's cone angle [28]. The cone angles of *sec*-butylamine, *tert*-butylamine, and benzylamine are 113°, 123°, and 106°, respectively. The cone angle of *n*-butylamine is unpublished. The formation constants were increased by decreasing the cone angles.

The electronic effect of amines is shown by Taft σ^* values, which are +0.85, +0.77, +0.68, and +1.2 for *n*-butylamine, *sec*-butylamine, *tert*-butylamine, and benzylamine, respectively [29]. On the base of the results in Table 1, the formation constants follow the sequence below:

benzylamine > n - butylamine > sec - butylamine > tert - butylamine

Aromatic amines as donors

We previously studied the effect of the base strength of the cyclic amines on the adduct formation constants of some symmetrical pentacoordinated Co(III) Schiff base

Table 4 Formation constants, $10^{-3}/K/dm^3 mol^{-1}$, for the interaction Co(III) complexes	<i>T/</i> K	[Co(5-Br-2,3- Salpyr)(PBu ₃)] ⁺	[Co(5-MeO-2,3- Salpyr)(PBu ₃)] ⁺	[Co(4-MeO-2,3- Salpyr)(PBu ₃)] ⁺	[Co(3-MeO-2,3 Salpyr)(PBu ₃)] ⁺
with <i>n</i> -butylamine in 96 %	283	4.1 ± 0.5	6.3 ± 1.0	4.7 ± 1.1	5.9 ± 1.2
methanol	293	3.6 ± 0.4	6.0 ± 0.4	4.4 ± 0.3	5.5 ± 1.2
	303	2.9 ± 0.3	3.5 ± 0.3	3.1 ± 0.6	3.4 ± 0.3
	313	1.9 ± 0.1	2.4 ± 0.3	2.1 ± 0.8	2.3 ± 0.0

Table 5 Formation constants, $10^{-2}/K/dm^3 mol^{-1}$, for the interaction Co(III) complexes with Im and its derivatives in 96 % methanol at 293 K

Compounds	Im	2-MeIm	2-EtIm	BzIm
[Co(2,3- Salpyr)(PBu ₃)] ⁺	45.2 ± 2.0	4.0 ± 0.6	1.6 ± 0.2	1.4 ± 0.2
[Co(2,3- Salpyr)(PPh ₂ Me)] ⁺	22.6 ± 1.0	1.3 ± 0.1	1.2 ± 0.1	0.8 ± 0.0

complexes [10]. In the present manuscript, the effects of these amines were examined on the formation constants of the unsymmetrical Co(III) Schiff base complexes derived from 2,3-DAP according to equation (d) in Scheme 4 (Table 2). The results show the following trend in the adduct formation between Co(III) Schiff base complexes as acceptors and the aromatic amines as donors:

Im > 2-MeIm > 2-EtIm > BzIm

As one can see, the formation constants for these bases with $[Co(2,3-Salpyr)(PPh_2Me)]^+$ are decreased with increasing the steric hindrance of the donor bases and it is in contrast with trend of the basic constants, $K_{\rm b}$, of these amines [10, 30] (Table 2).

Phosphines as donors

The adduct formations of some pentacoordinated cobalt(III) Schiff base complexes were studied according to equation (c) in Scheme 4 with two phosphines as donors. The steric and the electronic effects of the entering ligands of the Schiff base complexes were studied. Theses data are collected in Table 3.

The electronic effects of phosphines are expressed by Taft σ^* values. The σ^* value for PBu₃ is -0.390 and that for PPh₂Me was not reported in the literature (but for PPh₂Et is +1.10 and for PPhMe₂ is +0.60) [10, 31, 32]. Also, the phenyl electron-withdrawing groups decrease the basic properties of PPh₂Me with respect to PBu₃. The formation constants increased according to the order $PBu_3 > PPh_2Me$.

The phosphine ligands have an important steric effect that can decrease the tendency to form five-coordinated complexes with the donor bases. This factor is shown by Tolman's cone angle. The cone angles for PPh₂Me and Scheme 5

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

 $S = H_2O$ or solvent molecule

PBu₃ are 136° and 132°, respectively [33]. The steric effect increased with increase in the cone angle. So by increasing the cone angle in PPh₂Me, the formation constant is decreased. So, the steric and the electronic properties affect the formation constant of the complexes.

