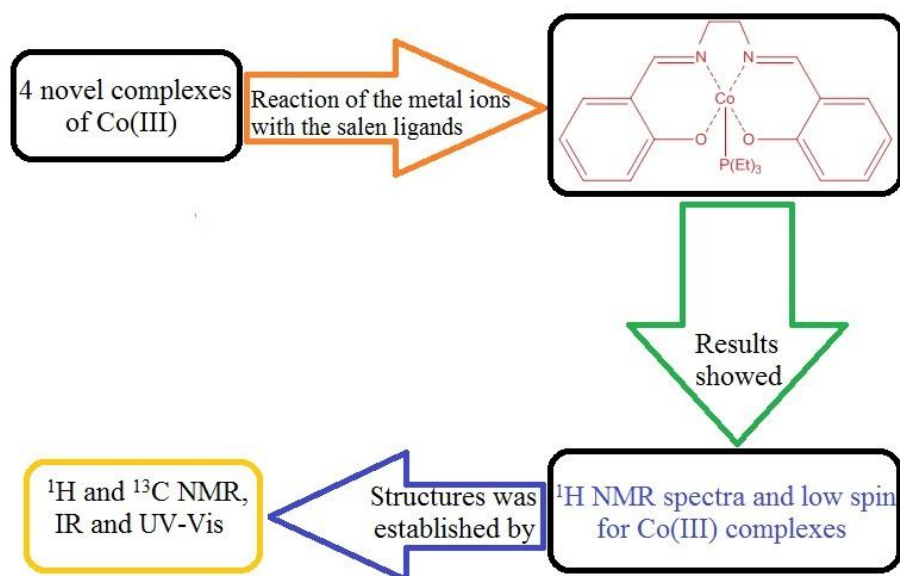


Synthesis, Experimental and Theoretical Characterization of Co (III) Complexes of 2-Hydroxynaphthaldehyde

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ARTICLE INFO	ABSTRACT
<p>Received: 12 January 2019 Revised: 29 January 2019 Accepted: 2 February 2019 Available online: 2 March 2019</p> <p>DOI: 10.29088/SAMI/AJCA.2019.2.184189</p> <p>KEYWORDS</p> <p>Cobalt (III) Complexes Structure NMR Spectroscopy Salen Ligands Schiff-Base Ligand Synthesis</p>	<p>The synthesis of some new cobalt (III) complexes: [Co (5-Xsalen) (PEt₃)] ClO₄.H₂O (where X= H, NO₂, Br, OMe) were synthesized and characterized using elemental analysis, ¹HNMR, IR and UV-Vis spectroscopy. The summarized results of these spectral evidences were in conformity with the structure of the synthesized complexes. In this study, we synthesized four novel complexes of Co (III) by the reaction of the metal ions with the salen ligands. The ligands coordinated with the metal ions through N- and O-donors. The complexes exhibited a geometry based on the coordination number 5. The results showed ¹HNMR spectra of these complexes are consistent with the suggest formulation and show that the cobalt in these complexes is low spin. Its structure was established by ¹HNMR, IR and UV visible spectroscopy.</p>

GRAPHICAL ABSTRACT



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Introduction

Schiff base are capable of forming coordinate bonds with many of metal ions through both azomethine group and phenolic group or via its azomethine or phenolic groups [1]. A large number of Schiff bases and their complexes are significant interest and attention because of their biological activity including anti-tumor, antibacterial, fungicidal and anti-carcinogenic properties [2]. Teridentate Schiff bases are well known to coordinate with various metal ions forming stable compounds, and some of these complexes are recognized as oxygen carriers [3]. Complexes of cobalt (II) involving derivatives of salicylaldehyde and aliphatic amines have received considerable attention because of their similarity to biological dioxygen carriers [3], as well as their potential as catalysts for the insertion of oxygen into organic substrates [4, 5]. In particular, the dioxygen adducts of [Co (salen)] and their ring substituted analogues have received intensive investigation. To continue investigation in the field of Schiff base complexes, we reported here preparation and characterization of the new cobalt (III) complexes. In this study, a series of complexes of the type [Co (5-Xsalen) (PEt₃)] ClO₄.H₂O (X= H, NO₂, Br, -OMe) has been synthesized and characterized by elemental analysis, UV-vis, IR, and ¹HNMR

spectroscopy.

Experimental

Materials and Apparatus

Ethylene diamine, 5-Methoxysalicylaldehyde, 5-nitro salicylaldehyde, salicylaldehyde, 5-Bromosalicylaldehyde, cobalt(II) acetate, tetrahydrate, triethylphosphine, methanol, and sodium perchlorate, all of which were obtained from Merck, Fluka and Aldrich. All of the scanning UV-Vis spectra were recorded by Jasco V-530 spectrophotometer. The ¹HNMR spectra were recorded by Bruker Avance DPX 250 MHz spectrometer; IR spectra were recorded by Perkin Elmer Infrared spectrophotometer. Elemental microanalysis (C.H.N), was performed using a Heraeus CHN-O-RAPID elemental analysis.

