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Structural Elucidation of Newly Synthesized Schiff Base Zr(IV) and Ce(IV) Chelates Using Physicochemical Methods

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ABSTRACT: The tetradentate Schiff base chelates of Zr(IV) and Ce(IV) ions were synthesized by the reaction of the Schiff base which formed by the refluxing of 2-hydroxyacetophenone and 1,6-diaminohexane in ethanol solution with the mentioned metal salts. The structures of the Zr(IV) and Ce(IV) chelates were identified by several physiochemical techniques. The CHN elemental analyses showed the formation of chelates in 1:1 [M:L] ratio. The molar conductance values revealed that the synthesized chelates are non-electrolyte in nature. The thermogravimetric analysis was performed for Ce(IV) chelate to satisfy the presence of hydrated and coordinated water molecules in the chelate. The spectral data suggested the existing of an octahedral geometrical structure for the chelates under investigation.

Keywords: Schiff base; Metal chelates and Physicochemical methods.

INTRODUCTION

Schiff bases are an important class of ligands in coordination chemistry due to not only their useful physical and chemical properties and large number of reactions, but also have very wide use in industry and due to their interesting pharmacological as well as physiological activities. [1 & 2] In this regard, Schiff base metal complexes have played a key role to the gradual development of the Ln(III) coordination chemistry, ranging from pure synthetic work to modern physicochemical and biochemically relevant studies of metal complexes.[3] Schiff-base ligands with N, O donor sets have often been used since the Schiff-base ligands may assemble coordination architectures directed by the lanthanide (III) ions.[4] Complexes of La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Dy(III), Yb(III), and Lu(III) with 2-(N-*o*-hydroxyacetophenone) amino-3-carboxyethyl-4,5,6,7-tetrahydrobenzo[b]thiophene (HAAT) formed by the condensation of *o*-hydroxyacetophenone and 2-amino-3-carboxyethyl-4,5,6,7-tetrahydrobenzo [b] thiophene were synthesized and characterized on the basis of elemental analyses, molar conductance measurements, magnetic susceptibility data, UV-Visible, IR, and NMR spectral studies. The spectral data revealed that the ligand acted as a neutral tridentate coordinating to the metal ion through ONO donor sequence. A coordination number nine was proposed for the complexes.[5] The Co (II), Ni (II), Cu (II), Cr (III), Mn (III), Fe (III) VO (IV), Zr (IV) and UO_2 (VI) chelates of a Schiff base derived from the refluxing of 2-hydroxy-5-bromo acetophenone with ethylenediamine were synthesized and characterized on the basis of elemental analysis, infrared, molar conductance, magnetic susceptibilities, electronic spectra and theromogravimetric analysis[6 & 7].

The aim of this study is to synthesis and characterize of the Schiff base and its chelates with hydrated metal salts of Zr(IV) and Ce(IV).

MATERIAL AND METHODS

All the used chemicals and solvents were reagent grade materials from BDH or Aldrich including; 2-

hydroxyacetophenone, 1,6-diaminohexane, $ZrOCl_2.8H_2O$, $Ce(SO_4)_2.4H_2O$, C_2H_5OH, $CHCl_3$, DMSO and NH_4OH solution from Prolabo Reagents. The synthesized Schiff base and its chelates were subjected to CHN elemental analyses using Perkin-Elmer 2400 elemental analyzer. The molar conductivity of the chelates was measured in DMSO solvent using digital conductivity meter CMD 650, at Chemistry Department, Sebha University, Sebha, Libya. The thermogravimetric analysis of the Ce(IV) chelate was achieved using Schimadzu thermal analyzer (Japan). The weight loss of the sample was measured from ambient temperature upto $1000^0C/min$. The infrared spectra were obtained by KBr disc technique by using IFS-25DPUSR\IR spectrometer (Bruker) in the range of 4000-400 cm^{-1}. Proton nuclear magnetic resonance spectrum of the Zr(IV) chelate was recorded on Varian Gemini200-200MHz spectrometer using TMS as internal standard and D^6- DMSO as a solvent. The electronic spectra of the Schiff base and its Zr(IV) and Ce(IV) 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. All the mentioned analyses were done at Micro analytical center, Cairo University, Giza, Egypt.

Synthesis of the Schiff base: The Schiff base was synthesized by adding (0.02 mole; 2.72 g) of o-hydroxyacetophenone dropwise to 1,6-diaminohexane (0.01 mole; 1.16 g) in 50 mL of absolute ethanol. The reaction mixture was heated under refluxing for one hour. The obtained mixture was allowed to cool, filtered, recrystallized from ethanol and then dried under vacuum to give light lemon-yellow crystals (m.p. 157.0 - 159.9°C); yield 75.95 %.

Synthesis of the Schiff base chelates: The chelates were synthesized in a similar way by following method. To a hot solution of Schiff base (0.02 moles) in 25ml of ethanol, 0.01mole; 3.22 and 4.04 g of $ZrOCl_2.8H_2O$ and $Ce(SO_4)_2.4H_2O$ salts in same ratio of an ethanolic solution were and few drops of ammonia solution were added to adjust the pH at 8 until the precipitates were isolated. Then the reaction mixtures were refluxed for three hours extra. The obtained products were filtered, washed, dried and recrystallized from ethanol. The yield of the products was ranged from 69.57 to 84.66 % and their melting points are above 300 ^OC.

