

Synthesis and Spectroscopic Investigation of Schiff Base Chelates with Zirconium(IV), Lanthanum(III) and Cerium(IV) Ions

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ABSTRACT: The 2-[(4-[(Z)-1-(2-hydroxyphenyl) ethylidene]hydrazonoethyl)phenol] has been synthesized by condensation of 2-hydroxyacetophenone and hydrazine monohydrate. The Schiff base chelates were synthesized from chloride, nitrate or sulphate salts of Zr(IV), La(III), and Ce(IV), respectively, in ethanol. The chemical structures of the Schiff base and its chelates were confirmed by various analyses such as CHN elemental analysis, molar conductivity, thermogravimetric analysis, IR, electronic, ¹HNMR and mass spectroscopies. The CHN elemental analysis data showed the formation of 1:1[metal: ligand] ratio. The TGA of the cerium(IV) chelate showed the existence of water molecules in the chelates. Based on the IR results, it is found that this Schiff base acts as neutral tetradentate ligand and coordinated to each metal ion through azomethine nitrogen and oxygen atoms. The participation of hydroxyl group of the Schiff base in complexation was confirmed by IR and ¹HNMR spectral data. The electronic spectral data exhibited the existence of $\pi \rightarrow \pi^*$ (phenyl ring), $n \rightarrow \pi^*$ (C=N and OH) and an octahedral geometry was proposed for all the chelates. The mass spectral data confirmed the purity of the Schiff base and its chelates.

Keywords: 2-[(4-[(Z)-1-(2-hydroxyphenyl)ethylidene]hydrazonoethyl)phenol]; Zr(IV), La(III), and Ce(IV) Chelates; Physicochemical tools.

INTRODUCTION: In view of broad applications of Schiff bases and their chelates, the research work in the field of coordination chemistry is improved, but still there is a lot of challenging work has been carried out on Schiff base metal chelates along with their different industrial and chemotherapeutic studies. Schiff base complexes are considered to be among the most important stereochemical models in main group and transition metal coordination chemistry due to their preparative accessibility and structural variety¹. Interest in the studies of hydrazides and corresponding hydrazones arises from the fact that hydrazides of organic acids and their hydrazones can function as antituberculous. The antituberculous activity was ascribed to their ability to form more or less stable chelates with the transition metal ions^{2&3}. Bidentate and tridentate (NO, ONO) Schiff bases have been synthesized by condensing methyl isobutyl ketone with 2-amino-4-chlorophenol and 2-hydroxyacetophenone with isonicotinic acid hydrazide. The 1:1 or 1:2 metal complexes have been prepared by interaction of the Schiff bases with Ni(II) and Cu(II) ions. These compounds have been synthesized by conventional as well as microwave methods and characterized by elemental analysis, FT-IR, UV-Vis, ESR, molar conductance, TGA and X-ray diffraction. The complexes were col-

ored and stable in air at room temperature. The TGA behavior of metal complexes showed that the hydrated complexes lose water molecules of hydration in the first step, followed by decomposition of ligand molecules in the subsequent steps⁴.

Our aim in this study is to establish and investigate the structures of the Schiff base and its chelates by using physicochemical techniques, including elemental analysis, molar conductivity, thermogravimetric analysis, IR, electronic, ¹HNMR and Mass spectroscopies.

MATERIAL AND METHODS: All chemicals were supplied from BDH and Fluka and used without any purification; 2-hydroxyacetophenone, hydrazine monohydrate, ZrOCl₂.8H₂O, La(NO₃)₃.6H₂O and Ce(SO₄)₂.4H₂O, C₂H₅OH, DMF, DMSO and NH₄OH solution from Prolabo Reagents. The synthesized Schiff base and its chelates were subjected to CHN elemental analyses using Perkin-Elmer 2400 elemental analyzer. Melting points were determined on a Tempo melting point apparatus and are uncorrected. The TGA of Ce(IV) chelate was achieved using Shimadzu thermal analyzer(Japan). The weight loss of the sample was measured from ambient temperature up to 1000°C in a rate of 10°C/min. Infrared spectra were obtained by KBr disc technique by using IFS-25DPUSR/IR spectrometer (Bruker) in the range of 4000-400cm⁻¹, ¹HNMR spectra

of the Schiff base and Zr(IV) chelate were recorded on Varian Gemini 200-200MHz spectrometer using TMS as internal standard and d_6 -DMSO as a solvent. The electronic spectra of the Schiff base and its chelates were measured in DMSO solvent using a Perkin-Elmer-Lambda β -spectrophotometer. The mass spectra were carried out by using Shimadzu QP-2010 Plus. The molar conductivity of the chelates was measured in DMSO solvent using digital conductivity meter CMD-650, at Chemistry Department, Sebha University, Sebha, Libya. All the mentioned analyses except molar conductivity were done at Micro analytical center, Cairo University, Giza, Egypt.

