

Synthesis, Spectral Characterization and Thermal Behavior of Newly Derived La(III), Co(III) and Mn(II) Complexes with Schiff Base Derived from Methionine and Salicylaldehyde

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Abstract

Many metal complexes of Schiff base derived from different amino acids are widely employed as biologically active materials, especially as antibacterial agents. Three new metal [Co(III), Mn(II) and La(III)] complexes with the Schiff base (L) derived from salicylaldehyde and amino acid (methionine) were synthesized and investigated by using various physico-chemical techniques such as elemental analysis, FTIR, UV-visible spectroscopy, magnetic measurement, thermo gravimetric analysis (TGA) and X-ray powder diffraction (XRD) method. From spectral studies, it has been concluded that the synthesized ligand acts as a tetra-dentate molecule, coordinates metal through azomethine nitrogen, sulfur, phenolic oxygen and carboxylate oxygen. UV-visible spectrophotometry showed the characteristic absorption bands corresponding to a square planar geometry for La(III) and Mn(II) metal complexes and tetrahedral geometry for Co(III) complex. The XRD data demonstrated that the manganese and cobalt complexes were crystalline but the lanthanum complex was amorphous in nature. The empirical formula of the synthesized complexes based on analytical data were $[\text{Co}(\text{C}_{12}\text{H}_{13}\text{SNO}_3)](\text{NO}_3)$, $[\text{La}(\text{C}_{12}\text{H}_{13}\text{SNO}_3)](\text{Cl})(\text{H}_2\text{O})$ and $[\text{Mn}(\text{C}_{12}\text{H}_{13}\text{SNO}_3)]$.

Keywords

Schiff Base, Metal Complexes, Spectral Studies, Thermal Behavior, X-Ray Powder Diffraction

1. Introduction

Schiff bases (also known as imine or azomethine) and their complexes are syn-

thesized from the condensation of an amino compound with carbonyl compounds under specific conditions. They exhibit a broad range of biological activities including antifungal, anti-bacterial, antimalarial, anti-proliferative, anti-inflammatory, antiviral, antipyretic properties and extensively used for industrial purposes [1]-[6]. A number of Schiff base complexes exhibit excellent catalytic activity in a wide range of chemical reactions both in homogeneous and heterogeneous catalysis [7]. Over the past few years, there have been many reports on their applications as catalyst in several reactions such as polymerization reaction, reduction of thionyl chloride, oxidation of organic compounds, reduction reaction of ketones, aldol reaction, Henry reaction, epoxidation of alkenes, hydrosilylation of ketones, synthesis of bis(indolyl) methanes and Diels-Alder reaction [8]-[14]. Structurally, a Schiff base is a nitrogen analogue of an aldehyde or ketone in which the carbonyl group (CO) has been replaced by an imine or azo-methine group, as shown in **Figure 1** [15] [16] [17] [18].

Methionine[2-amino-4-(methylthio) butanoic acid] is an essential amino acid that is used in the biosynthesis of proteins. It contains an α -amino group (which is in the protonated $-\text{NH}_3^+$ form under biological conditions), an α -carboxylic acid group (which is in the deprotonated $-\text{COO}^-$ form under biological conditions), and an S-methylthio ether side chain, classifying it as a nonpolar, aliphatic amino acid. Methionine is a bidentate ligand which has greater interest in coordination chemistry, as shown in **Figure 2(a)**. Salicylaldehyde (2-hydroxybenzaldehyde) is the organic compound with the formula $\text{C}_6\text{H}_4\text{CHO}-2\text{-OH}$. Salicylaldehyde is a key precursor to a variety of chelating agents, some of which are commercially important, as shown in **Figure 2(b)**. Schiff base ligands can form very stable complexes compared to some other ligands, as shown in **Figure 2(c)** [19] [20] [21].

2. Experimental

Chemicals and Instruments

All chemicals used were of analytical grade (AR) and of the highest purity

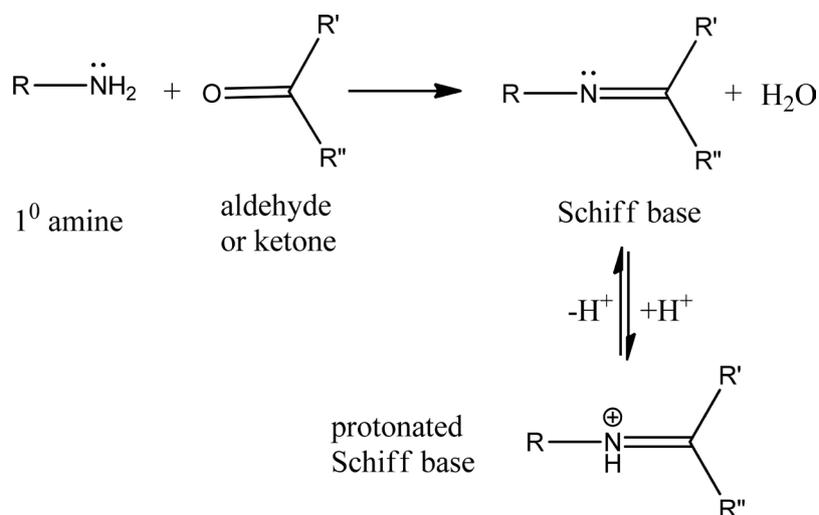


Figure 1. General scheme for formation of Schiff bases.