Electronic effect of the equatorial Schiff base ligands

The equatorial ligands play an important role in the stability and the reactivity of the complexes. We determined the role of four equatorial ligands in the stability of the five-coordinated complexes. The formation constants for $[Co(5-MeO-2,3-Salpyr)(PBu_3)]^+$ in methanol are larger than those of all the other complexes with all donors (Table 4).

The addition of a methoxy group to 2,3-Salpyr decreased the stability of the solvated five-coordinated complex and increased the formation constants of the sixcoordinated adduct. It seems that in the five-coordinated complexes, a water or a solvent molecule occupies the sixth position (Scheme 5) and this would decrease the tendency of the complexes toward the interaction with donors.

Concerning the stabilization of the five-coordinate complex, the donation power of the Schiff base is important. The cobalt atom in $[Co(5-Br-2,3-Salpyr)(PBu_3)]^+$ complex has a more powerful acceptor property than that in the other types of complexes and forms more stable complexes with H_2O or a solvent molecule (Scheme 5). Therefore its tendency for the reaction with donors decreases and hence its formation constant, K, with donors is lower [10].

To study the effect of the position of substituents on the interaction of the Co(III) complexes, 3-MeO, 4-MeO, and 5-MeO were selected. The results show the following trend in the adduct formation between cobalt(III) Schiff bases and *n*-butyl amine as donor: 5 - MeO > 3 - MeO > 4 - MeO.

Table 6 $\Delta G^{\circ}/kJ \text{ mol}^{-1}$ values for the interaction between [Co(5-Br-2,3-Salpyr)(PBu₃)]⁺ and various amines in 96 % methanol

Donors	283 K	293 K	303 K	313 K
Benzyl	-20.1 ± 1.1	-20.5 ± 0.7	-20.1 ± 0.8	-20.0 ± 0.2
<i>n</i> -Butyl	-19.5 ± 0.3	-19.9 ± 0.9	-20.1 ± 0.3	-19.6 ± 0.1
sec-Butyl	-19.3 ± 0.2	-19.8 ± 0.7	-19.9 ± 0.5	-19.2 ± 0.6
tert-Butyl	-17.06 ± 0.4	-16.8 ± 0.9	-16.5 ± 0.4	-16.7 ± 0.5

Table 7 $\Delta G^{\circ}/kJ \text{ mol}^{-1}$ values for the interaction between [Co(2,3-Salpyr)(PPh₂Me)]⁺ and Im and its derivatives in 96 % methanol

Donors	283 K	293 K	303 K	313 K
Im	-18.4 ± 1.0	-18.7 ± 0.7	-18.9 ± 0.2	-18.5 ± 0.3
2-MeIm	-12.0 ± 0.3	-11.9 ± 0.5	-12.2 ± 0.1	-10.4 ± 0.0
2-EtIm	-11.5 ± 0.7	-11.7 ± 0.4	-10.7 ± 0.1	-7.5 ± 0.2
BzIm	-10.9 ± 0.6	-10.8 ± 0.2	-10.6 ± 0.8	-9.7 ± 0.4

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 σ^* in PPh₂Me, the cobalt atom in [Co(2,3-Salpyr)(PPh₂Me)]⁺ complex has a more powerful acceptor property than that in the other types of complexes and forms more stable complexes with H₂O or a solvent molecule (Scheme 5). Therefore, its tendency for the reaction with donors decreases and its formation constant, *K*, with donors is lower [10]. So, the formation constants increased according to the order PBu₃ > PPh₂Me.

Effect of temperature on the formation constants

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

Thermodynamic free energy change

The free energy change values, ΔG° , of the studied cobalt(III) Schiff base complexes were calculated from $\Delta G^{\circ} = -\text{RT} \ln K_f$ at various temperatures (Tables 6, 7, 8). The linear plot of [Co(5-Br-2,3-Salpyr)(PBu₃)]ClO₄·H₂O titrated with *n*-butylamine at various temperatures in 96 % methanol is shown in Fig. 3.