Synthesis of 2-[(4-[(Z)-1-(2-hydroxyphenyl) ethylidene]hydrazonoethyl)phenol]: This compound was synthesized by refluxing of 2-hydroxyacetophenone (0.02mole; 2.72g) in ethanolic solution (50mL) with the same amount of the solvent of hydrazine monohydrate (0.01mole; 0.50 mL), then few drops of glacial acetic acid was added slowly to the reaction mixture. The obtained mixture was heated under refluxing with continuous stirring at about 60°C for 2hrs and light-yellowish needle crystals were collected by filtration and washed with sufficient quantity of hot ethanol. The obtained crystals were dried in a vacuum desiccator with 79.59% yield and the melting point ranged from 198.9-200.0°C. The formation of the Schiff base was confirmed by its purity and elemental analysis data.

Synthesis of the chelates: These chelates were synthesized by mixing 25mL ethanolic solution of 0.5mmol of the metal salts ($ZrOCl_2 \cdot 8H_2O$, $La(NO_3)_3 \cdot 6H_2O$ and $Ce(SO_4)_2 \cdot 4H_2O$), respectively, and same amount of the ethanolic solution of the Schiff base. The mixtures were heated under refluxing with continuous stirring for 3hrs

after adding 10% of ammonia solution to adjust the pH \cong 8 at which the chelates separated out and the obtained products filtered then washed several times with absolute hot ethanol. The formed products were dried in desiccator under silica gel. The yields of the products were of about 79.50-93.50% and their purity was confirmed by the elemental analysis data and they decomposed above 300°C.

RESULTS AND DISCUSSION: The reaction of 2-hydroxyacetophenone with the hydrazine monohydrate in 2:1[Ketone:Amine] ratio gave a product which is a Schiff base as shown in Fig-1.

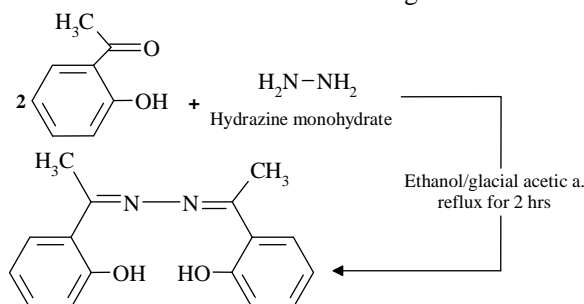


Figure 1: Structure of 2-[(4-[(Z)-1-(2-hydroxyphenyl) ethylidene]hydrazonoethyl)phenol].

CHN elemental analyses and molar conductivity: In all chelates, the calculated values are in a good agreement with the experimental values as shown in Table-I. The molar conductivity was measured in $10^{-3}M$ DMF solvent and their values are in the range of 11.55-20.40 $ohm^{-1}cm^2mol^{-1}$ at room temperature. These values confirm the existence of non- electrolytic nature⁵.

Table I: Physical characterization, analytical and molar conductance data of the Schiff base and its chelates.

Ligand/ chelates	M. wt g/mole	Colour	m.p(⁰ C)	Yield %	Elemental analysis Calc. (Found)			Molar Conductance $Ohm^{-1}cm^2mol^{-1}$
					C%	H%	N%	
L; ($C_{16}H_{16}N_2O_2$)	268.32	Yellowish needle	198– 200	79.59	71.62 (71.72)	6.01 (5.59)	10.44 (10.72)	–
[ZrO (L)(OH) ₂].3H ₂ O	445.709	Pale canary powder	>300	86.27	43.23 (43.42)	4.76 (4.82)	6.38 (6.63)	20.40
[La (L)(OH)(H ₂ O)].H ₂ O	458.368	Light canary yellow powder	>300	79.51	43.55 (43.59)	4.11 (4.47)	6.35 (6.67)	11.55
[Ce (L)(OH) ₂]. 3H ₂ O	510.600	Dark creamy green powder	>300	93.43	38.39 (38.71)	4.31 (4.87)	5.97 (5.46)	18.02

Thermogravimetric analysis for Ce(IV) chelate: The TGA was performed to assist in predicting the molecular structures of the chelates and the weight losses were

measured from the ambient temperature up to 1000°C using a heating rate of 10°C/min⁶. The TGA curve of Ce(IV) chelate of the formula $[Ce(L)(OH)_2] \cdot 3H_2O$ oc-

curs in three stages of decomposition, while the first step estimated weight loss of 7.83% with the calculated value 7.47% attributed to the loss of the three hydrated water molecules found outside the coordination sphere usually take place in the temperature range 50-291°C. In the second stage, a continuous weight loss in the temperature range 291-525°C is observed due to the decomposition of the Schiff base as carbonate or oxalate ion. In the third stage, the mass of final residue of metal oxide (CeO₂) reveals a weight loss of 48.33% was appeared stable state above 756°C coincide fairly with the calculated value 50.63%⁷. Thermal stability places the chelate in the following order:

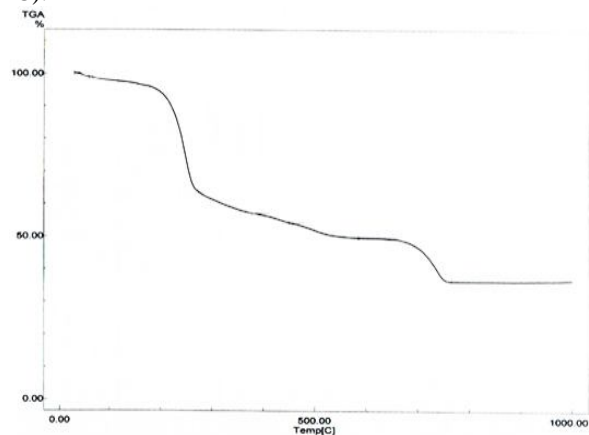
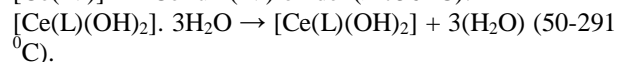
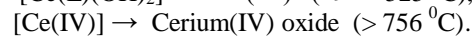
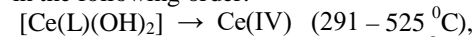


Figure 2: Thermogravimetric analysis of Ce(IV) chelate Infrared spectra.

A comparative study of the IR spectrum of the Schiff base with that of the chelates are summarized in Table-2 and their spectra are shown in Figures-3-6. The bands at 1604, 1617 and 1600 cm⁻¹ which have assigned to characteristic of azomethine (-C=N-) moiety of the Schiff base chelates. The observed change in comparison to the position of this group in the free Schiff base (1601 cm⁻¹) indicating the participation of azomethine group in coordination with the metal ions through nitrogen atoms⁸. Moreover, the presence of water molecules in the coordination sphere of the chelates is indicated by the appearance of νOH band which was observed as broad band centered in the range 3397-3544 cm⁻¹⁹. The bands which are not present in the Schiff base assigned to ν(M-N) and ν(M-O) appeared at 424-457 and 518-663 cm⁻¹, respectively, suggesting the engagement of both nitrogen and oxygen atoms in chelation¹⁰. The spectrum of the Zr(IV) chelate exhibits a band at 1155cm⁻¹ due to the existence of Zr=O bond¹¹.

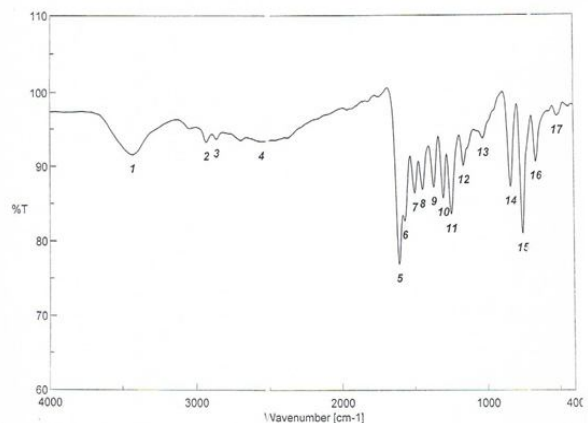


Figure 3: IR spectrum of 2-[(4-[(Z)-1-(2-hydroxyphenyl)ethylidene]hydrazonoethyl)phenol].

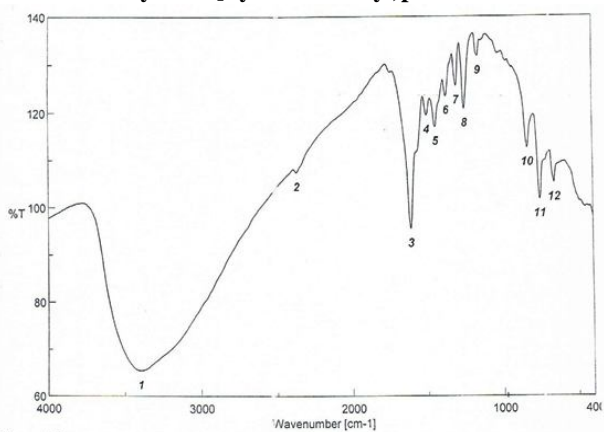


Figure 4: IR spectrum of Zr(IV) chelate.