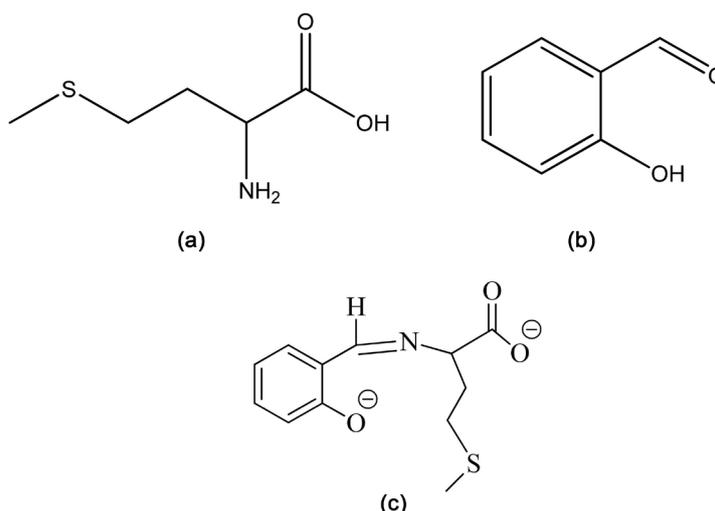


Figure 2. Chemical structure of methionine (a) salicylaldehyde (b) and Schiff base (c).

available. Salicylaldehyde and methionine (Sigma-Aldrich, Germany) were used to prepare the Schiff base that was mixed with (each) Mn(II) chloride tetrahydrate, La(III) chloride hexahydrate and Co(III) nitrate hexahydrate (Merck, Germany) in order to synthesize their complexes. The organic solvents used included methanol, ethanol, chloroform, acetone and DMSO. These solvents were either spectroscopically pure from Merck, Germany or purified by the recommended methods and tested for their spectral purity.

Percentage of carbon, hydrogen, sulfur and nitrogen present in the complex were recorded in a CHNS elemental analyzer (VARIO-MICRO V1.6.1, GmbH, Germany). Melting points of the studied compounds were taken in a melting points apparatus (SMP 11, Stuart, England), which have the capacity of recording the temperature up to 350°C. Infrared spectra of the compounds were recorded in a FTIR spectrophotometer (IRPrestige-21, Shimadzu, Japan) in the range of 400 - 4000 cm^{-1} using KBr pellets. Ultraviolet-visible spectral analysis was carried out at room temperature in dimethyl sulfoxide (DMSO) in a double beam Shimadzu UV-visible spectrophotometer, model UV-1650 PC. Magnetic susceptibility of the complexes were determined using SHERWOOD SCIENTIFIC Magnetic Susceptibility Balance, Cambridge, England, and Model Magway MSB Mk1. Thermo gravimetric analysis of the complexes was performed in nitrogen atmosphere, using a TGA-50 analyzer, Shimadzu, Japan.

Synthesis of the Schiff base ligand (L)

Methionine-salicylaldehyde Schiff base was synthesized from 10 mL water containing 0.1497 g (1×10^{-3} M) methionine and 20 mL ethanol that had been dissolved in advance 0.1209 g (1×10^{-3} M) salicylaldehyde. In order to maintain the *pH* value 9.0 of the mixture, 1×10^{-3} M NaOH solution was added and the mixture was refluxed for 2 hours. The reaction is clarified in **Figure 3**:

Synthesis of the metal complexes (ML)

The metal complexes were synthesized in the same manner by mixing 1×10^{-3} M ethanolic solution (20 mL) of methionine-salicylaldehyde Schiff base with 20

mL ethanol containing $\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (1×10^{-3} M) or $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$ (1×10^{-3} M) or $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (1×10^{-3} M). Then the mixtures were refluxed for 4 hours. Finally, the volume of solutions was reduced and in all cases, an occurrence of colored precipitate was observed this being assigned to Co(III) complex or Mn(II) complex or La(III) complex respectively. It was filtered, washed with water and dried at room temperature. The reaction is clarified in **Figure 4**.

3. Results and Discussion

The Schiff base ligand was synthesized by refluxing the appropriate amount of methionine with salicylaldehyde in mixed medium (water-ethanol). The metal complexes of Schiff base ligand were prepared by the stoichiometric reaction of the corresponding metal(II) chloride, metal(III) nitrate and metal(III)chloride with the ligand in a molar ratio of 1:1. The complexes were obtained as air-stable solids, which are insoluble in water, partially soluble in acetone, methanol, ethanol and soluble in dimethyl sulfoxide (DMSO). The color, elemental analysis data along with some other physical properties of the synthesized complexes are listed in **Table 1** [22] [23] [24].