Conclusions

thermodynamic formation constants, K, and the thermodynamic free energy change values for the above adducts of the mentioned complexes with various donors were determined spectrophotometrically and the following conclusions have been drawn:

- 1. The reactions are exothermic, because by increasing temperature, the formation constant is decreased: $\Delta H^{\circ} < 0.$
- 2. The formation constants change according to the following trend owing to the steric and the electronic factors of the Co(III) complexes:
 - 5 MeO > 5 H > 5 Br

5 - MeO > 3 - MeO > 4 - MeO

- The order of the formation constants of Co(III) Schiff base complexes toward a given donor according to the phosphine axial ligand is as follows: PBu₃ > PPh₂Me
- 4. The following binding trend of the donors toward a given cobalt(III) Schiff base complex is as follows: benzylamine > n butylamine > sec butylamine
 > tert butylamine
 Im > 2 MeIm > 2 EtIm > BzIm
 PBu₃ > PPh₂Me

Experimental

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.

The infrared spectra of all ligands and their complexes were recorded in the range 4,000–400 cm⁻¹ using a Shimadzu FTIR-8300 spectrophotometer applying the KBr disc technique. The UV–Vis absorption spectra were recorded using a Perkin-Elmer Lambda 2 spectrophotometer at room temperature. The elemental analysis was carried out using a Thermo Finnigan-Flash-1200. The ¹H NMR spectra were recorded by a Bruker Avance DPX 250 MHz spectrometer.

Preparation of Schiff bases

The mono Schiff base 1 was prepared by mixing stoichiometric amounts of analytically pure salicylaldehyde with 2,3-DAP dissolved in ethanol and refluxing for 3 h on a water bath. The separated brown-yellow crystals were recrystallized from hot ethanol [7]. The mono Schiff base 1 were mixed with the appropriate aldehyde in a 1:1 ratio using the same condensation procedure to afford the bis

Compounds	283 K	293 K	303 K	313 K
[Co(5-Br-2,3-Salpyr)(PBu ₃)] ⁺	-19.5 ± 0.3	-19.9 ± 0.2	-20.1 ± 0.9	-19.6 ± 1.0
[Co(5-MeO-2,3-Salpyr)(PBu ₃)] ⁺	-20.5 ± 1.1	-21.1 ± 1.4	-20.5 ± 0.7	-20.2 ± 0.9
[Co(4-MeO-2,3-Salpyr)(PBu ₃)] ⁺	-19.9 ± 0.7	-20.4 ± 0.9	-20.2 ± 0.8	-19.8 ± 0.6
[Co(3-MeO-2,3-Salpyr)(PBu ₃)] ⁺	-20.4 ± 0.5	-21.0 ± 0.6	-20.5 ± 0.7	-20.1 ± 0.4



Fig. 3 Plot of *K* against 1/T for [Co(5-Br-2,3-Salpyr)(PBu₃)] ClO₄·H₂O with *n*-butylamine in 96 % methanol

Schiff bases **2**. The resulting solution was concentrated to half its initial volume and the separated crystals were filtered and recrystallized from ethanol.

(*N*-Salicyliden-N'-5-bromosalycyliden-2,3-diaminopyridine (5-Br-2,3-Salpyr) (**2a**, C₁₉H₁₄BrN₃O₂)

Yellow crystals; yield 50 %; m.p.: 120 °C; ¹H NMR (DMSO-*d*₆): $\delta = 6.9$ (1H, H¹¹), 7.0 (1H, H¹⁰), 8.9 (1H, H¹²), 7.4–7.9 (6H, Ar–H), 7.9 (1H, H⁶), 8.4 (1H, H¹³), 9.5 (1H, H⁷), 12.6 (1H, H²), 13.1 (1H, H¹) ppm; ¹³C NMR (DMSO-*d*₆): $\delta = 160.5$ (C⁷=N), 160.1 (C¹³=N), 149.1 (C¹²), 123.6 (C¹¹), 136.4 (C¹⁰), 141.3 (C⁹), 151.9 (C⁸), 163.6, 161.8, 133.1, 132.6, 130.3, 126.3, 122.0, 120.8, 118.1, 117.1, 114.7 (12 signals for Ar–C) ppm; FT-IR (KBr): $\bar{\nu} = 3,427$ (v_{O–H}), 1,612 (v_{C=N}), 1,558 (v_{C=C}), 1,184 (v_{C–O}) cm⁻¹; UV–Vis (MeOH): $\lambda_{max} = 330$, 460 (sh) nm.