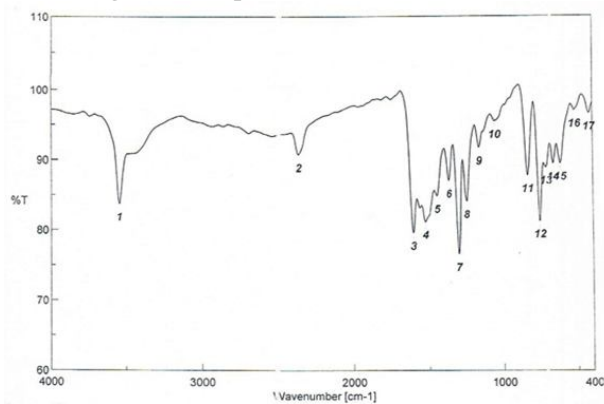


Figure 5: IR spectrum of La(III) chelate.

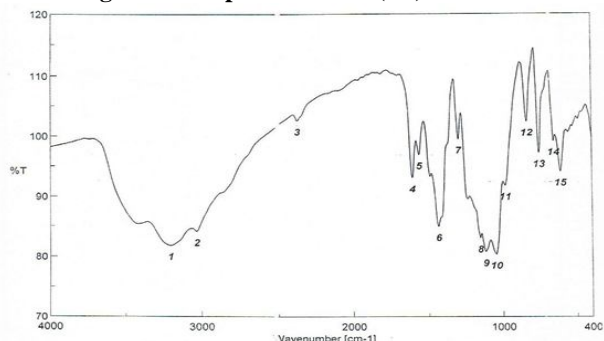


Figure 6: IR spectrum of Ce(IV) chelate.

Electronic spectra of the chelates: The electronic spectral data of the Schiff base and its chelates are listed in table 2. The ultraviolet spectrum results of the 2-[(Z)-1-(2-hydroxyphenyl) ethylidene]hydrazonoethyl)phenol exhibits two bands at 294 nm (34014 cm⁻¹) and 329 nm (30395 cm⁻¹) which can be assigned to the $\pi \rightarrow \pi^*$ (phenyl) and $n \rightarrow \pi^*$ (C=N and OH)¹². The electronic system (d⁰) of Zr(IV) chelate was found to be diamagnetic. The diffuse reflectance spectrum of this chelate did not show any d-d transition but abroad bands are observed in the region 294 nm (34013cm⁻¹) and 363nm (27548 cm⁻¹) due to charge transfer transition suggesting an octahedral geometry for Zr(IV) chelate¹³. On the other hand, the electronic spectrum of diamagnetic La(III) chelate exhibits two absorption observed at 293nm (34129 cm⁻¹) and 360 nm (27778cm⁻¹) attributed to the charge transfer transition and an octahedral configuration was proposed for this chelate¹⁴. In addition, the electronic spectrum of Ce(IV) chelate shows two bands at 294 nm (34013cm⁻¹) and 363nm (27548 cm⁻¹) due to charge transfer transition and an octahedral geometry was suggested for this chelate¹⁵.

Table-2: Infrared band assignments (cm⁻¹) and electronic spectral data (nm, cm⁻¹) of Schiff base and their chelates

Ligand/ chelates	IR spectral data , cm ⁻¹				Electronic spectral data,(nm,cm ⁻¹)
	v(OH) (H ₂ O)	v(C=N)	v(M -O)	v(M- N)	
L; (C ₁₆ H ₁₆ N ₂ O ₂)	3430	1601	-	-	294 (34014), 329 (30395)
[ZrO (L)(H ₂ O)] 3H ₂ O	3413	1617	663	457	294 (34013), 363 (27548)
[La (L)(OH)(H ₂ O)]].H ₂ O	3397	1604	656	454	293 (34129), 360 (27778)
[Ce (L)(OH) ₂] 3H ₂ O	3544	1600	518	424	294 (34013), 363 (27548)

¹HNMR spectra of the Schiff base and its Zr(IV) chelate: The ¹HNMR spectral data of the 2-[(4-[(Z)-1-(2-hydroxyphenyl) ethylidene]hydrazonoethyl)phenol in DMSO solvent exhibits two doublet signals of the substituted phenyl ring in the range of 7.596-7.784ppm, and the other signal at 12.899 ppm due to phenolic -OH protons in the Schiff base. Moreover, the signal at 2.533 ppm is assigned to the proton of -CH₃ group¹⁶. The ¹HNMR spectra of the Schiff base and its diamagnetic Zr(IV) chelate were recorded in d₆-DMSO solvent at room temperature as shown in figures-7& 8). In comparison to the ¹HNMR spectral data of the Schiff base and its chelate; [ZrO(L)(OH₂)]₃H₂O, the mode of coordination between the Schiff base and metal ions was clarified, showed two doublet signals of the substituted phenyl ring are obtained in range 7.756-7.789ppm is assigned to doublet two protons of aromatic ring of the proposed chelate have resonated. Also the signal of -OH group at 12.899 ppm which is absent in the chelate, suggesting coordination of this group with the metal ions through deprotonated phenolic oxygen¹⁷.