RESULTS AND DISCUSSION

The reaction between o-hydroxyacetophenone and 1, 6-diaminohexane in 2:1[ketone:amine) gives a Schiff base presented in figure 1:

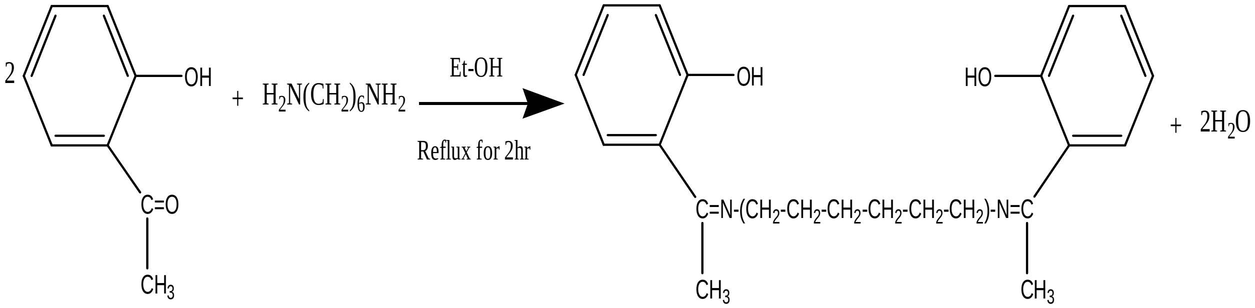


Figure 1: Structure of the Schiff base

CHN elemental analyses and molar conductivity: Analytical data and physical properties of the Schiff base and its chelates were shown in table 1. The chelates were colored, insoluble in common organic solvents but soluble in DMF and DMSO solvents. The theoretical CHN elemental analysis data of the Schiff base and its chelates are in good agreement with the found values and showed the formation of 1:1 [M: L] ratio. The molar conductance values of the chelates in 10^{-3}M DMSO solvent are 3.68 and 3.87 Ω^{-1} cm^2 mol^{-1}, respectively, which are relatively low, indicating their non-electrolytic nature.[8]

Table 1: Analytical data and some physical properties of the Schiff base and its chelates

Compound abbreviation	Empirical Formulae	Mol. Wt	Colour and Nature	m.p (^{0}C)	Yield %	Elemental analysis % Cal (Obs)			Λ
						C	H	N	
SB	$C_{22}H_{28}N_2O_2$	352.48	Light lemon-yellow	157 – 159	75.95	74. 97 (74.41)	8.01 (7.51)	7.95 (8.61)	-
[Zr (L) $(OH_2)_2$].H_2O	$C_{22}H_{32}N_2O_6$ Zr	511.49	Light creamy powder	>300	78.38	51. 89 (51.64)	6.73 (6.30)	5.75 (5.47)	3.68
[Ce (L)$(OH)_2$].3H_2O	$C_{22}H_{34}N_2O_7$ Ce	578.64	Dark canary powder	>300	84.66	45.67 (45.91)	5.92 (6.14)	4.84 (5.03)	3.87

Λ = Ω^{-1} cm^2 Mol^{-1}, Cal = Calculated values and M. Wt. = Molecular weight

Thermal analysis of Ce(IV) chelate: The thermogravimetric analysis techniques is used to determine the decomposition nature of the Ce(IV) chelate of the formula [Ce(L) $(OH)_2$].3H_2O. The sample was measured from the ambient temperature up to 1000 ºC using a heating rate of 10 ºC⁄ min. The Ce(IV) chelate decomposed in three stages; the first stage shows weight-loss of 10.30% at temperature range of 55 -305^{o}C which is consistent with the theoretical weight loss of 11.01%. This agreement confirms the existence of three hydrated water molecules out the coordination sphere of Ce(IV) chelate. The second stage; Further at 305 -756^{o}C has not shown any weigh-losses in the temperature which indicates the absence of lattice water as well as coordinated water. The loss in the weight can be dueto the decomposition of the Schiff base as carbonate or oxalate ion. The third stage decomposition. At 756^{o}C horizontal nature of the curve indicates the presence of thermally stable residual metal oxide. The percentage of residual metal oxide (CeO_2) at 39.26% is in good agreement to the theoretical value of 40.57%. The following scheme shows the thermal decomposition of the Ce(IV) chelate.

$$[Ce(L)(OH)_2].3H_2O \rightarrow [Ce(L)(OH)_2] + n(H_2O), \quad (55 – 305\ ^{\circ}C)$$
$$[Ce(L)(OH)_2] \rightarrow [Ce(L)] + nOH, \quad (305 – 756\ ^{\circ}C)$$
$$[Ce(L)] \rightarrow CeO_2\ (\text{Metal oxide})\ \ (\text{Above } 756\ ^{\circ}C)$$

