

Synthesis and Characterization of Cobalt(III) Octahedral Complexes with Flexible Salpn Schiff Base in Solution. Structural Dependence of the Complexes on the Nature of Schiff Base and Axial Ligands

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For a long time tetradentate Schiff base complexes of transition metal ions have attracted many researchers interest in the field of coordination chemistry.¹⁻⁵ Co(III) complexes of Schiff base are an important class of coordination compound not only because of them being interesting B₁₂ models and oxygen carriers but also due to their interesting magnetic properties, spectroscopic characteristics and the interaction of metal-to-ligand bonds.⁴⁻⁹

Many studies initially focus on simple Schiff base ligand such as salphen, salen and acacen (*n* = 2) Scheme 1^{1,4,5,10,11} but interest quickly shift to more intricate species which have extra functional groups, side chains and more methylene groups in the amine backbone.¹²⁻¹⁵ A number of structural studies on the effect of the number of CH₂ groups between the two imine moieties in VO²⁺, Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ complexes¹⁶⁻²² of tetradentate Schiff bases derived from salicylaldehyde and a variety of diamines (1:2 ratio) have been carried out previously. They have been shown that an increase in the methylene chain length allows adequate flexibility for the complexes to change their structure from a planar towards a distorted or pseudo-tetrahedral motif. In addition, the longer chains cause the ligand field strength to decrease.^{19,21}

Among the cobalt Schiff base complexes, the best known is Co(salen), which has a square planar geometry about the cobalt(II) ion.^{18,19} Magnetic susceptibility measurements indicate that a low spin electronic configuration with the single unpaired electron residing in a molecular orbital of primarily d_{z²} character, which is consistent with esr measurements.^{8,19,23,24} Although Co(III) octahedral complexes with salphen, salen and acacen (*n* = 2) have been known,^{4,5,10,11} octahedral complexes with higher number of CH₂ groups in Schiff base (*n* ≥ 3) such as salpn or acacpn have not been reported. The Co^{II}(salpn) complex's reactivity toward bases was markedly different from that of Co^{II}(salen). The

Co^{II}(salen) complex is extremely oxygen sensitive and in the presence of an additional donor group forms six coordinated octahedral cobalt(III) complexes, whereas the Co^{II}(salpn) complex shows a low tendency to increase its coordination number in the presence of additional donors such as σ-donor bases. In order to investigate the effect of the number of methylene groups on the coordination behaviors, we have synthesized the cobalt(III) octahedral complexes with the H₂salpn Schiff base (*n* = 3).

Experimental

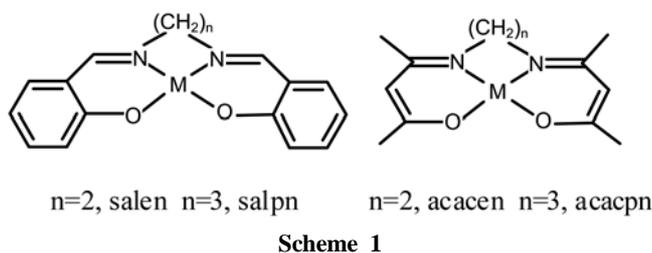
Physical measurements. UV-Vis spectra in solution were recorded in acetone solvent on a Jasco 7800 spectrophotometer. IR spectra were recorded as KBr pellets in an Equinox 55 Bruker spectrophotometer. All NMR measurements were made in CDCl₃ or DMSO-*d*₆ on a Bruker Avancer 500 (500 MHz) NMR spectrometer. Proton chemical shifts are reported in parts per million (ppm) relative to an internal TMS standard. Elemental analyses were performed by using a Heraeus CHN-O-RAPID elemental analyzer.