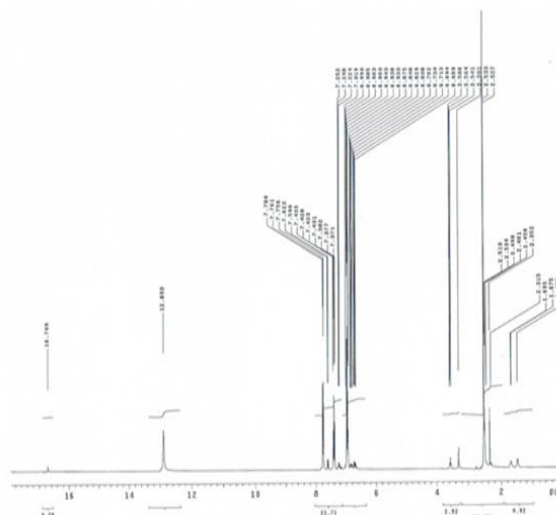


Figure 7: ¹HNMR spectrum of 2-[(4-[(Z)-1-(2-hydroxyphenyl) ethylidene]hydrazonoethyl)phenol.

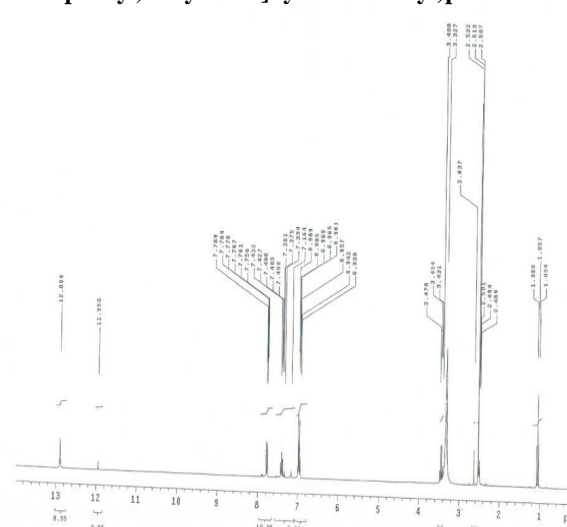
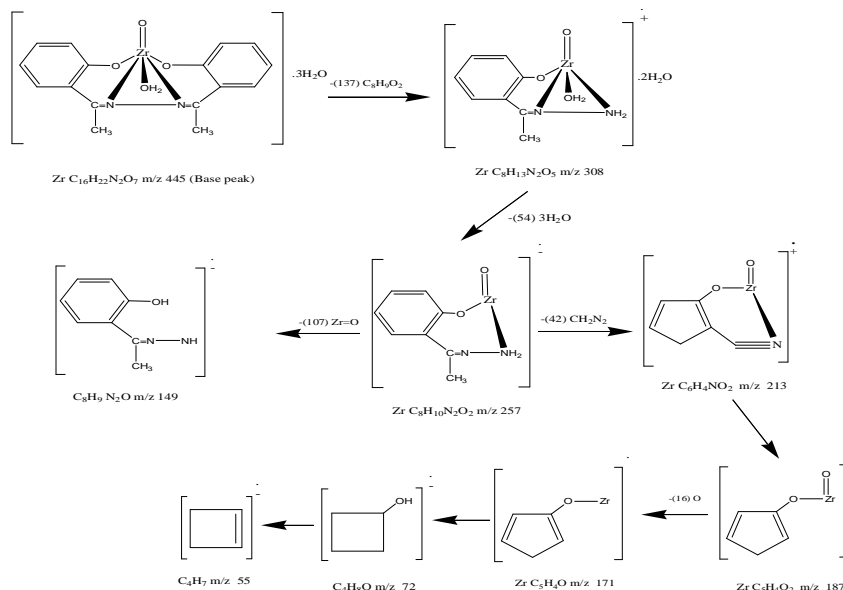
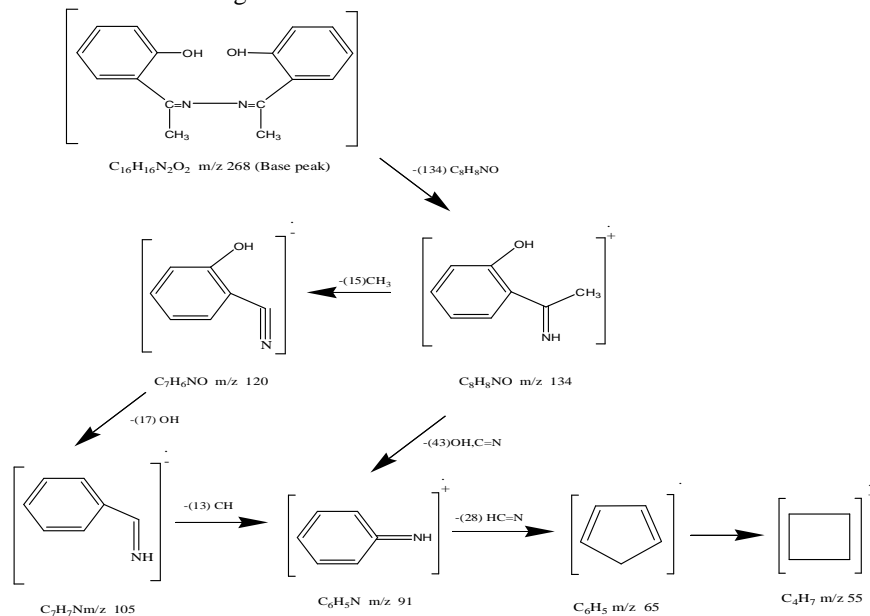