(*N-Salicyliden-N'-5-methoxysalycyliden*)-2,3-diaminopyridine (5-MeO-2,3-Salpyr) (**2b**, C₂₀H₁₇N₃O₃)

Yellow crystals; yield 51 %; m.p.: 115 °C; ¹H NMR (DMSO-*d*₆): δ = 7.1 (1H, H¹¹), 7.6 (1H, H¹⁰), 7.9 (1H, H¹²), 6.6–7.1 (7H, Ar–H), 8.7 (1H, H¹³), 8.9 (1H, H⁷), 12.9 (1H, H²), 13.3 (1H, H¹), 3.7 (OCH₃) ppm; ¹³C NMR (DMSO-*d*₆): δ = 160.6 (C⁷=N), 160.1 (C¹³=N), 148.2 (C¹²), 123.1 (C¹¹), 137.1 (C¹⁰), 140.6 (C⁹), 152.4 (C⁸), 162.4, 161.8, 161.1, 133.2, 132.3, 130.1, 121.3, 117.9, 116.2, 111.8, 108.1, 107.3 (12 signals for Ar–C), 55.8 (OCH₃) ppm; FT-IR (KBr): $\bar{\nu}$ = 3,417 (v_{O–H}), 1,624 (v_{C=N}), 1,556 (v_{C=C}), 1,151 (v_{C–O}) cm⁻¹; UV–Vis (MeOH): λ_{max} = 305, 334, 504 nm.

(N-Salicyliden-N'-4-methoxysalycyliden)-2,3-diaminopyridine (4-MeO-2,3-Salpyr) (2c, C₂₀H₁₇N₃O₃)

Yellow crystals; yield 55 %; m.p.: 200 °C; ¹H NMR (DMSO- d_6): $\delta = 6.6-7.2$ (1H, H¹¹), 8.0 (1H, H¹⁰), 8.6 (1H, H¹²), 6.6-7.2 (6H, Ar–H), 8.6 (1H, H⁶), 8.8 (1H, H¹³), 9.0 (1H, H⁷), 12.3 (1H, H²), 12.6 (1H, H¹), 3.8 (OCH₃) ppm; ¹³C NMR (DMSO- d_6): $\delta = 160.5$ (C⁷=N), 160.2 (C¹³=N), 148.4 (C¹²), 122.6 (C¹¹), 135.9 (C¹⁰), 139.8 (C⁹), 150.3 (C⁸), 162.9, 159.9, 153.1, 132.3, 130.0, 120.8, 118.5, 118.2, 117.8, 116.3, 116.1, 110.3 (12 signals for Ar–C), 55.6 (OCH₃) ppm; FT-IR (KBr): $\bar{\nu} = 3,444$ (ν_{O-H}), 1,612 ($\nu_{C=N}$), 1,558 ($\nu_{C=C}$), 1,107 (ν_{C-O}) cm⁻¹; UV–Vis (MeOH): $\lambda_{max} = 388, 445$ (sh) nm.

$(N-Salicyliden-N'-3-methoxysalycyliden)-2,3-diaminopyridine (3-MeO-2,3-Salpyr) (2d, C_{20}H_{17}N_3O_3)$

Orange crystals; yield 59 %; m.p.: 205 °C; ¹H NMR (CDCl₃): $\delta = 6.8-7.3$ (1H,H¹¹), 7.4 (1H, H¹⁰), 8.4 (1H, H¹²), 6.8-7.3 (6H, Ar–H), 7.8 (1H, H⁶), 8.8 (1H, H¹³), 9.5 (1H, H⁷), 12.5 (1H, H²), 13.2(1H, H¹), 3.8 (OCH₃) ppm; ¹³C NMR (CDCl₃): $\delta = 160.6$ (C⁷=N), 160.1 (C¹³=N), 147.8 (C¹²), 121.0 (C¹¹), 137.6 (C¹⁰), 143.5 (C⁹), 151.1 (C⁸), 163.4, 161.7, 161.1, 132.7, 132.3, 130.1, 121.4, 118.0, 116.3, 112.2, 108.1, 104.9 (12 signals for Ar–C), 55.9 (OCH₃) ppm; FT-IR (KBr): $\bar{\nu} = 3,456$ (v_{O–H}), 1,605 (v_{C=N}), 1,556 (v_{C=C}), 1,107 (v_{C–O}) cm⁻¹; UV–Vis (MeOH): $\lambda_{max} = 330, 465$ (sh) nm.