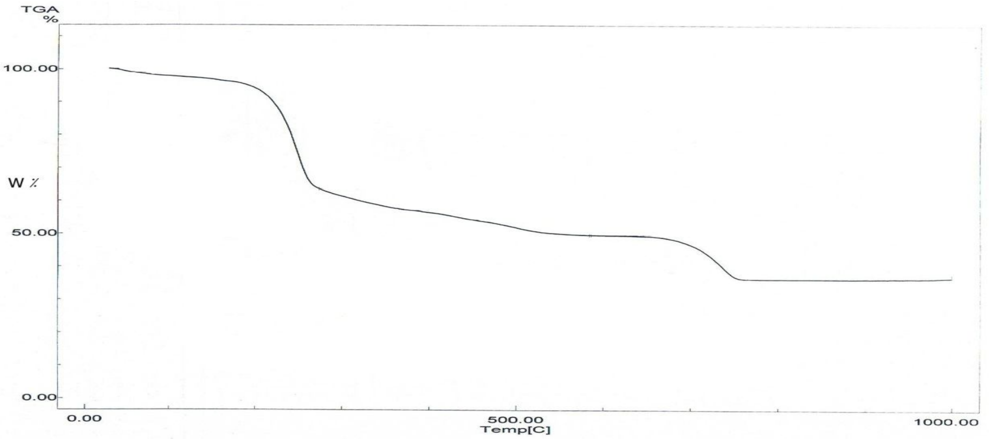


Figure 2: Thermogravimetric analysis of the Ce(IV) chelate

Infrared spectra: The infrared spectra provide valuable information regarding the nature of the functional group attached to the metal atom. The most important infrared spectral bands that provide conclusive structural evidence for the coordination of the ligand to the central metal ions are given in Table-2 and their spectra are shown in figures 3 and 4. It is observed that in all the chelates the metal ions are coordinated to the Schiff base through the azomethine group (-C=N) at 1610 cm^{-1}. The position of this group is changed to higher frequencies (1618-1633cm^{-1}) during the chelate formation indicating the participation of azomethine group in chelation towards the metal atom through the nitrogen atom. [9] The bands due to the intermolecular hydrogen bonded OH, appearing in the region 3415-3585 cm^{-1} in the chelates illustrated the involvement of this group in complexation through the oxygen atom.[10] New vibrations at 431-468 cm^{-1} and 567-614 which are not present in the free Schiff base are attributed to the existence of ν(M-O) and ν(M-N). [11 & 12] The spectrum of $[Zr(L)(H_2O)_2].H_2O$ chelate displays a band at 1140 cm^{-1} assigned to υ(M=O) vibration suggesting the involvement of this group as a coordinated band with Zr-O vibration. [13]

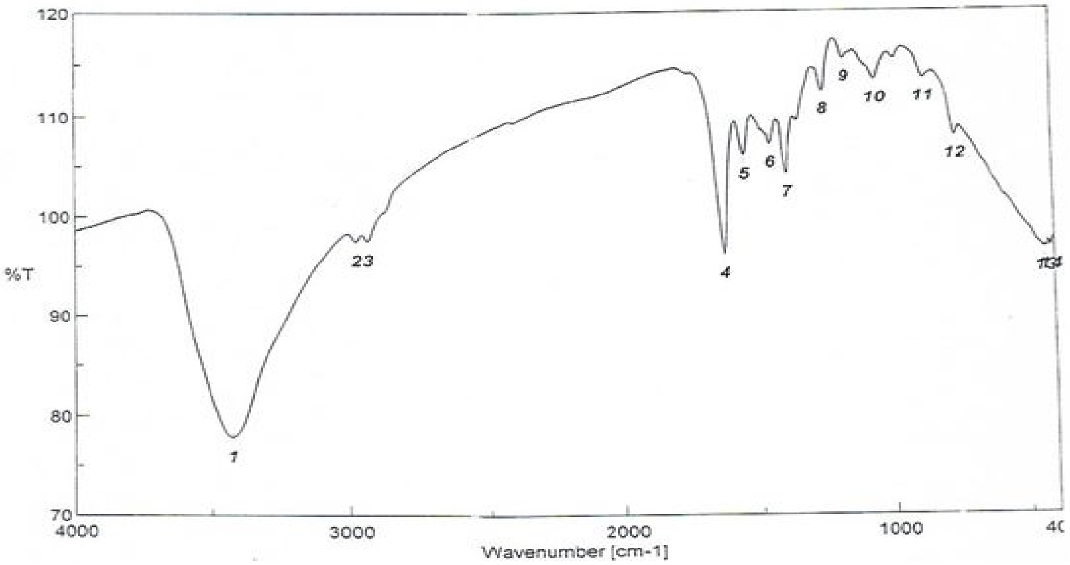


Figure 3: Infrared spectrum of Zr(IV) Chelate

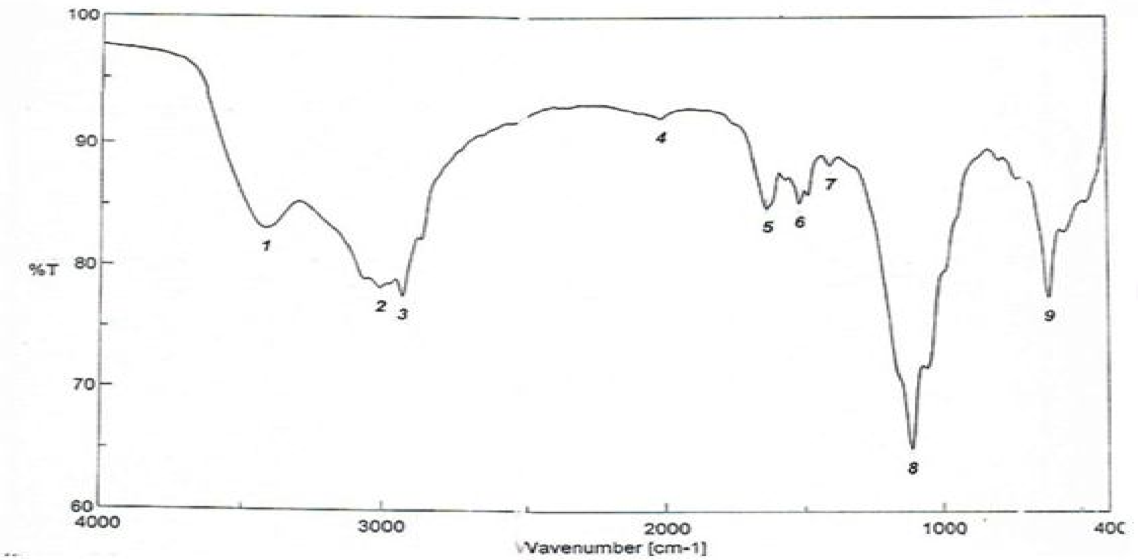


Figure 4: Infrared spectrum of Ce(IV) Chelate

Electronic spectra and magnetic moments of the chelates: The electronic spectra of all the chelates were recorded in DMSO solvent and their spectral data are given in Table-2. The obtained UV-Vis spectral data of the Schiff base exhibits two bands at 267 nm (37453 cm^{-1}) and 330 nm (30303 cm^{-1}) due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. [14] The spectrum of Zr(IV) chelate exhibits two bands at 313 nm (36496 cm^{-1}) and 274 nm (31948 cm^{-1}) assigned to charge transfer transitions and an octahedral geometry was proposed for this chelate. [15] In the present study, the Ce(IV) chelate shows the absorption band of 256 nm (39062 cm^{-1}) which can be assigned to the charge transition. This transition suggests an octahedral geometry for the chelate. [16] The diamagnetic character of these chelates supports the geometrical structure which is obtained from the electronic spectral data.