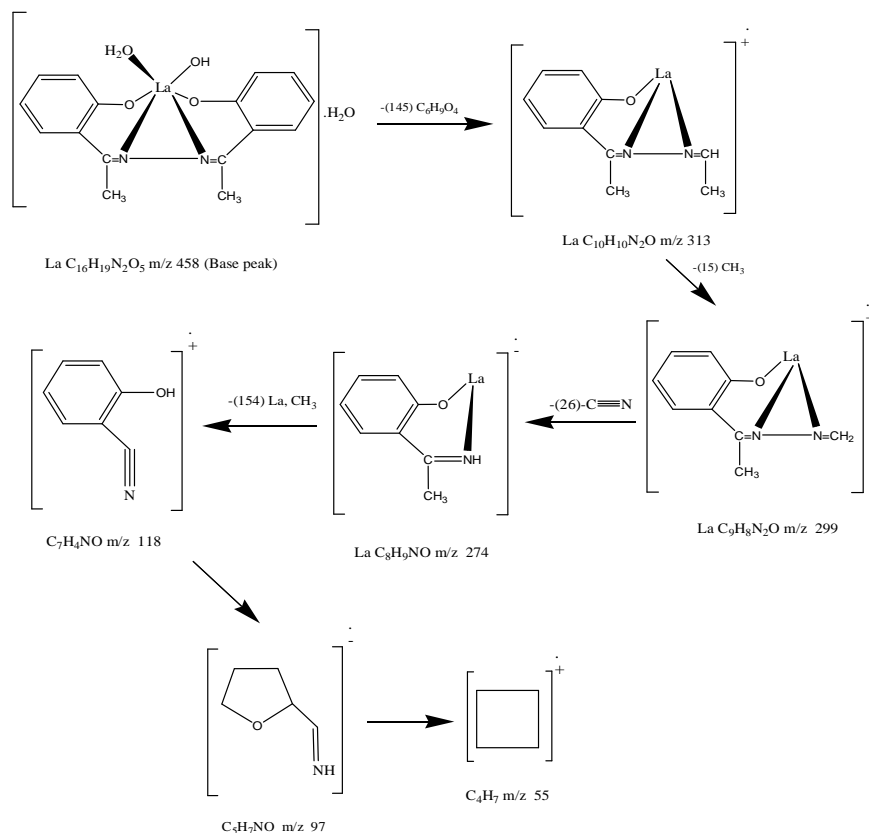
Figure 8: Proton magnetic resonance spectrum of the Zr(IV) chelate.

Mass spectra of Schiff base and Schiff base chelates: The mass spectrum of 2-[(4-[(Z)-1-(2-hydroxyphenyl) ethylidene]hydrazonoethyl)phenol (Fig.-9) exhibits a pattern characteristic of the target molecule. The peak at m/z= 268 (base peak) is attributed to the original molecular weight of the Schiff base. Fragment at m/z= 134 is due to C₈H₈NO ion. The fragments at m/z values; 120 and 105 suggesting various fragments and the second fragment at m/z= 91 is attributed to the loss of hydroxyl and cyano groups, respectively. Other important fragment at m/z= 65 is corresponding to the loss of second cyano group. The final fragment at m/z= 55 is analogous to the appearance of C₄H₃⁺ ion, (Scheme-1). The mass spectral fragmentation data of [ZrO(L)(OH₂)]₃H₂O chelate show molecular ion peak at m/z= 445 as shown in Fig.-10 is analogous to the original molecular weight of the chelate. Several fragmentations were observed in