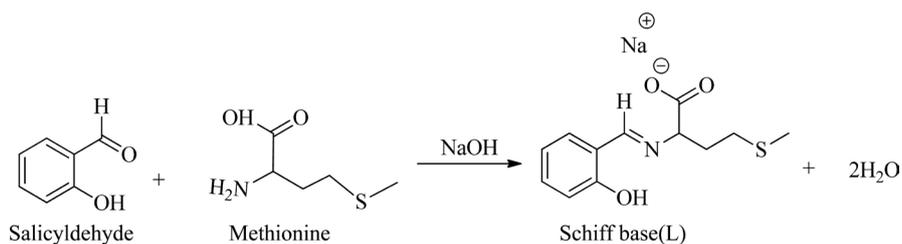


Figure 3. Synthesis route of methionine-salicylaldehyde Schiff base.

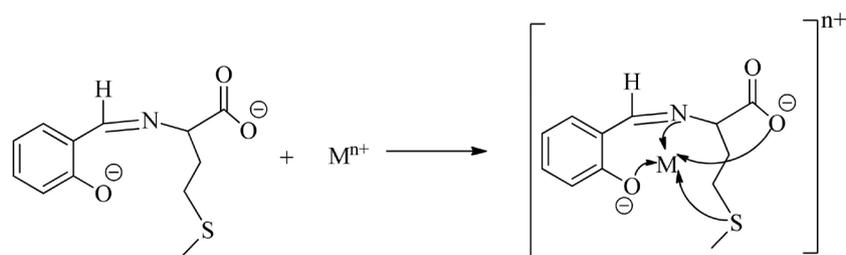


Figure 4. Synthesis route of metal-Schiff base complex.

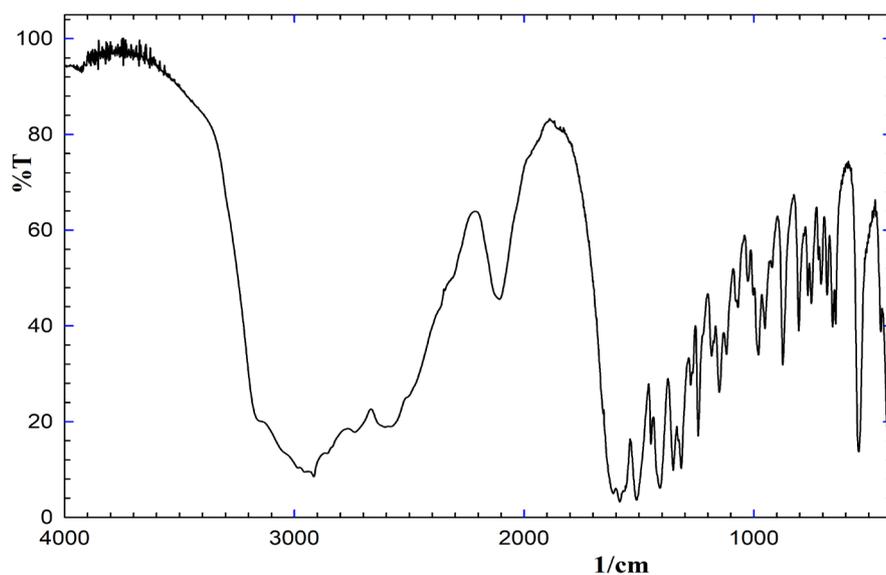
Table 1. Analytical and physical data of the metal complexes.

Complex formula Molecular weight (g/mol)	Color	m.p °C (Decomp.)	Elemental and metal analysis calculated (Found)				
			C%	H%	N%	S%	M%
[LaL](H ₂ O)(Cl) 443.68	Yellow	>340	36.92 (37.42)	3.36 (3.98)	3.59 (4.07)	8.23 (8.67)	45.97 (46.30)
[CoL](NO ₃) 372.24	Brown	225 - 230	46.44 (45.39)	4.22 (4.95)	4.51 (4.80)	10.34 (9.76)	34.49 (33.65)
[MnL] 306.24	Greenish yellow	220 - 226	47.04 (46.83)	4.28 (4.88)	4.58 (4.87)	10.47 (10.02)	33.63 (34.56)

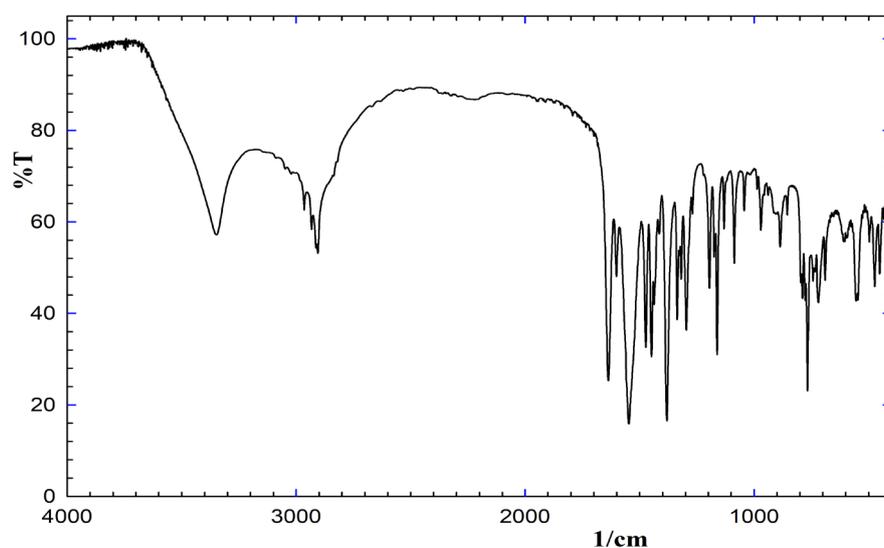
Here, L = C₁₂H₁₃SNO₃.