Synthesis of the Ligands and Complexes

The Schiff bases ligands were prepared from the condensation of 5-Methoxysalicylaldehyde, 5-nitrosalicylaldehyde, salicylaldehyde and 5-Bromo salicylaldehyde, with ethylene diamine in methanol as a solvent. The reaction molar ratio is (X-salicylaldehyde: ethylenediamine; 2:1). The separated precipitate was filtered, washed several times with minimum amount of methanol and dried under vacuum at room temperature. Cobalt (III) complexes under investigation were synthesized as follows; the ligand was dissolved in (100 mm)

methanol and added to a metal salt (cobalt (II) acetate) methanolic solution (20 mm). The mixture was refluxed for 2h; the volume of the mixture was reduced to one-third. On

cooling a crude product was formed, which is collected by filtration and washed several times with methanol (according to the literature [6-8]).

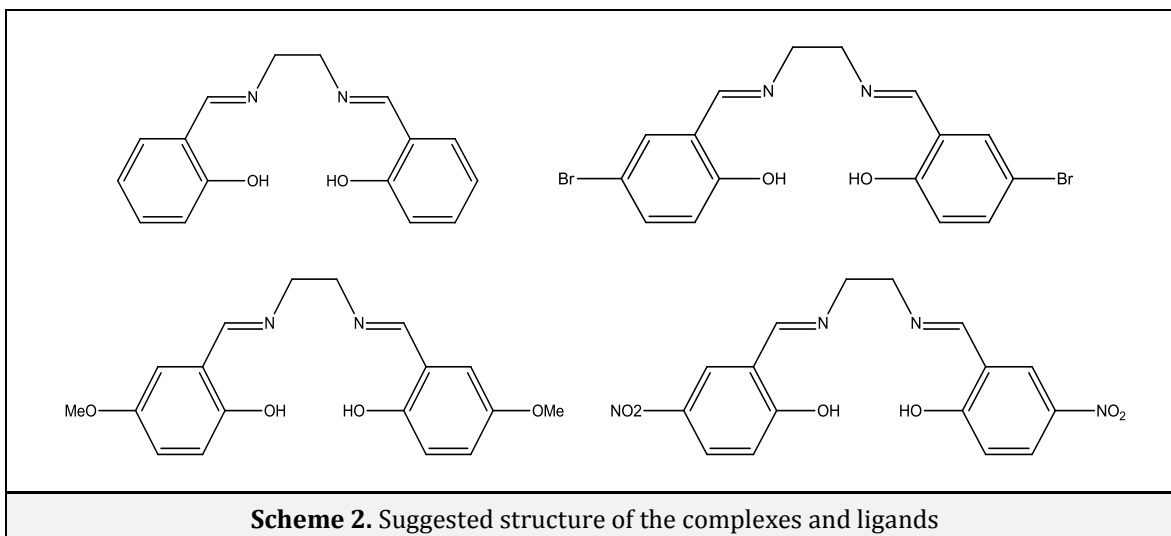
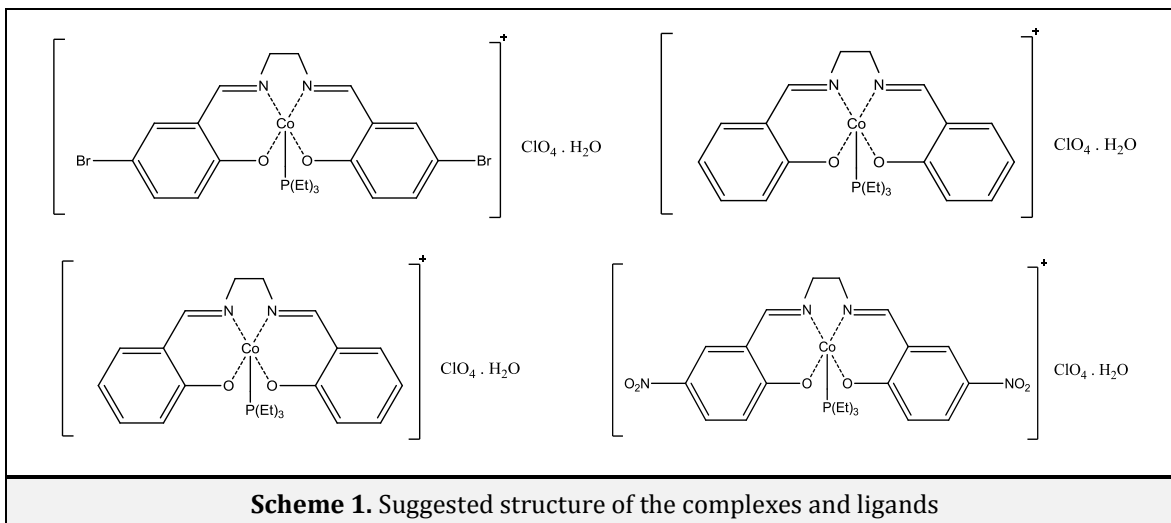