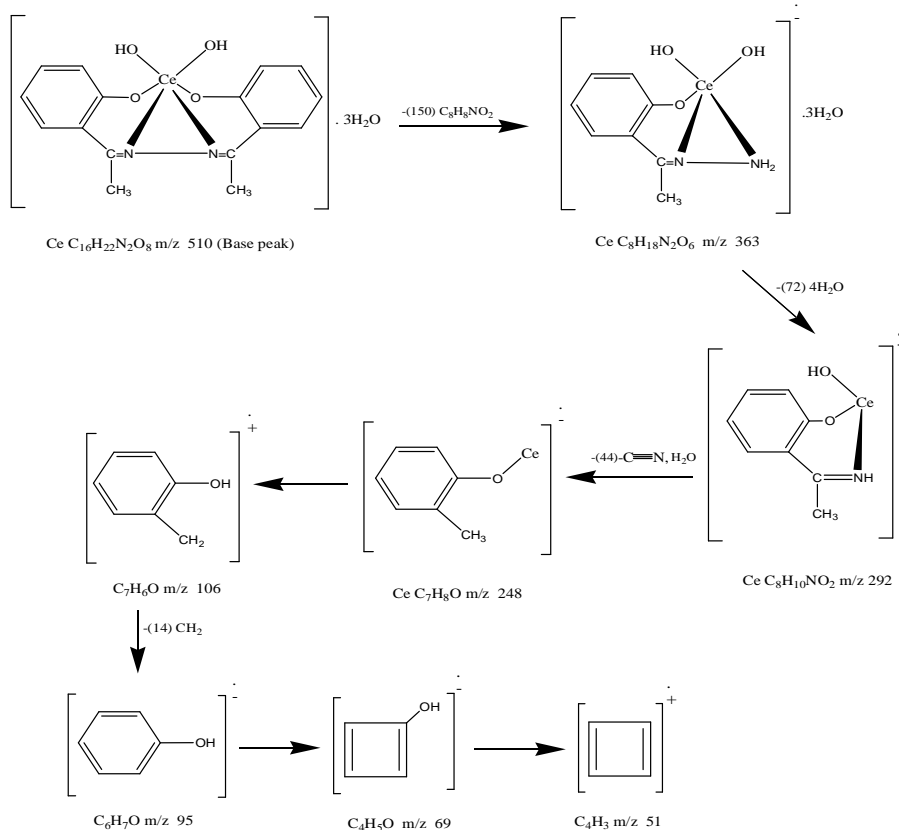
mass spectrum at m/z values; 308, 257, 213, 187 and 171, 149 which can due to the fragmentation pattern (Scheme-2). On the other hand for the same chelate, the most prominent peak observed at $m/z=72$ is corresponding to the loss of Zr(IV) oxide and cyano group and other important fragment at $m/z=55$ is assigned to the existence of the stable $C_4H_4^-$ ion. The mass spectral fragmentation of $[La(L)(OH)(H_2O)] H_2O$ chelate (Fig.-11) exhibit the molecular ion (M^+) peak at $m/z=458$ suggesting the monomeric nature of the chelate. The other important peaks of appreciable intensity have been observed at m/z values, 313, 299 and 274 due to the ion species after the successive fragmentation of different groups. Meanwhile; the m/z value of 118 is attributed to the loss of La(III) ion and methyl group from the chemical structure for the chelate. Other fragment at $m/z=97$

assigned to the loss of hydroxyl group and the final fragment at $m/z=55$ which is $C_4H_5^-$ ion, (Scheme-3). The mass fragmentations of $[Ce(L)(HO)_2] 3H_2O$ chelate show a characteristic molecular ion (M^+) peak at $m/z=510$, which corresponds to the molecular weight confirming the molecular formula of the chelate. The fragmentation of appreciable intensity have been observed at m/z values, 363, 292 and 248 due to various fragments (Scheme-4). Meanwhile; the m/z values at 106, 95 and 69 are corresponding to the loss of Ce(IV) ion, two azomethine groups, and other fragment at $m/z=51$ is assigned to the existence of the stable $C_4H_3^+$ ion, Scheme-4 and Fig.-12. The above fragmentations illustrate the formation of the Schiff base and the formation of the chelates in 1:1 [M:L] ratio.





Scheme 3: Mass spectral fragmentations of the La(III) chelate.



Scheme 4: Mass spectral fragmentations of the Ce(IV) chelate.