Table-2: Infrared band assignments (cm^{-1}) and electronic spectral data (nm, cm^{-1}) of Schiff base and its chelates

Comp.	***ν*(OH)**	***ν*(C=N)**	***ν*(M-O)**	***ν* (M-N)**	**nm (cm^{-1})**
SB	3437	1610	-	-	**267** (37453), **330** (30303)
$[Zr(L)(OH_2)_2].H_2O$	3426	1618	612	468	**274** (36496), **313** (31948)
$[La (L)(OH_2)_2]. 2H_2O$	3585	1633	567	433	**258** (38759), **318** (31446)
$[Ce(L)(OH)_2].3H_2O$	3415	1623	614	431	**256** (39062)

^{1}HNMR spectrum of the Zr(IV) chelate: ^{1}HNMR spectral studies of the Schiff base (Figure 5) display multiplet signals at 6.764 -7.282 ppm corresponding to aromatic protons and at 7.628 ppm is attributable to the azomethine (-C=N) proton. Strong signals at 12.368 ppm assignable to phenolic -OH group of the Schiff base.[17] In Zr(IV) metal chelate (Figure 6), the spectrum shows the disappearance of -OH group indicating the participation of this group in complexation with the metal ion.

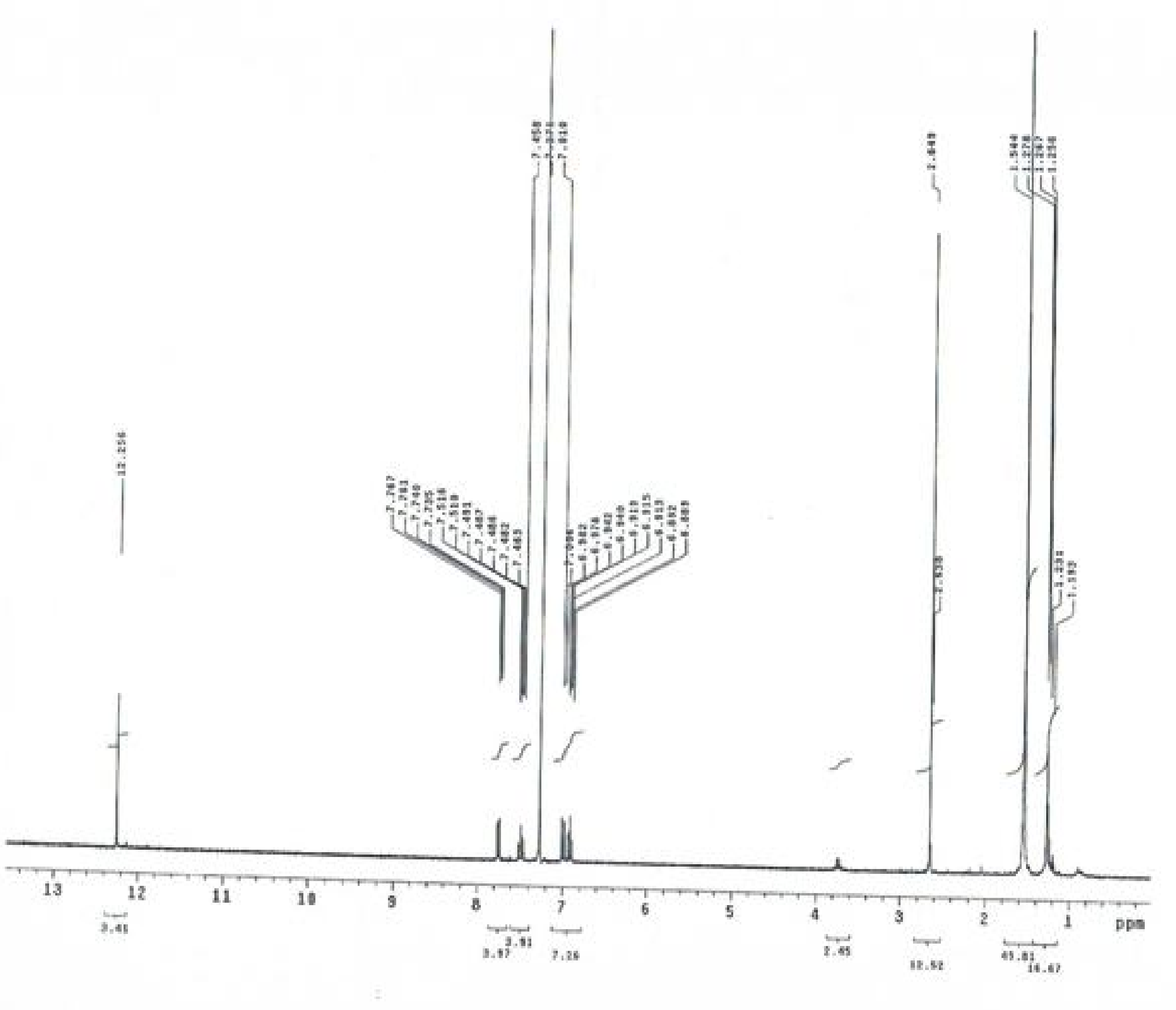


Figure 5: Proton nuclear magnetic resonance spectrum of the Schiff base

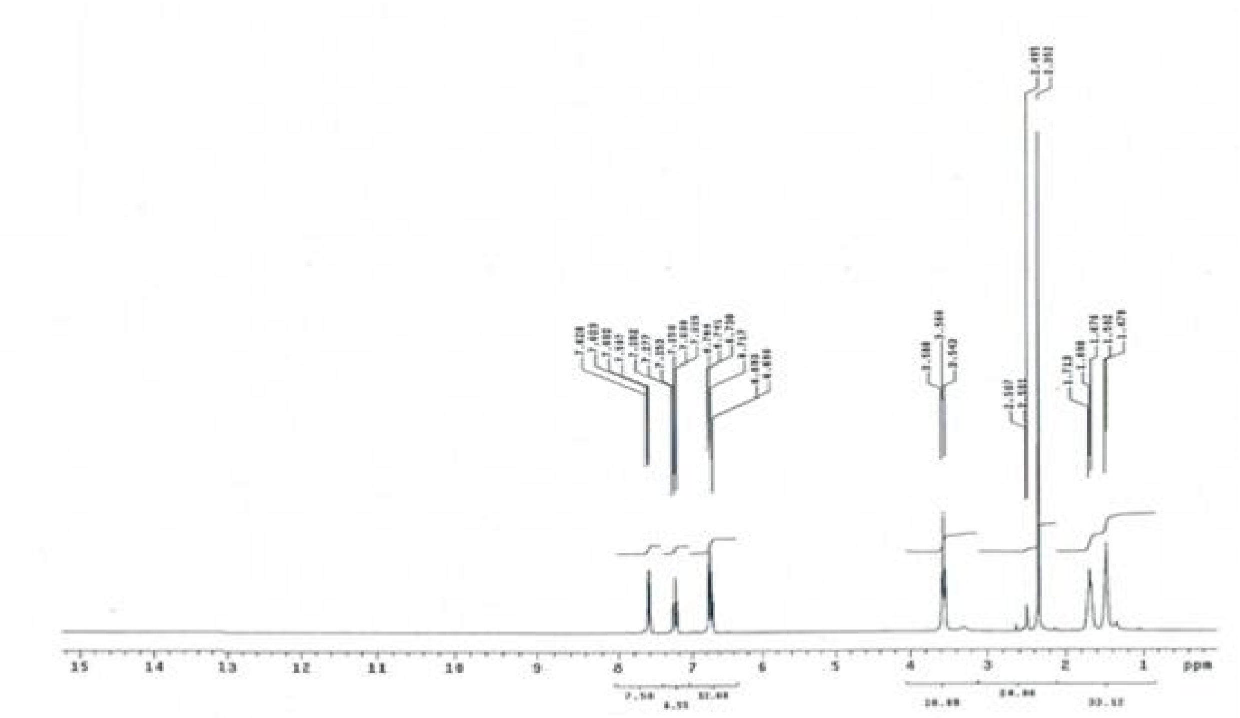


Figure 6: Proton nuclear magnetic resonance spectrum of the Zr(IV) chelate

Mass spectra of Schiff base and its chelates: The electron impact mass spectra of Schiff base and its chelates were recorded and investigated at 70 eV of electron energy. The mass spectra give additional information about the analyzed species. The mass spectral features of the Schiff base (Figure 8) was