Infra red Spectra

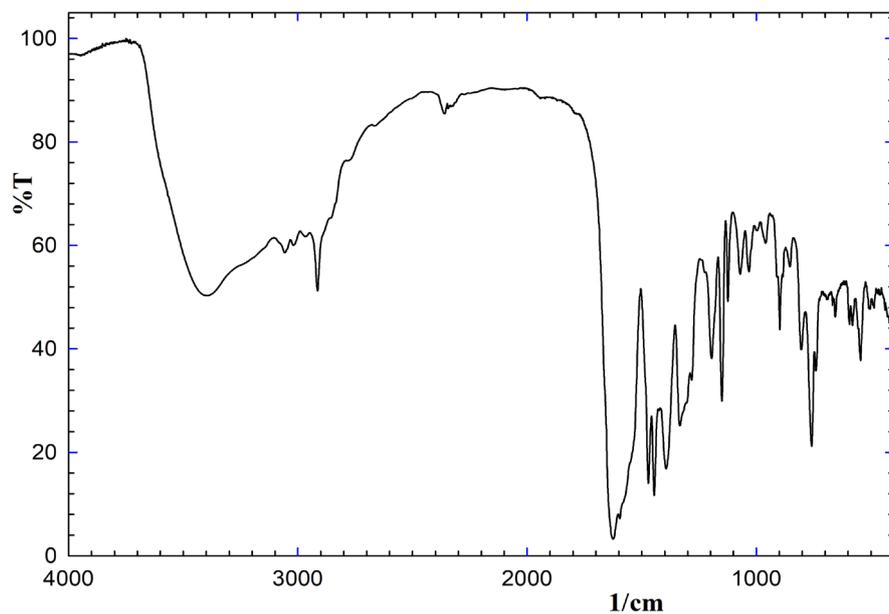
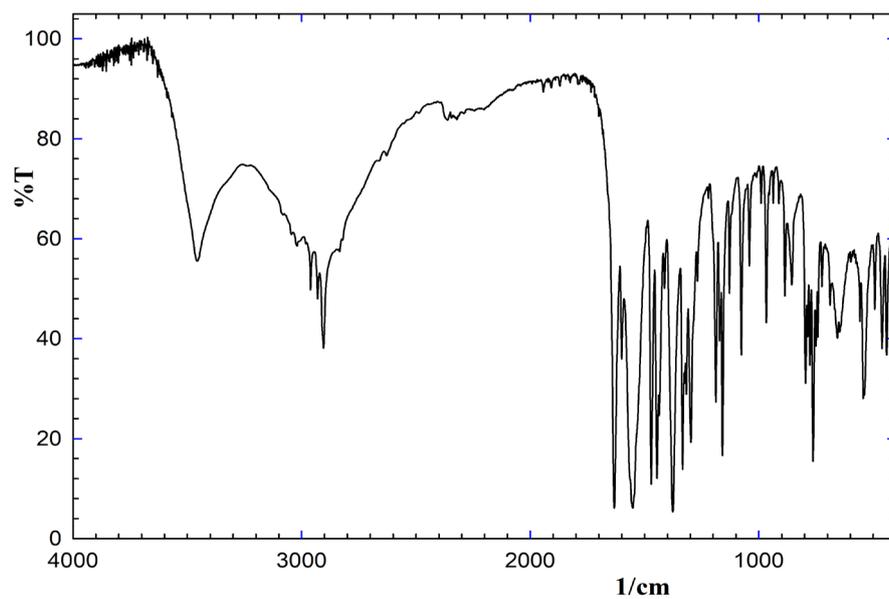
IR spectra for methionine, Schiff base ligand and metal complexes were recorded in wavenumber range between 400 - 4000 cm^{-1} . IR spectrum of methionine showed absorption bands at 3000 - 2850, 2800 - 2550, 2106, 1350 - 1000 and 900 - 690 cm^{-1} corresponding to $\nu(\text{N-H})_{\text{sym}}$, $\nu(\text{O-H})_{\text{carboxylic}}$, $\nu(\text{N-H})_{\text{asym}}$, $\nu(\text{C-N})_{\text{amines}}$ and $\nu(\text{C-H})_{\text{bent}}$ stretching frequencies, respectively. A comparison of the IR spectra of methionine and Schiff base ligand provides proof of the formation of the Schiff base between methionine and salicylaldehyde. The principal band responsible for this is the new absorption band at 1636 cm^{-1} attributed to $\nu(\text{C=N})$ stretching vibration. The IR spectra of different metal complexes are given below **Figure 5**. The most important absorption bands and their assignments are listed in **Table 2**.