Synthesis of the five-coordinate Co(III) complexes

The cobalt(III) Schiff base complexes were prepared by the methods described in the literature [34]. To a refluxing solution of the tetradentate ligands (1 mmol) in 10 cm³ methanol was added 0.25 g Co(OAc)₂·4H₂O (1 mmol). After 15 min, the appropriate phosphine (0.8 mmol) was added to the solution. 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 then 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 purified by recrystallization in dichloromethane/ethanol. The complex was dried in vacuo at 323 K for 48 h (Fig. 4).



 $\begin{array}{l} \mathsf{X} = \mathsf{PBu}_3, \, \mathsf{R} = 5\text{-}\mathsf{Br} \; (\textbf{3a}), \, 5\text{-}\mathsf{OCH}_3 \; (\textbf{3b}), \, 4\text{-}\mathsf{OCH}_3 \; (\textbf{3c}), \, 3\text{-}\mathsf{OCH}_3 \; (\textbf{3d}) \\ \mathsf{X} = \mathsf{PPh}_2\mathsf{Me}, \, \mathsf{R} = \mathsf{H} \; (\textbf{3e}) \end{array}$

Fig. 4 Proposed structure of the unsymmetrical $\operatorname{Co}(\operatorname{III})$ Schiff base complexes

[(N-Salicyliden-N'-5-bromosalycyliden)-2,3-diaminopyri dine](tributylphosphine)cobalt(III) perchlorate monohy drate ([5-Br-Co(Salpyr)(PBu₃)]ClO₄·H₂O) (2a, C, H, BrClCaN, Q, P)

 $(\mathbf{3a}, \mathbf{C}_{31}\mathbf{H}_{41}\mathbf{BrClCoN}_{3}\mathbf{O}_{7}\mathbf{P})$

Brown crystals; yield 65 %; m.p.: >250 °C; ¹H NMR (DMSO-*d*₆): δ = 6.7–7.8 (2H, pyridine), 8.2 (1H, H¹²), 6.7–7.8 (7H, Ar–H), 9.1 (1H, H¹³), 9.5 (1H, H⁷), 0.7–0.8 (9H, CH₃), 1.2–1.3 (18H, CH₂) ppm; ¹³C NMR (DMSO-*d*₆): δ = 163.9 (C⁷=N), 163.4 (C¹³=N), 148.8 (C¹²), 124.1 (C¹¹), 131.4 (C¹⁰), 142.5 (C⁹), 168.5(C⁸), 160.2, 158.3, 133.1, 132.6, 130.3, 126.3, 122.0, 120.8, 118.9, 118.1, 117.1, 114.7 (12 signals for Ar–C), 29.1, 23.8, 23.3, 13.8 (PBu₃) ppm; FT-IR (KBr): $\bar{\nu}$ = 3,444 (v_{O–H}), 1,604 (v_{C=N}), 1,510 (v_{C=C}), 1,170 (v_{C–O}), 1,097 (v_{CIO4}), 563 (v_{Co–N}), 462 (v_{Co–O}) cm⁻¹; UV–Vis (MeOH): λ_{max} = 324, 400, 489 nm.