Syntheses. H₂salpn Schiff base was prepared as reported in the literature.¹⁹ [Co^{II}(salpn)] complex was synthesized according to the reported method.¹⁹

trans-[Co^{III}(salpn)(amine)(N₃)] complexes. To a stirred suspension of 1 mmol (0.34 g) of the Co^{II}(salpn) complex in 70 mL dry methanol, 2 mmol of the appropriate amine was added. Air was bubbled slowly through the reaction mixture for 3.5 h. To the resulting solution 1 mmol (0.065 g) of solid KN₃ was added and air was bubbled in for a further 0.5 h. The resulting solution was left overnight, giving a green oil form. The green oil obtained was resuspended in ether (15 ml) and stirred at room temperature until a precipitate formed. The green solid product was recrystallized from suitable solvents according to the following procedures:

– The [Co^{III}(salpn)(py)(N₃)] complex (**1**) was recrystallized from dichloromethane:cyclohexane (2:1 v/v) as a green powder. The powder was filtered off, washed with cyclohexane and dried under vacuum. Yield 40% (0.4 mmol, 0.184 g). Anal. Calc. for C₂₂H₂₁N₆O₂Co: C, 57.38; H, 4.60; N, 18.26, Found: C, 57.32; H, 4.81; N, 17.96%. FT-IR (KBr cm⁻¹): 2027s (ν N₃); 1623s (ν C=N); 1538m (ν C=C). UV-Vis (acetone) dd, 611 nm (ε = 199 M⁻¹cm⁻¹).

– The [Co^{III}(salpn)(3-Mepy)(N₃)] complex (**2**) was



recrystallized from dichloromethane:ethanol:cyclohexane (2:2:1 v/v/v) as a green powder. The powder was filtered off, washed with cyclohexane, and dried under vacuum. Yield 35% (0.35 mmol, 0.166 g). Anal. Calc. for $C_{23}H_{23}N_6O_2Co$: C, 58.21; H, 4.89; N, 17.72, Found: C, 57.94; H, 5.05; N, 17.42%. FT-IR (KBr cm^{-1}): 2027s (νN_3); 1622s ($\nu C=N$); 1538m ($\nu C=C$). UV-Vis (acetone) dd, 612 nm ($\epsilon = 192 M^{-1} cm^{-1}$).

– The $[Co^{III}(salpn)(4-Mepy)(N_3)]$ complex (**3**) was purified by a similar method to the complex (**1**). Yield 44% (0.44 mmol, 0.209 g). Anal. Calc. for $C_{23}H_{23}N_6O_2Co$: C, 58.21; H, 4.89; N, 17.72, Found: C, 57.87; H, 5.11; N, 17.54%. FT-IR (KBr cm^{-1}): 2028s (νN_3); 1624s ($\nu C=N$); 1538m ($\nu C=C$). UV-Vis (acetone) dd, 611 nm ($\epsilon = 156 M^{-1} cm^{-1}$).

– The $[Co^{III}(salpn)(3-CNpy)(N_3)]$ complex (**4**) was recrystallized from dichloromethane:cyclohexane (1:1 v/v) as a green powder. The powder was filtered off, washed with cyclohexane and dried under vacuum. Yield 25% (0.25 mmol, 0.125 g). Anal. Calc. for $C_{24}H_{22}N_7O_2Co$: C, 57.72; H, 4.44; N, 19.63, Found: C, 57.52; H, 4.67; N, 19.31%. FT-IR (KBr cm^{-1}): 2028s (νN_3); 1623s ($\nu C=N$); 1539m ($\nu C=C$). UV-Vis (acetone) dd, 610 nm ($\epsilon = 162 M^{-1} cm^{-1}$).

trans-[Co^{III}(salpn)(amine)₂]ClO₄ complexes. To a stirred suspension of 1 mmol (0.34 g) of the $Co^{II}(salpn)$ complex in 70 mL dry methanol, 3 mmol of the appropriate amine was added. Air was bubbled slowly through the reaction mixture for 3 h. To the resulting solution 0.15 g of solid $NaClO_4$ was added and air was bubbled in for 1 more hour. The resulting clear brown solution was left overnight to give a brown precipitate. The following complexes were recrystallized as shown below, filtered off, wash with ethanol and dried in vacuum at room temperature.