Infrared Spectrum of methionine



Infrared Spectrum of $[\text{Co}(\text{C}_{12}\text{H}_{13}\text{SNO}_3)]$ complex

Infrared Spectrum of $[\text{La}(\text{C}_{12}\text{H}_{13}\text{SNO}_3)]$ complexInfrared Spectrum of $[\text{Mn}(\text{C}_{12}\text{H}_{13}\text{SNO}_3)]$ complex**Figure 5.** Infra red spectrum of methionine and metal complexes.**Table 2.** Relevant IR data of the Schiff base and its metal complexes (cm^{-1}).

Compounds	$\nu(\text{N-H})$	$\nu(\text{O-H})$	$\nu(\text{C=C})$	$\nu(\text{C=N})$	$\nu(\text{C-N})$	$\nu(\text{C-O})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
Schiff base	3450 br	-	-	1636 m	1375 s	1225 s	-	-
$[\text{CoL}](\text{NO}_3)$	3348 br	-	1472 m	1640 sh	1335 m	1182 sh	766 sh	545 m
$[\text{LaL}](\text{H}_2\text{O})\text{Cl}$	3401 br	2914 m	1626 b	1645 w	-	1070 m	759 m	539 m
$[\text{MnL}]$	3050 br	3418 b	1612 sh	-	1149 sh	-	897 m	656 m

Sh = sharp, m = medium, br = broad, w = weak, s = small.

The main bands in the IR spectrum of the free Schiff base are at 3450, 1636, 1375 and 1225 cm^{-1} attributed to $\nu(\text{OH})$, $\nu(\text{C}=\text{N})$ azomethine, $\nu(\text{C}-\text{N})$ amine and $\nu(\text{CO})$ phenolic, respectively [25] [26] [27] [28]. The band at 3450 cm^{-1} in the ligand spectrum disappears from the complexes as an indicative of phenolic group deprotonation. Instead, the band at 1252 cm^{-1} assigned to $\nu(\text{CO})$ phenolic vibration is shifted left in comparison with the ligand, as a result of both deprotonation and coordination of phenolic oxygen. These shifts indicate the participation of the oxygen atom of the deprotonated hydroxyl group which is situated in a favorable position (orto) towards the azomethine group. The spectra of metal complexes exhibited a broad band around 3348 cm^{-1} , 3401 cm^{-1} and 3050 cm^{-1} which is assigned to different $\nu(\text{N}-\text{H})$, associated with the complexes. IR spectra of the ligand presented a band at 1636 cm^{-1} attributed to $\nu(\text{C}=\text{N})$ azomethine group, which is shifted to a higher value in two complexes at 1640 and 1645 cm^{-1} suggesting that the ligand is coordinated to the metal ion through nitrogen atom from azomethine group. The new absorption bands $\nu(\text{M}-\text{N})$, $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{S})$ observed in spectra of complexes at 545, 766, 486 cm^{-1} ; 539, 759, 416 cm^{-1} and 656, 897, 448 cm^{-1} respectively (see inserted spectrum in **Figure 5**) shows the coordination of the ligand through nitrogen and oxygen [29] [30]. The IR spectra of the complexes contain several absorption bands from the Schiff base and also new absorption bands, these being attributed to the coordination of the ligand to metal ions through phenolic oxygen atom, carboxylic oxygen atom, sulphur atom and imino nitrogen atom from azomethine bond.

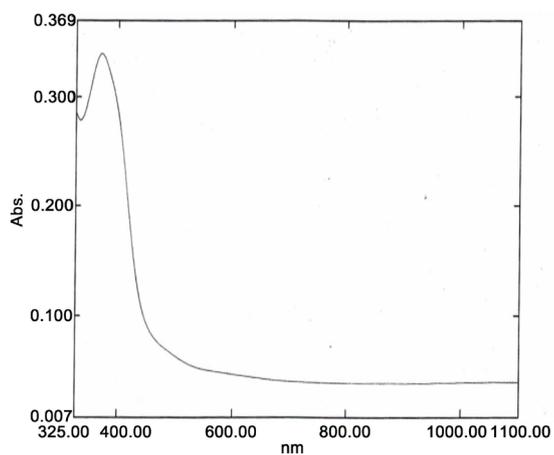
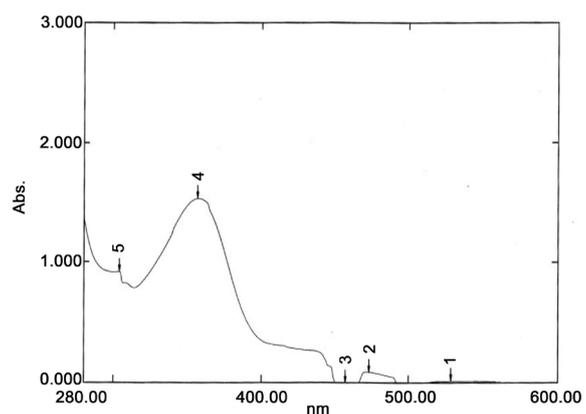
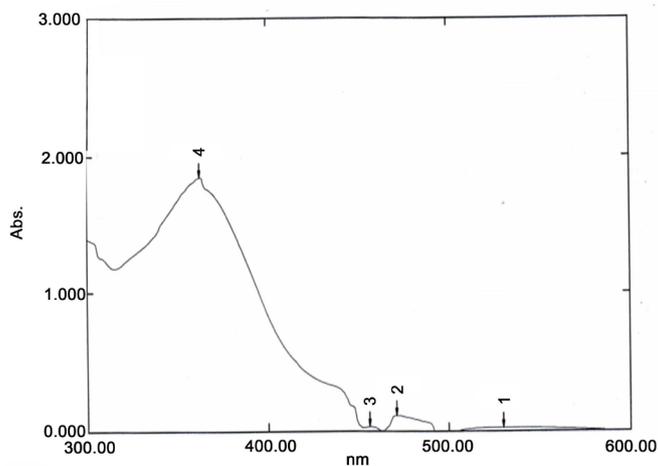
Magnetic measurements and electronic spectra