[(*N*-Salicyliden-*N*'-5-methoxysalycyliden)-2,3-diaminopyridine](tributylphosphine)cobalt(III) perchlorate monohydrate ([5-MeO-Co(Salpyr)(PBu₃)]ClO₄·H₂O) (**3b**, C₃₂H₄₄ClCoN₃O₈P)

Brown crystals; yield 62 %; m.p.: > 250 °C; ¹H NMR (DMSO-*d*₆): $\delta = 6.7$ -7.6 (2H, pyridine), 8.7 (1H, H¹²), 6.7-7.6 (6H, Ar–H), 8.5 (1H, H⁶), 9.0 (1H, H¹³), 9.3 (1H, H⁷), 0.7-0.8 (9H, CH₃), 1.2–1.3 (18H, CH₂) ppm; ¹³C NMR (DMSO-*d*₆): $\delta = 163.5$ (C⁷=N), 163.1 (C¹³=N), 148.4 (C¹²), 123.9 (C¹¹), 131.3 (C¹⁰), 142.3 (C⁹), 168.7 (C⁸), 159.6, 158.2, 157.3, 133.1, 132.9, 130.5, 121.2, 118.0, 115.4, 107.8, 107.0, 100.5 (12 signals for Ar–C), 55.8 (OCH₃), 29.1, 23.8, 23.3, 13.8 (PBu₃) ppm; FT-IR (KBr): $\bar{\nu} = 3,402$ (v_{O–H}), 1,606 (v_{C=N}), 1,525 (v_{C=C}), 1,153 (v_{C–O}), 1,093 (v_{CIO4}), 540 (v_{CO–N}), 466 (v_{CO–O}) cm⁻¹; UV–Vis (MeOH): $\lambda_{max} = 341, 381, 503$ nm.

[(*N*-Salicyliden-*N*'-4-methoxysalycyliden)-2,3-diaminopyridine](tributylphosphine)cobalt(III) perchlorate monohydrate ([4-MeO-Co(Salpyr)(PBu₃)]ClO₄·H₂O) (**3c**, C₃₂H₄₄ClCoN₃O₈P)

Brown crystals; yield 64 %; m.p.: >250 °C; ¹H NMR (DMSO- d_6): $\delta = 6.3-7.7$ (2H, pyridine), 8.4 (1H, H¹²),

6.3–7.7 (7H, Ar–H), 8.8 (1H, H¹³), 9.1 (1H, H⁷), 0.7–0.8 (9H, CH₃), 1.2–1.3 (18H, CH₂) ppm; ¹³C NMR (DMSOd₆): δ = 163.6 (C⁷=N), 163.2 (C¹³=N), 148.2 (C¹²), 123.1 (C¹¹), 130.3 (C¹⁰), 142.1 (C⁹), 168.4 (C⁸), 158.4, 155.4, 152.3, 133.5, 131.2, 120.8, 118.7, 117.9, 117.5, 116.3, 114.1, 110.3 (12 signals for Ar–C), 55.7 (OCH₃), 29.1, 23.8, 23.3, 13.8 (PBu₃) ppm; FT-IR (KBr): $\bar{\nu}$ = 3,421 (ν_{O-H}), 1,608 ($\nu_{C=N}$), 1,562 ($\nu_{C=C}$), 1,122 (ν_{C-O}), 1,095 (ν_{CIO4}), 524 (ν_{CO-N}), 462 (ν_{CO-O}) cm⁻¹; UV–Vis (MeOH): λ_{max} = 307, 381, 464 nm.

[(N-Salicyliden-N'-3-methoxysalycyliden)-2,3-diaminopyridine](tributylphosphine)cobalt(III) perchlorate monohydrate ([$3-MeO-Co(Salpyr)(PBu_3)$]ClO₄·H₂O) (**3d**, C₃₂H₄₄ClCoN₃O₈P)

Light brown crystals; yield 60 %; m.p.: >250 °C; ¹H NMR (DMSO-*d*₆): $\delta = 6.6-8.7$ (3H, pyridine), 6.6–8.7 (7H, Ar–H), 9.0 (1H, H¹³), 9.3 (1H, H⁷), 0.7–0.8 (9H, CH₃), 1.2–1.3 (18H, CH₂) ppm; ¹³C NMR (DMSO-*d*₆): $\delta = 163.8$ (C⁷=N), 163.5 (C¹³=N), 147.6 (C¹²), 122.8 (C¹¹), 130.4 (C¹⁰), 142.8 (C⁹), 167.8 (C⁸), 159.2, 158.8, 157.7, 133.6, 131.5, 130.8, 121.9, 118.1, 115.9, 112.1, 108.8, 106.8 (12 signals for Ar–C), 55.7 (OCH₃), 29.1, 23.8, 23.3, 13.8 (PBu₃) ppm; FT-IR (KBr): $\bar{\nu} = 3,404$ (v_{O–H}), 1,606 (v_{C=N}), 1,564 (v_{C=C}), 1,193 (v_{C–O}), 1,093 (v_{CIO4}), 549 (v_{Co–N}), 462 (vCo–O) cm⁻¹; UV–Vis (MeOH): $\lambda_{max} = 342$, 378, 491 nm.