– $[Co^{III}(salpn)(py)_2]ClO_4$ complexes. (**5**): was recrystallized from dichloromethane-ethanol (2:1 v/v) as a green powder. Yield 34% (0.34 mmol, 0.203 g). Anal. Calc. for $C_{27}H_{26}N_4O_6ClCo$: C, 54.33; H, 4.39; N, 9.39, Found: C, 54.21; H, 4.35; N, 9.52%. FT-IR (KBr cm^{-1}): 1624s ($\nu C=N$); 1540m ($\nu C=C$); 1095vs (νClO_4^-). UV-Vis (acetone) dd, 565 nm ($\epsilon = 235 M^{-1} cm^{-1}$).

– $[Co^{III}(salpn)(4-Mepy)_2]ClO_4$ complexes. (**6**): was recrystallized from dichloromethane-ethanol (3:1 v/v) as a green powder. Yield 39% (0.39 mmol, 0.244 g). Anal. Calc. for $C_{29}H_{30}N_4O_6ClCo$: C, 55.73; H, 4.84; N, 8.96, Found: C, 55.94; H, 4.91; N, 8.86%. FT-IR (KBr cm^{-1}): 1623s ($\nu C=N$); 1540m ($\nu C=C$); 1095vs (νClO_4^-). UV-Vis (acetone) dd, 567 nm ($\epsilon = 219 M^{-1} cm^{-1}$).

Results and Discussion

Synthesis of octahedral $Co(III)$ complexes with salen or other Schiff bases having $n = 2$ is easily accomplished by addition of appropriate axial ligands to $Co^{II}(salen)$ and oxidation of $Co(II)$ to $Co(III)$.^{25,26} However, the $Co^{II}(salpn)$ complex shows only a low tendency to increase its coordination number. The observed difference in behavior is due to the structural differences between $Co^{II}(salpn)$ and $Co^{II}(salen)$.

The $Co^{II}(salen)$ complex has a low spin square planar structure with a single unpaired electron and a magnetic moment of about 2.5 BM,¹⁷ and it is extremely oxygen sensitive. In contrast the observed value of μ (4.56 BM) for the $Co^{II}(salpn)$ complex eliminates a low spin square planar or a high spin octahedral formation.¹⁹ The magnetic moment is instead in agreement with tetrahedral or pseudo tetrahedral structure.

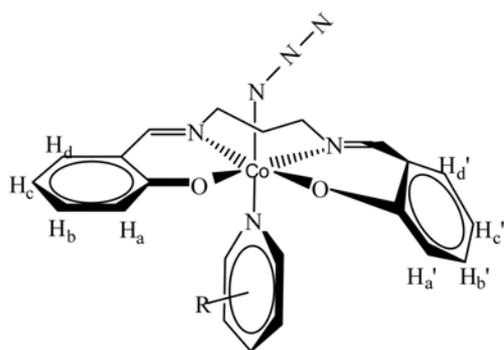
Increasing the number of the methylene units in diamine chain of the Schiff base ligand (Schem 1) allows the $Co(II)$ complexes to change from a square planar ($n = 2$) to a tetrahedral motif.^{20,21,27} While the $Co(salen)$ complex has no geometrical distortion with respect to the primary ligand, $Co(salpn)$ has a distorted structure. This is in contrast to the $Ni(II)$ series, which maintains a square planar geometry with an increase in the number of the methylene groups, or adopts an octahedral geometry if additional donor (MeOH, DMF, DMSO) are present.^{19,20}

The distortion about the cobalt center due to the extra methylene groups which causes an apparent weakening of the ligand field strength. In other words, the increasing chain length in salpn allows more flexibility to form a tetrahedral coordination geometry about the cobalt (The cobalt(II) shows a more pronounced tendency for the formation of tetrahedral complexes than either $Ni(II)$ or $Cu(II)$ does).²⁸ Therefore, $Co^{II}(salpn)$ complex shows a low tendency to increase its coordination number by forming octahedral complexes in the presence of addition donors.^{8,29} However, relatively strong π -acceptor ligands (for example pyridine and its derivatives, or anions such as N_3 , CN) increase effectively the ligand field strength. The increase in ligand field strength should facilitate the oxidation of the $Co(II)$ and the formation of $Co(III)$ with a trans octahedral structure.