The complex $[\text{CoL}](\text{NO}_3)$ showed 4.59 BM, indicated a tetrahedral geometry, which is related to three unpaired electrons. Furthermore, the square planar geometry of the complex $[\text{MnL}]$ showed 5.24 BM which is related to four unpaired electron. On the other hand, square planar complex of $[\text{LaL}](\text{H}_2\text{O})\text{Cl}$ have one unpaired electron which showed the magnetic moment 1.47 BM, as shown in **Table 3**.

Electronic spectra of the complexes showed in the **Figure 6**. The electronic spectra of the cobalt (III) complex exhibit one absorption band at 364 nm which could be assigned ligand to metal charge transfer transition and the other absorption band at 478 nm corresponds to intra ligand charge transfer transition. These transitions suggest tetrahedral and square planar structure respectively. On the other hand, the lanthanide (III) complex shows absorption band at 362

Table 3. Magnetic moments and electronic spectra of metal complexes.

Complex	$\mu_{\text{eff.}}$ (B.M)	λ_{max} (nm)	Band assignment	Geometry
$[\text{CoL}](\text{NO}_3)$	4.59	364 478	ligand to metal charge transfer intra ligand charge transfer	tetrahedral
$[\text{LaL}](\text{H}_2\text{O})\text{Cl}$	1.47	362 480	ligand to metal charge transfer intra ligand charge transfer	square planar
$[\text{MnL}]$	5.24	376	intra ligand charge transfer	square planar

UV-visible spectrum of 0.0005M $[\text{Mn}(\text{C}_{12}\text{H}_{13}\text{SNO}_3)]$ UV-visible spectrum of 0.001M $[\text{La}(\text{C}_{12}\text{H}_{13}\text{SNO}_3)](\text{Cl})(\text{H}_2\text{O})$ UV-visible spectrum of 0.001M $[\text{Co}(\text{C}_{12}\text{H}_{13}\text{SNO}_3)](\text{NO}_3)$ **Figure 6.** Electronic spectra of the complexes.

nm and 480 nm respectively. The intense transition at 362 nm occur due to the ligand to metal charge transfer transition. The manganese (II) complex shows only one intense absorption band at 376 nm due to intra ligand charge transfer transition [31]. The electronic spectra of the complexes are agreed with magnetic

values.

Thermal analysis (TGA)

Thermogravimetric analysis of the metal complexes are used to: i) get information about the thermal stability of these new complexes, (ii) decide whether the water molecules (if present) are inside or outside the inner coordination sphere of the central metal ion, and iii) suggest a general scheme for thermal decomposition of these complexes [32]. In the present investigation, heating rate were suitably controlled at $10^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere, and the weight loss was measured from the ambient temperature up to 800°C . The data are provided in **Table 4**.

The thermogram of the $[\text{Co(III)L}](\text{NO}_3)$ complex shows three decomposition steps within the temperature range $25^{\circ}\text{C} - 800^{\circ}\text{C}$. The first step of decomposition within the temperature range $150^{\circ}\text{C} - 320^{\circ}\text{C}$ correspond to the loss of salicylaldehyde molecule with a mass loss of 33.27% (calc: 39.38%). The second step of decomposition within the temperature range $320^{\circ}\text{C} - 640^{\circ}\text{C}$ correspond to the loss of methionine molecule with a mass loss of 38.19% (calc: 39.88%). The subsequent step (upto 799°C) correspond to the removal of the organic part of the ligand, leaving metal oxide as a residue. The remaining residue corresponding to a mass of 24.45% (calc: 23.70%).

The thermogram of the $[\text{La(III)L}](\text{H}_2\text{O})\text{Cl}$ complex shows four decomposition steps within the temperature range $28^{\circ}\text{C} - 800^{\circ}\text{C}$. The first step of decomposition within the temperature range $28^{\circ}\text{C} - 166^{\circ}\text{C}$ correspond to the loss of water

Table 4. Characteristics of the thermal degradation steps of Co(III), La(III) and Mn(II) complexes.