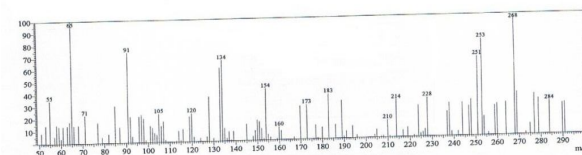
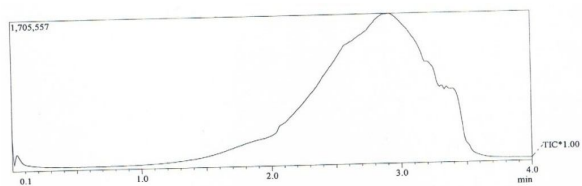


Figure 9: Mass spectrum of 2-[(4-[(Z)-1-(2-hydroxyphenyl) ethylidene]hydrazonoethyl)phenol].

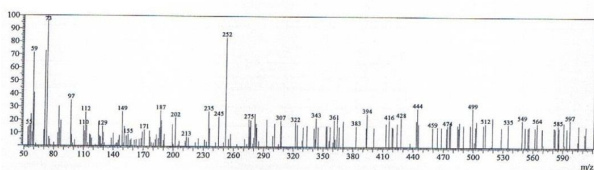
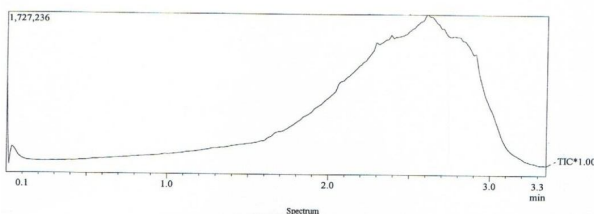


Figure 10: Mass spectrum of the Zr(IV) chelate.

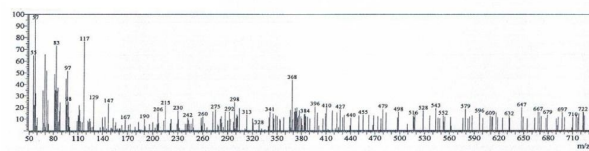
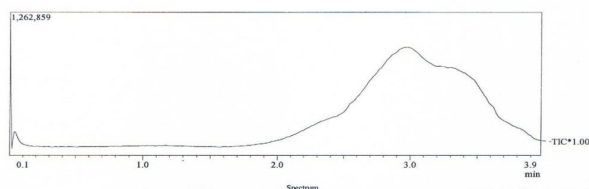


Figure 11: Mass spectrum of the La(III) chelate.

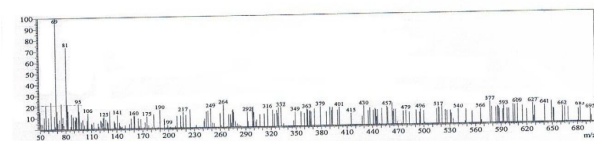
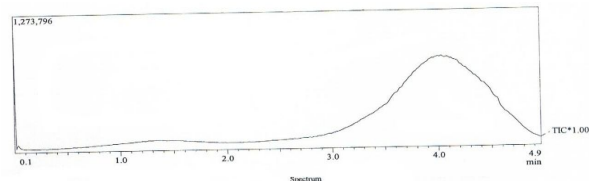
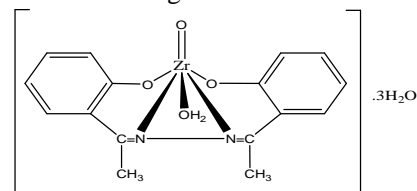
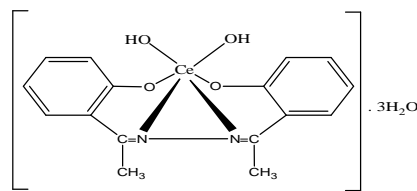
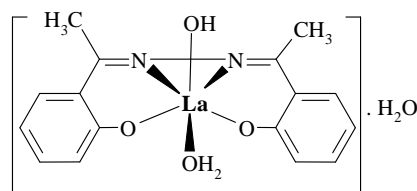


Figure 12: Mass spectrum of the Ce(IV) chelate.

CONCLUSION: In the present investigation, all the synthesized Schiff base chelates found to be mononuclear and characterized by different techniques basically on CHN analyses, molar conductivity, TGA, IR, electronic, $^1\text{H-NMR}$ and mass spectroscopies. The Schiff base coordinates to the metal ions in a bidentate form and an octahedral structure was suggested for all chelates as shown in Fig.-13.



[Zr (L)(OH₂)₂]. 3H₂O



[Ce (L) (OH)₂]. 3H₂O

Figure 13: Structures of the chelates

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