Spectral characterization. The O-H stretching frequency of the free ligand is displaced to the 2500-2600 cm^{-1} region due to the internal hydrogen bond $OH-N=C$.^{30,31} The ligand is relatively planar, with a geometrical arrangement favoring the formation of the hydrogen bond.³⁰ The C-O stretching frequency is found as a medium band near 1280 cm^{-1} in the free ligand and 1318 cm^{-1} in these complexes. The IR spectrum of the free ligand exhibited a strong band at 1636 cm^{-1} due to $\nu C=N$.^{32,33} In the coordinated of the Schiff base ligand, the C=N stretching frequency is displaced to a lower frequency, $\sim 1620 cm^{-1}$. The decrease in the frequency indicate a decrease in the C=N bond order due to the coordination of the azomethine nitrogen to the cobalt.^{31,34} The IR spectra of the complexes **1-4** exhibit a band about 2027 cm^{-1} , which is characteristic of a coordinated azido ligand.³⁵

Electronic spectra for the free Schiff base ligand in acetone recorded in the 300-800 nm range. The spectrum exhibits a band at 402 nm ($\epsilon = 219 M^{-1} cm^{-1}$) due to $n \rightarrow \pi^*$ transition.³⁶

Electronic absorption spectra of the cobalt complexes in acetone recorded in UV-Vis region. The $n \rightarrow \pi^*$ band appears to be absent in the spectra of the $Co(III)$ complexes. The complexes exhibit a strong band in the UV region



R = H (**1**) R = 3-Me (**2**) R = 4-Me (**3**) R = 3-CN (**4**)

Figure 1. *trans*-[Co(salpn)(amine)(N₃)] complexes **1-4**.

corresponding to $d \rightarrow \pi^*$ charge transfer. The band at about 610 nm (**1-4**) and 565 nm (**5** and **6**) is assigned to d-d transition.

The ¹H NMR spectra data for the Schiff base region of complexes **1-6** are summarized in Table 1. The spectrum of the free ligand exhibits a signal at $\delta = 13.52$, due to the intramolecular hydrogen bonded phenolic protons.^{37,38} The two equivalent imine protons (-CH=N) appear as a singlet at 8.58 ppm. The aromatic protons of the two equivalent phenyl rings in the free Schiff base appear as three well resolved signals centered at 6.90 (**H_{a,c}**), 7.33 (**H_b**), and 7.43 (**H_d**) ppm³⁸ (Fig. 1). The propanediamine protons show a quintet at 2.02 ppm due to two protons (CH₂CH₂-CH₂) and a triplet signal at 3.68 ppm due to four protons (CH₂CH₂CH₂).

The chemical shift pattern of the free ligand H₂salpn is relatively simple spectrum, the two half of the Schiff base being equivalent by symmetry. It is clear that the ligand H₂salpn has a plane of symmetry passing through the carbon