Complex	Step	Temperature range/ $^{\circ}\text{C}$	Mass loss /%	Associated process
$[\text{Co(III)L}](\text{NO}_3)$	1	150 - 320	33.27	loss of salicylaldehyde molecule
	2	320 - 640	38.19	loss of methionine molecule
	3	640 - 799	2.10	gradual loss of mass due to the elimination of some gases
		residue	24.45	Cobalt oxide
$[\text{La(III)L}](\text{H}_2\text{O})\text{Cl}$	1	28 - 166	9.14	loss of one molecule hydrated water
	2	166 - 360	31.11	loss of methionine molecule
	3	360 - 625	22.67	loss of salicylaldehyde molecule
	4	625 - 799	1.68	gradual loss of mass due to the elimination of some gases
	residue	35.40	Lanthanum oxide	
$[\text{Mn(II)L}]$	1	166 - 408	45.96	loss of methionine molecule
	2	408 - 708	24.66	loss of salicylaldehyde molecule
	3	708 - 799	3.68	gradual loss of mass due to the elimination of some gases
		residue	23.44	Manganese oxide

molecules of hydration with a mass loss of 9.14% (calc: 8.40%). The second step of decomposition within the temperature range 166°C - 360°C correspond to the loss of methionine molecule with a mass loss of 31.11% (calc: 34.90%). The third step of decomposition within the temperature range 360°C - 625°C correspond to the loss of salicylaldehyde molecule with a mass loss of 22.67% (calcd: 29.93%). The subsequent step (upto 799°C) correspond to the removal of the organic part of the ligand, leaving metal oxide as a residue. The remaining residue corresponding to a mass of 35.40% (cala: 36.23%).

The thermogram of the [Mn(II)L] complex shows three decomposition steps within the temperature range 31°C - 800°C. The first step of decomposition within the temperature range 166°C - 408°C correspond to the loss of methionine molecule with a mass loss of 45.96% (calc: 43.42%). The second step of decomposition within the temperature range 408°C - 708°C correspond to the loss of salicylaldehyde molecule with a mass loss of 24.66% (calc: 35.56%). The subsequent step (upto 799°C) correspond to the removal of the organic part of the ligand, leaving metal oxide as a residue. The remaining residue corresponding to a mass of 23.44% (cala: 25.30%).

X-ray Powder Diffraction (XRD)

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined. X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector. Cu K α or Mo K α radiations are used in the x-ray powder diffractometer. For typical powder patterns, data is collected at 2θ from $\sim 5^\circ$ to 70° , angles that are preset in the X-ray scan. X-ray powder diffraction is most widely used for the identification of unknown crystalline material.

The XRD pattern of different metal complexes is given in **Figure 7**.

The sharp line diffractogram indicates that Co(III) and Mn(II) complexes are crystalline in nature. The XRD pattern of lanthanum complex indicates that it is amorphous in nature.

From literature we know, for body centred crystal ($h + k + l = 2n$) or the ratio of $\text{Sin}2\theta$ must be 2:4:6:8:10:12:14:16:18. The XRD data in **Table 5** fulfills the condition. So the structure of the complex [Mn(C₁₂H₁₃SNO₃)] and [Co(C₁₂H₁₃SNO₃)](NO₃) is body centred.

From the result of various studies described and discussed here and the concept of essential criteria of complex formation that the associated ligands must fulfill the coordination number and the oxidation state of the metal ion, the most probable structure of the complexes are given in **Figure 8**.

4. Conclusion

The new Co(III), Mn(II) and La(III) complexes with the Schiff base derived from methionine and salicylaldehyde were synthesized and characterized. The