described by base peak as well as molecular ion peak that agreeing with the m/z value of 352 (Figure 7), which matched with the original molecular weight of the Schiff base ($C_{22}H_{28}N_2O_2$). Its fragmentation pattern is shown in (Scheme 1). Several fragment peaks observed in the mass spectrum at m/z 216, 188, 136, 107and 91 (see scheme 1). The final fragment at m/z = 55 is analogous to the appearance of $C_4H_7^-$ ion. In the chelates; the mass spectrum of the chelate $[Zr(L)(OH_2)_2].H_2O$ (Figure 8) shows a peak at m/z 511 suggesting the existing of the chelate in monomeric form. The same spectrum exhibits a fragment at m/z 340 is due to the loss of one coordinated water molecule from the chelate. Also it shows a series of peaks at m/z 312, 259, 226, 276 and 211(Scheme 2) corresponding to various fragments. The most prominent fragment observed at m/z 91 attributed to C_6H_5N ion. Meanwhile, the fragment at m/z 65 due to the loss cyano group and the final fragment at m/z 52 is analogous to $C_4H_3^+$. The m/z value at 579 corresponds to $[Ce(L)(OH)_2].3H_2O$ chelate (Figure 9), which suggests the monomeric nature of the chelate, thus confirming the proposed formula. The spectrum of the chelate shows a series of peak at 400, 305, 262, 232 and 223 (Scheme 3) due to various fragments. Meanwhile; the value of 83 corresponds to cerium (IV) ion. The value at m/z 66 assigned to the loss of hydroxyl group and the final fragment at m/z 51 which is $C_4H_3^+$.