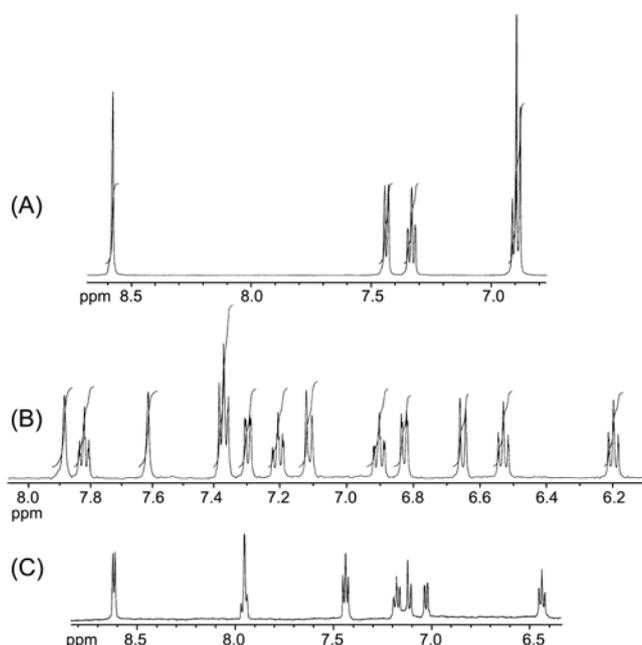


Figure 2. ¹H NMR spectra for the Schiff base region of free Schiff base (A), *trans*-[Co(salpn)(py)(N₃)] complex (B) and *trans*-[Co(salpn)(py)₂] complex (C).

atom in the middle of the propanediamine fragment.

The ¹H NMR spectra of complexes **1-4** are very complex and showed more peaks than expected. The spectra showed that the two halves of the Schiff base moiety are not equivalent. For example, in complexes **1-4**, the two imine protons appear as two individual singlets (Table 1, Fig. 2). Also the eight protons of the two phenyl rings in the complexes **1-4** exhibit eight peaks with equi-integration (Table 1, Fig. 2).

The number of signals from the Schiff base moiety in the complexes **1-4** in the ¹H NMR spectra rules out the presence

Table 1. ¹H NMR spectra data for the Schiff base region of complexes **1-6**^{a,b,c}

complex	-CH=N	-CH ₂ CH ₂ CH ₂ -	-CH ₂ CH ₂ CH ₂ -	Protons of phenyl rings
1	7.62 (1H, s); 7.89 (1H, s)	2.16, 2.45 (2H, m)	3.63 (1H, m); 3.76 (2H, m); 5.03 (1H, m)	6.20 (1H, t, $J = 7.64$, H_c); 6.53 (1H, t, $J = 7.64$, H_b); 6.65 (1H, d, $J = 8.48$, H_a); 6.83 (1H, dd, $J_o = 7.78$, $J_m = 1.57$, H_d); 6.90 (1H, td, $J_o = 7.64$, $J_m = 1.69$, H_c); 7.11 (1H, d, $J = 8.4$, H_{a'}); 7.20 (1H, td, $J_o = 7.64$, $J_m = 1.69$, H_{b'}); 7.29 (1H, dd, $J_o = 7.61$, $J_m = 1.53$, H_{d'})
2	7.46 (1H, s); 7.87 (1H, s)	2.17, 2.45 (2H, m)	3.53 (1H, m); 3.70 (2H, m); 4.90 (1H, m)	6.26 (1H, t, $J = 7.16$, H_c); 6.59 (1H, t, $J = 7.37$, H_b); 6.62 (1H, d, $J = 8.52$, H_a); 6.81 (1H, d, $J = 7.24$, H_d); 6.92 (1H, t, $J = 7.15$, H_c); 7.08 (1H, d, $J = 8.23$, H_a); 7.21 (1H, t, $J = 6.64$, H_b); 7.31 (1H, d, $J = 7.6$, H_d)
3	7.61 (1H, s); 7.88 (1H, s)	2.16, 2.43 (2H, m)	3.62 (1H, m); 3.76 (2H, m); 5.02 (1H, m)	6.21 (1H, t, $J = 7.28$, H_c); 6.52 (1H, t, $J = 7.28$, H_b); 6.64 (1H, d, $J = 8.48$, H_a); 6.84 (1H, d, $J = 6.65$, H_d); 6.90 (1H, t, $J = 6.98$, H_c); 7.09 (1H, d, $J = 8.41$, H_a); 7.18 (1H, t, $J = 7.21$, H_b); 7.28 (1H, d, $J = 7.68$, H_d)
4	7.68 (1H, s); 7.87 (1H, s)	2.18, 2.45 (2H, m)	3.67 (1H, m); 3.76 (2H, m); 5.07 (1H, m)	6.25 (1H, t, $J = 7.48$, H_c); 6.56 (1H, t, $J = 7.49$, H_b); 6.70 (1H, d, $J = 8.45$, H_a); 6.88 (1H, d, $J = 6.50$, H_d); 6.96 (1H, td, $J_o = 7.15$, $J_m = 1.50$, H_c); 7.14 (1H, d, $J = 8.47$, H_a); 7.24 (1H, t, $J_o = 6.89$, $J_m = 1.60$, H_b); 7.31 (1H, d, $J = 7.60$, H_d)
5	7.95 (2H, s)	2.63 (2H, m)	3.90 (4H, t, $J = 5.13$)	6.44 (2H, t, $J = 7.33$, H_{c,c'}); 7.03 (2H, dd, $J_o = 7.79$, $J_m = 1.52$, H_{d,d'}); 7.11 (2H, d, $J = 8.37$, H_{a,a'}); 7.20 (2H, td, $J_o = 7.65$, $J_m = 1.65$, H_{b,b'})
6	7.93 (2H, s)	2.60 (2H, m)	3.87 (4H, t, $J = 5.18$)	6.43 (2H, t, $J = 7.30$, H_{c,c'}); 7.04 (2H, dd, $J_o = 7.74$, $J_m = 1.54$, H_{d,d'}); 7.11 (2H, d, $J = 8.42$, H_{a,a'}); 7.21 (2H, td, $J_o = 7.61$, $J_m = 1.62$, H_{b,b'})