[N,N'-bis(Salicyliden)-2,3-diaminopyridine]-(diphenylmethylphosphine)cobalt(III) perchlorate monohydrate $(<math>[Co(2,3-Salpyr)(PPh_2Me)]ClO_4\cdot H_2O$) (**3e**, C₃₂H₂₈ClCoN₃O₇P)

Brown crystals; yield 60 %; m.p.: >250 °C; ¹H NMR (DMSO-*d*₆): $\delta = 6.6-7.4$ (2H, pyridine), 8.6 (1H, H¹²), 6.6-7.4 (6H, Ar–H), 8.5 (1H, H⁶), 8.7 (1H, H¹³), 8.9 (1H, H⁷), 1.4 (CH₃) ppm; ¹³C NMR (DMSO-*d*₆): $\delta = 163.6$ (C⁷=N), 163.3 (C¹³=N), 148.1 (C¹²), 123.6 (C¹¹), 131.4 (C¹⁰), 142.8 (C⁹), 167.8 (C⁸), 158.2, 157.6, 133.0, 132.9, 131.2, 130.9, 122.5, 122.2, 122.1, 121.8, 116.9, 116.2 (12 signals for Ar–C), 142.8, 137.6, 130.1, 127.1, 12.1 (PPh₂Me) ppm; FT-IR (KBr): $\bar{\nu} = 3,398$ (v_{O–H}), 1,608 (v_{C=N}), 1,562 (v_{C=C}), 1,149 (vC–O), 1,093 (v_{CI04}), 543 (v_{CO–N}), 469 (v_{CO–O}) cm⁻¹; UV–Vis (MeOH): $\lambda_{max} = 330(sh), 375, 479$ nm.

[N,N'-bis(Salicyliden)-2,3-diaminopyridine]bis(tributylphosphine)cobalt(III) perchlorate monohydrate ([Co(2,3-Salpyr)(PBu₃)₂]ClO₄:H₂O) (**4**, C₄₄H₇₃ClCoN₃O₇P₂)

To a solution 0.16 g of the ligand 2,3-Salpyr (0.5 mmol) and 0.4 cm³ tributylphosphine (1.6 mmol) in 6 cm³ methanol was added a solution of 0.136 g of Co(OAc)₂·4H₂O (0.6 mmol) in 1.5 cm³ methanol. The reaction mixture was refluxed for 2 h to give a brown-red solution. A solution of 0.42 g NaClO₄·H₂O (3 mmol) in 7 cm³ methanol was then added and the mixture was stirred for 2 h. The resulting brown precipitate was collected by filtration and recrystallized from dichloromethane/methanol. The product was dried in vacuo. Brown crystals; yield 61 %; m.p.: >250 °C; ¹H NMR (DMSO-*d*₆): $\delta = 6.4$ –7.4 (2H, pyridine), 7.5 (1H, H¹²), 6.4–7.4 (7H, Ar–H), 8.7 (1H, H¹³), 9.0 (1H, H⁷), 0.7–0.8 (18H, CH₃), 1.2–1.3 (36H, CH₂) ppm; FT-IR (KBr): $\bar{\nu} = 3,342$ (ν_{O-H}), 1,602 ($\nu_{C=N}$), 1,548 ($\nu_{C=C}$), 1,149 (ν_{C-O}), 1,093 (ν_{CIO4}), 536 (ν_{CO-N}), 472 (ν_{CO-O}) cm⁻¹; UV–Vis (MeOH): $\lambda_{max} = 306, 437$ nm.

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