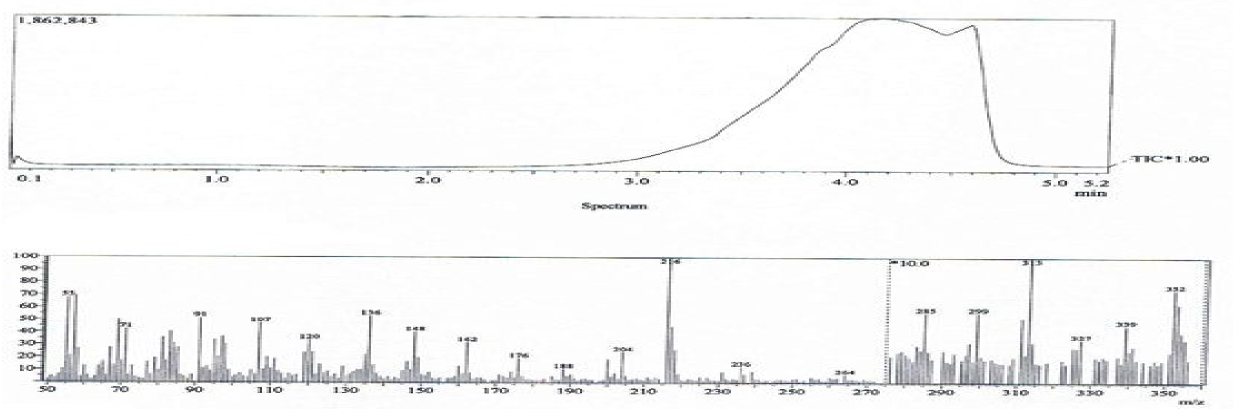
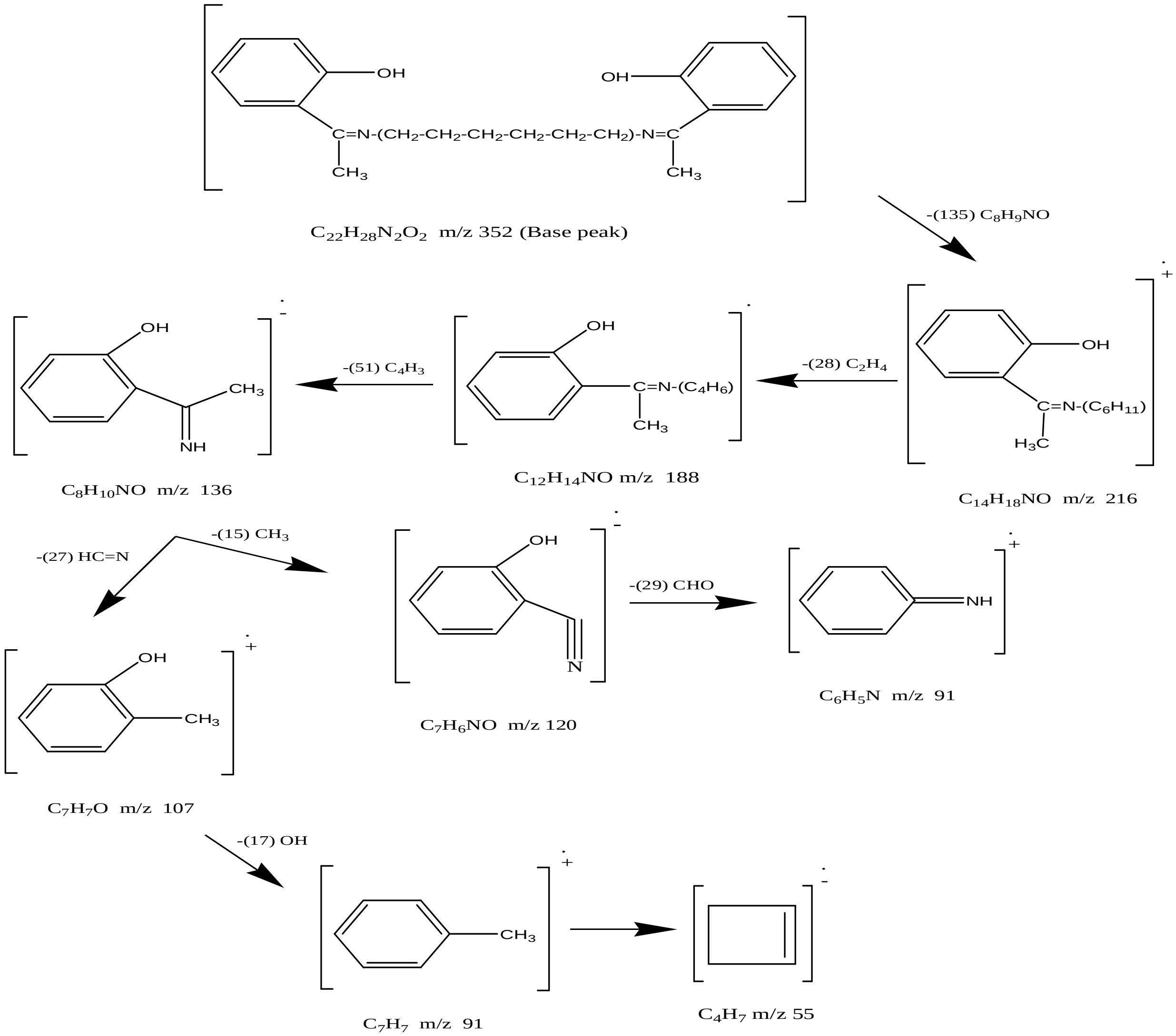