^aIn ppm relative Me₄Si. ^bCD₃COCD₃ solvent. ^cs = singlet, d = doublet, t = triplet, q = quintet, m = multiplet, dd = doublet of doublet, td = triplet of doublet

of plane symmetry. Increasing the number of the methylene groups in diamine chain of the Schiff base causes distortion of the geometry of the salpn ligand in the complexes **1-4**. The distortion of the Schiff base moiety from planarity could be due to the bonding geometry of the axial azido ligand. Bending of the Co-N₃ bond (angle of 116° and 120° has been reported for similar complexes^{39,40}), causes steric interactions between the azido axial ligand and salpn ligand. The *trans*-[Co(salpn)(amine)₂]ClO₄ complexes were studied in order to further establish the importance of steric factors. The ¹H NMR spectra of solution of the complexes **5** and **6** were simple. Only four different signals were observed due to the Schiff base moiety, indicating the presence of symmetry plane, like that found in the free ligand. This indicates that the flexibility of salpn itself is not enough to cause distortion of the complexes, and another factor (steric interactions) must be present. However, steric interaction alone could not be responsible for distortion of the Schiff base moiety, as Complexes with acacen or salen and azido axial ligand have not shown distortion from planarity.¹¹ Both the flexibility of the salpn Schiff base, due to the long alkyl chain, and the steric repulsion of the azido axial ligand, are necessary to cause part of the Schiff base to be forced away from the azido axial ligand toward the amine axial ligand. We suggest the existence of remarkable intramolecular π - π interactions in the complexes 1-4. The distorted structure is further stabilized by π - π interactions between the amine aromatic ring and the π -system of the salpn Schiff base. The greater complexity of the ¹H NMR spectra is due to steric interaction between axial N₃ and Schiff base ligand, which cause the difference in orientations of the two half Schiff base with respect to the axial amine. The up field shifts of this half of the Schiff base proton signals with respect to the other half are attributed to the shielding effect of the amine aromatic ring located near these protons.⁴¹

Conclusion

A series of octahedral cobalt(III) complexes with the salpn Schiff base ligand and relatively strong π -acceptor ligands have been synthesized and their coordination chemistry has been investigated. Our results from the ¹H NMR studies on the complexes show that their geometric structure is affected by not only the structure of Schiff base ligand but also the steric effect of the axial ligand.

In all these complexes, the ¹H NMR spectrum showed that salpn Schiff base moiety had a distorted shape about the cobalt center. The differences observed in the ¹H NMR spectrum of salpn complexes **1-4** in comparison with the free ligand and with the symmetrical complexes **5** and **6** suggest that the complexes **1-4** lack symmetry plane in solution.

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