Table 1. Elemental analyses [found (calcd.) (%)] and wavelengths selected (λ , nm) of the complexes

Co(5- XSalen)	C	H	N	Wavelengths (nm)
Co(Salen)	41.98(42.55)	5.11(5.03)	4.60(4.51)	230 400 620
Co(5-NO ₂ Salen)	45.37(37.17)	4.4(4.11)	4.02(3.92)	210 370 570
Co(5-Br Salen)	36.07(36.75)	4.02(4.07)	3.95(3.89)	220 240 613
Co(5-OMe Salen)	42.63(42.33)	5.15(5.18)	4.18(4.15)	230 450 656

Table 2. Infrared spectral data of the schiff base ligands and cobalt complexes (cm⁻¹)

Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{o})$	$\nu(\text{C}-\text{NO}_2)$	$\nu(\text{C}-\text{Br})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
H ₂ -Salen	1653	1283	-	-	-	-
H ₂ (5-NO ₂ Salen)	1655	1216	1300	-	-	-
H ₂ (5-Br Salen)	1590	1270	-	690	-	-
H ₂ (5-OMe Salen)	1650	1280	-	-	-	-
Co(Salen)	1637	1300	-	-	550	510
Co(5-NO ₂ Salen)	1630	1110	1300	-	563	531
Co(5-Br Salen)	1625	1085	-	690	555	513
Co(5-OMe Salen)	1605	1210	-	-	578	522

Results and discussion

All the newly synthesized complexes were colored solids and soluble in DMSO, DMF and methanol. The analytical data were in good agreement with the proposed stoichiometry of the complexes. The electronic spectral and analytical data of cobalt complexes are presented in Tables 1.

IR spectra

In the complexes, the absorption band around 1600 cm⁻¹ is assigned to an azomethine (C=N) group [9]. The phenolic (C-O) stretching band is observed at 1230–1290 cm⁻¹[9, 10]. The ring skeletal vibrations (C=C) were consistent in the region of 1440–1465 in all complexes [11]. Intense band in 1090–1100 is assigned to perchlorate stretching vibrations, which are typical of non-coordinating perchlorate [12]. The weak bands at 2845–2985 cm⁻¹ in the ligands are related to C-H modes of vibrations. In cobalt (III) complexes containing PEt₃ these bands were very stronger, assignable to (CH₃; CH₂) vibrations of PEt₃. The vibration band in 3000–3400

cm⁻¹ is assigned to O-H stretching due to H₂O of the complexes [13]. The IR spectral frequencies of tetra dentate ligands and cobalt complexes are given in Table 2.

¹HNMR spectra

The ¹HNMR spectra of these complexes are consistent with the suggest formulation and show that the cobalt in these complexes is low spin. In the ligands, the signals observed at 12.84 to 16.10 ppm are attributed to the hydroxyl protons. The second signals observed around 12.00 to 12.52 ppm are assigned to NH protons [14]. The absences of these protons in the complexes show that the Schiff bases are coordinated. The azomethine proton signals appeared at 8.22 to 8.63 ppm. By comparing the ¹HNMR spectra of all the Schiff bases with those of their corresponding Co(III) complexes, it is noted that there is a down field shift in the frequency of azomethine protons aliphatic bridge confirming coordination of the metal ion to these groups. The proton chemical shifts for the coordinated PEt₃ appear at 0.70–1.76 ppm. ¹HNMR spectra of,

substituted phenyl ring of Schiff bases show additional signals. A singlet signal at 3.42 ppm is assigned in the [Co (5 OMeSalen) (PEt₃)] ClO₄.H₂O that have OMe group. These results are in agreement with the observed previous results for metal complexes of phosphine as axial ligand [15-18].

Conclusion

In this study, we synthesized four novel complexes of Co (III) by the reaction of the metal ions with the salen ligands. The ligands coordinated with the metal ions through N- and O-donors. The complexes exhibited a geometry based on the coordination number 5. An attempt at prediction the structure and geometry of the complexes was made by elemental analysis, UV-vis, IR, and ¹HNMR spectroscopy. All these characterizations put together lead us to propose the structures shown in Figs 1.

Acknowledgements

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