Figure 7: Mass spectrum of the Schiff base



Scheme 1: Mass fragmentation of the Schiff base

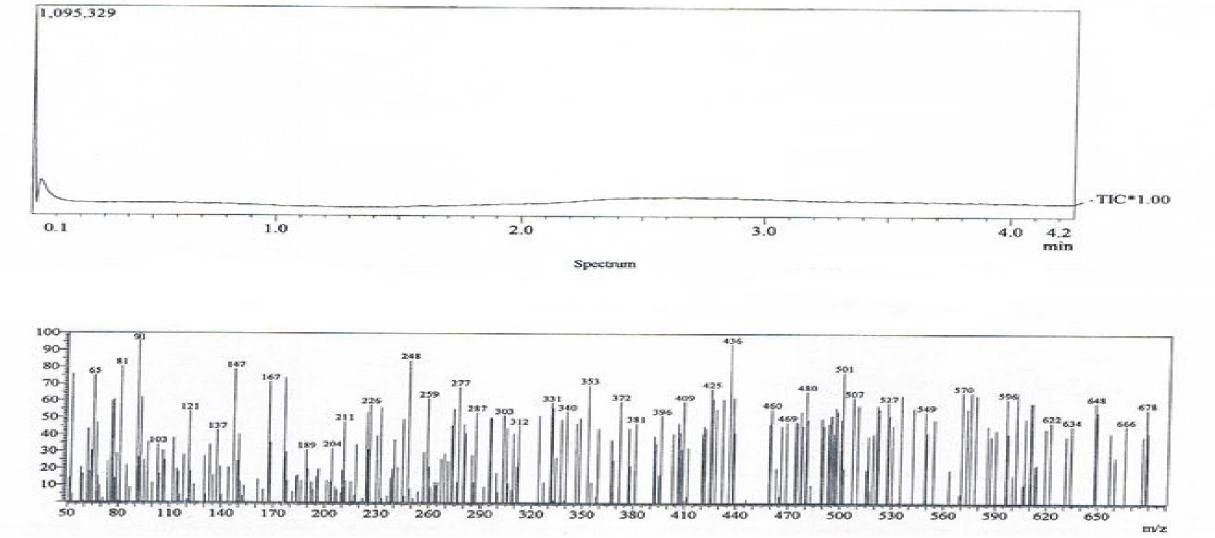
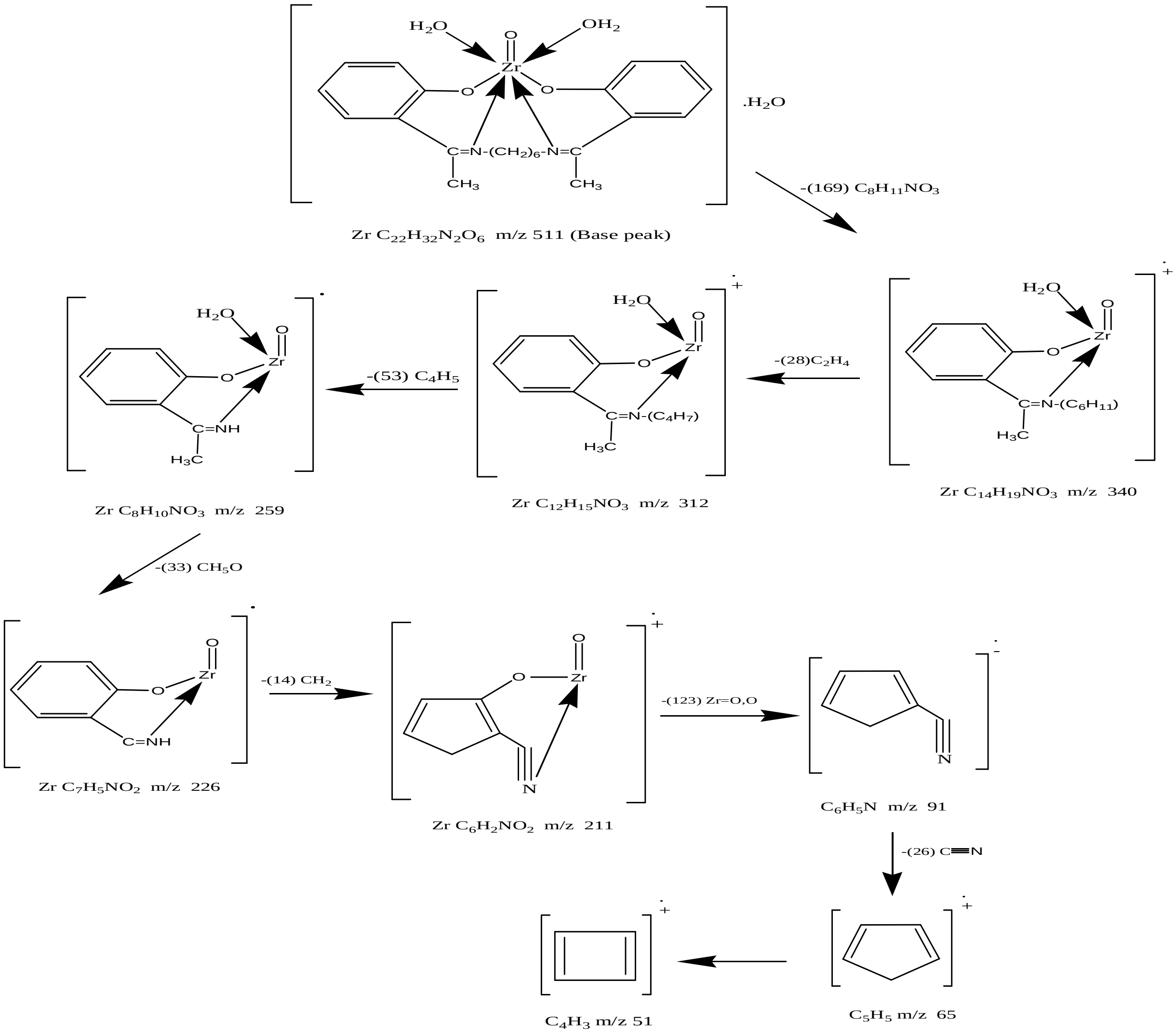