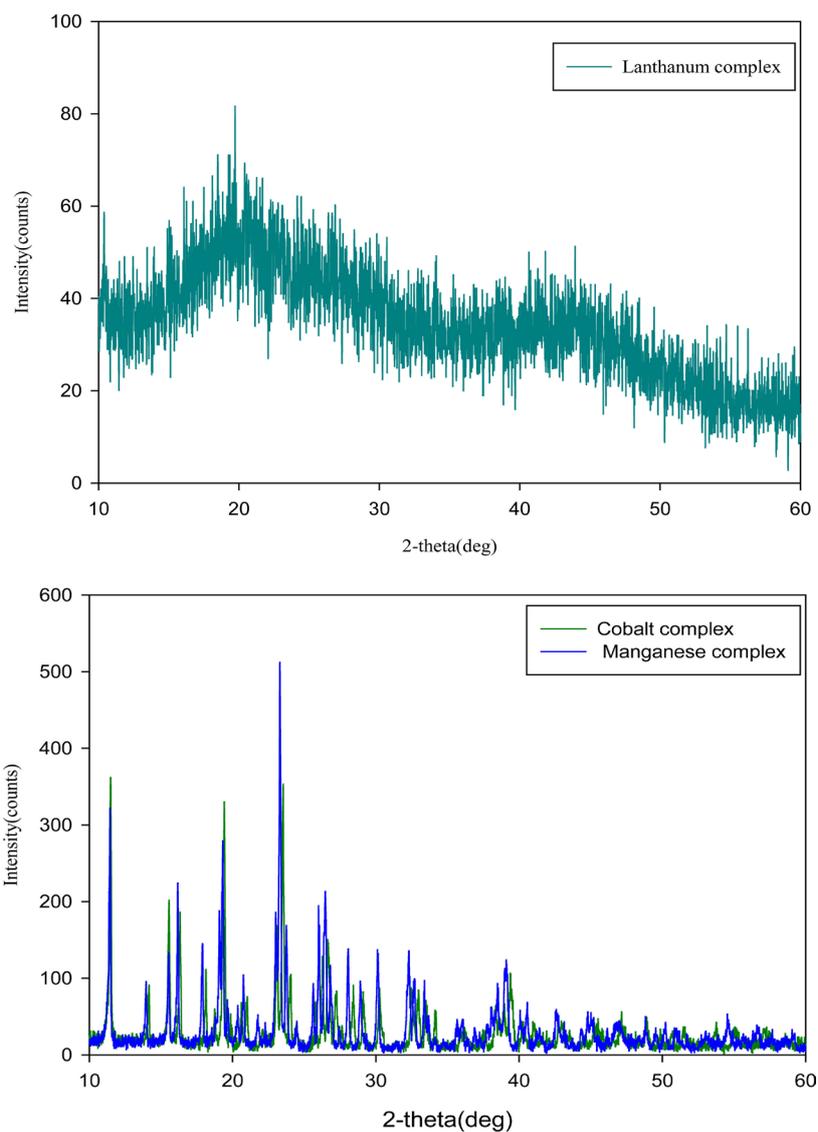


Figure 7. XRD pattern of Co(III), La(III) and Mn(II) complexes.

Table 5. XRD data of $[\text{Mn}(\text{C}_{12}\text{H}_{13}\text{SNO}_3)]$ and $[\text{Co}(\text{C}_{12}\text{H}_{13}\text{SNO}_3)](\text{NO}_3)$ complexes.

2θ	θ	$\text{Sin}2\theta$	$\frac{h^2 + k^2 + l^2}{\text{Ratio}}$	2^*ratio	2θ	θ	$\text{Sin}2\theta$	$\frac{h^2 + k^2 + l^2}{\text{Ratio}}$	2^*ratio
11.448	5.724	0.010	1.0	2.0	11.490	5.745	0.010	1.0	2.0
16.179	8.090	0.020	2.0	4.0	16.339	8.169	0.020	2.0	4.0
19.647	9.824	0.029	3.0	6.0	19.910	9.955	0.030	3.0	6.0
23.018	11.509	0.040	4.0	8.0	23.107	11.554	0.040	4.0	8.0
25.611	12.809	0.049	5.0	10.0	25.790	12.895	0.050	5.0	10.0
28.074	14.037	0.060	6.0	12.0	28.440	14.220	0.060	6.0	12.0
30.154	15.078	0.069	7.0	14.0	30.120	15.060	0.069	7.0	14.0
32.640	16.320	0.079	8.0	16.0	33.003	16.502	0.080	8.0	16.0
34.700	17.350	0.089	9.0	18.0	34.130	17.065	0.089	9.0	18.0

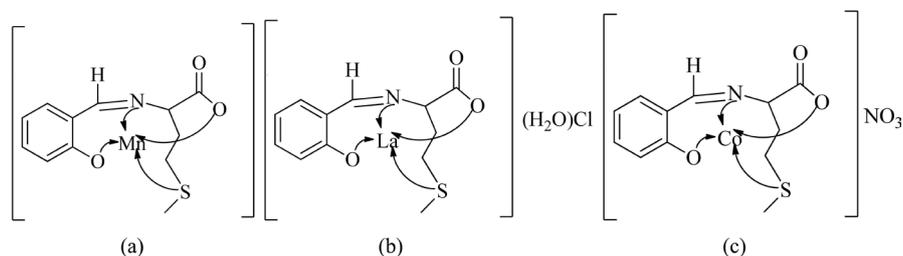


Figure 8. Probable structure of $[\text{Mn}(\text{C}_{12}\text{H}_{13}\text{SNO}_3)]$ complex (a), $[\text{La}(\text{C}_{12}\text{H}_{13}\text{SNO}_3)](\text{Cl})(\text{H}_2\text{O})$ complex (b) and $[\text{Co}(\text{C}_{12}\text{H}_{13}\text{SNO}_3)](\text{NO}_3)$ complex (c).

data collected from IR spectra showed that the Schiff base behaves as a tetra-dentate ligand coordinated in the lanthanum, cobalt and manganese complexes. Electronic spectra and magnetic measurements indicated tetrahedral geometry for the cobalt complex and square planer geometry for lanthanum and manganese complexes. The thermal analysis presented the thermal degradation data of the three complexes. The XRD data revealed that the manganese and cobalt complexes were crystalline whereas the lanthanum complex was amorphous in nature.

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