Figure 8: Mass spectrum of the Zr(IV) Chelate



Scheme 2: Mass spectral fragmentations of the Zr(IV) Chelate

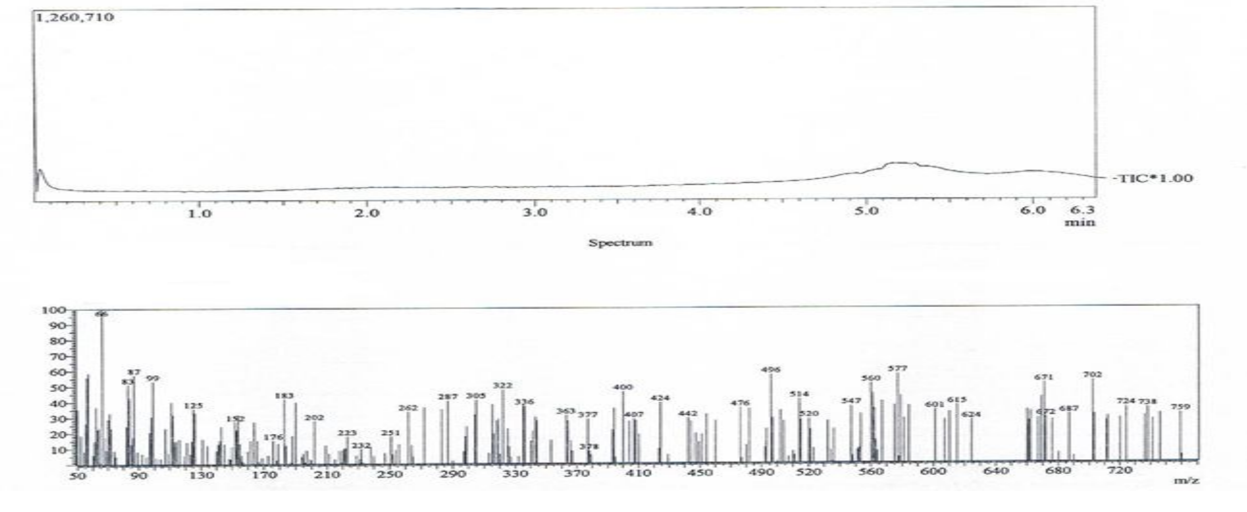
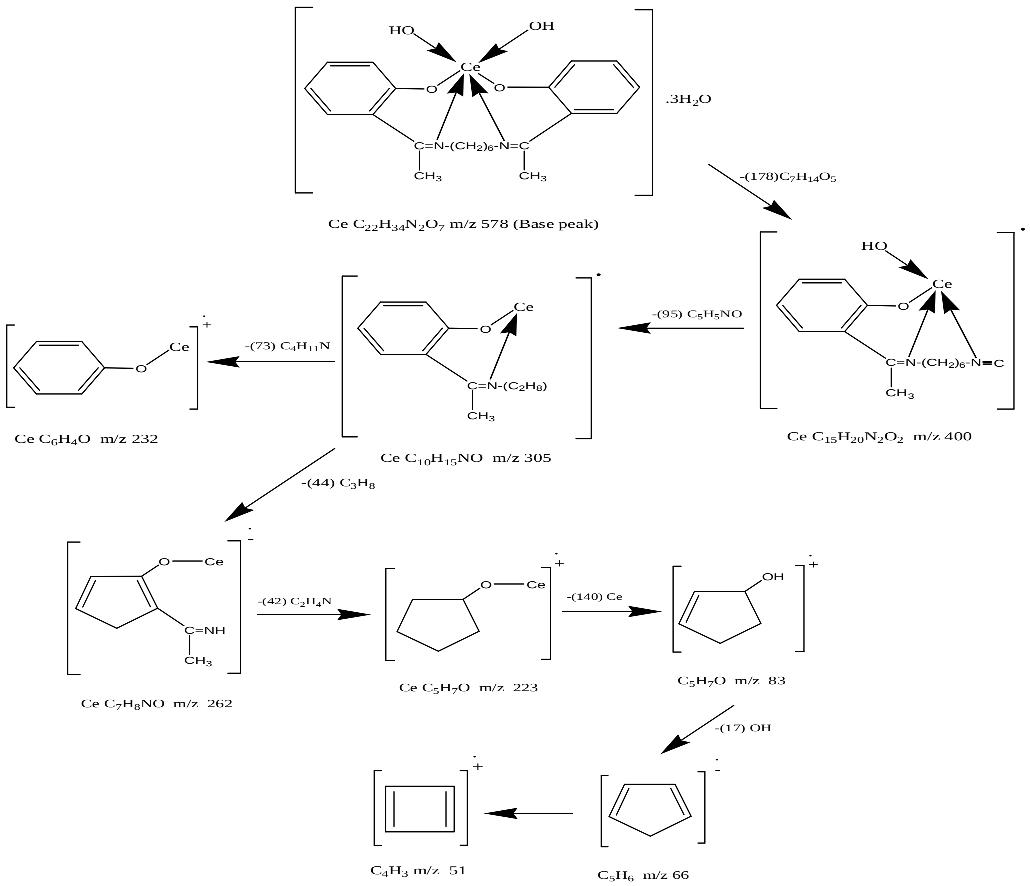


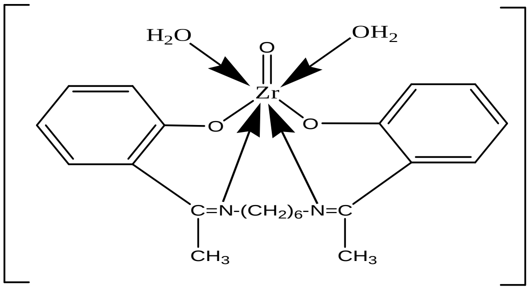
Figure 9: Mass spectrum of the Ce(IV) Chelate



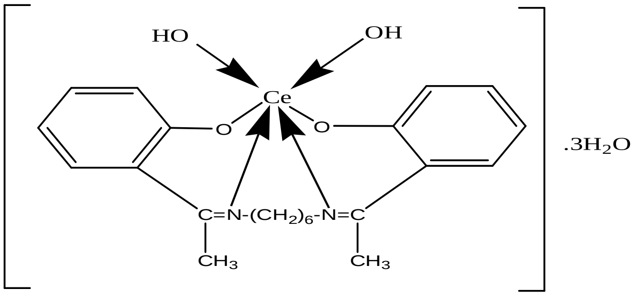
Scheme 3: Mass spectral fragmentations of the Ce(IV) Chelate

CONCLUSION

In this study, we have explored the synthesis and coordination chemistry of some mononuclear chelate. This is a neutral ligand, with behaves as a dibasic tetradentate species upon chelation with the involvement of phenolic oxygen and the nitrogen atoms of the azomethine (-C=N-) group in coordination for all the chelates. The newly synthesized Schiff base and its chelates have been confirmed by the analytical data, molar conductance measurements and thermogravimetric analysis infrared, electronic, ^{1}HNMR and mass spectroscopy. Based on the analytical and spectral studies, an octahedral geometry was proposed for the chelates. From the mentioned physiochemical analyses, the suggested structures were shown below:



[Zr (L)(OH$_2$)$_2$].H$_2$O



[Ce(L)(OH)$_2$].3H$_2$O

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