

Research Article

Preparation, Spectroscopic Investigation and Biological evaluation of Schiff's base La(III), Zr(IV) and Ce(IV) chelates

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ABSTRACT

M(III) and M(IV) chelates of La(III), Zr(IV) and Ce(IV) ions with Schiff base formed from the condensation of *o*-hydroxyacetophenone and 2,2'.diamino.diethylene were prepared and investigated by several tools, such as, CHN elemental analyses, molar conductivity, infrared, electronic and mass spectral studies. On the basis of these analyses, an octahedral geometry was proposed for all chelates. The Schiff base and metal chelates were tested against a strain of Gram +ve bacteria (*Lactobacillus fermentum* & *Streptococcus faecalis*), Gram-ve bacteria (*Escherichia coli* and *Salmonella Kentucky*), and fungi (*Aspergillus niger* and *Fusarium solani*). The antimicrobial results also indicate that the metal chelates are better antimicrobial agents as compared to the Schiff bases with standard.

Keywords: Schiff's base, *o*-hydroxyacetophenone, 2,2'.diamino.diethylene, chelates.

INTRODUCTION

Acetophenone compound has a good ability to form several complexes with transition and non-transition metal ions¹. Many Schiff bases and their chelates have been widely studied because of their biological and industrial applications². Some transition metal complexes of 2-1-[(E)-6-[(E)-1-2(2-hydroxyphenyl)ethylidene] aminoethylidene) aminoethylphenol were synthesized and characterized by physicochemical studies and an octahedral geometry was suggested for all complexes. The synthesized Schiff base and its complexes were screened against some pathogenic bacteria³. The complexes of Co(II), Ni(II) and Cu(II) with the Schiff base derived from salicylaldehyde and 2-aminophenol or 2-aminobenzoic acid were synthesized and characterized by using several different tools, in particular; CHN elemental analyses and spectral techniques⁴. Fifteen lanthanide(III) complexes of Schiff base formed from 2-amino-4,6-dimethylbenzothiazole with 2,5-dihydroxyacetophenone, pyridine-2-aldehyde were synthesized and characterized on the basis of physicochemical studies viz. elemental analysis and spectral studies. All of the representative Schiff bases and their complexes were also screened for the antimicrobial activity against some pathogenic bacteria and fungi⁵. A Schiff base derived from 2-amino-4-methylphenol with *o*-hydroxyacetophenone and its Ti(IV) and Zr(IV) complexes were synthesized and characterized on the basis of elemental analysis, spectral studies and X-ray diffraction. The analytical data indicate that the metal to ligand ratio in the complexes were 1:1 and the X-ray diffraction studies indicate monoclinic crystal system for all complexes. The synthesized Schiff base and its complexes have been evaluated for their antimicrobial activity⁶.

In this paper, we have described the synthesis, physicochemical characterization and biological activities of La(III), Zr(IV) and Ce(IV) chelates with ligand derived from *o*-hydroxyacetophenone with 2,2'.diamino.diethylene. The reaction was carried out by condensation method. The Schiff' base ligand system coordinates with the metal ions in a bidentate manner through the oxygen and azomethine nitrogen. The formed metal chelates may be used as precursors for the synthesis of new compounds. Some of which they may exhibit interesting physical and chemical properties and potentially useful biological activities.

EXPERIMENTAL SECTION

Chemicals and reagents

All chemicals and reagents used in this study were analytical reagent grade of BDH and Aldrich including La(NO₃)₃.6H₂O, ZrOCl₂.8H₂O and Ce(SO₄)₂.4H₂O, NH₄OH, C₂H₅OH, CHCl₃, DMF, DMSO,

o-hydroxyacetophenone and 2,2'.diamino.diethylene. Distilled water were used through the experimental.

Preparation of Schiff base

The Schiff base (SB) under investigation was prepared by mixing an ethanolic solution (25 mL) of 0.02 mole; 2.72g) of *o*-hydroxyacetophenone with the same amount of the solvent of 0.01 mole; 1.03 g) of 2,2'.diamino.diethylene under reflux for two hours. The obtained product was then removed from the reaction mixture by filtration, washed several times with hot ethanol until the filtrate becomes clear and dried in desiccator over anhydrous calcium chloride. Obtained product is dried and stored in a sample glass bottle. The color of the product was pale lemon-yellow precipitate with 65.30% yield and its melting point is in the range of 115-117°C.

Preparation of Schiff base chelates

The chelates were prepared by mixing of 50 mL ethanolic solution of the Schiff base (0.01 mole; 3.39 g) with the same amount of the metal salts (0.01 mole; 4.33, 3.22 and 4.04g) of La(NO₃)₃.6H₂O, ZrOCl₂.8H₂O and Ce(SO₄)₂.4H₂O. If the chelates did not isolated, few drops of ammonia solution were added to adjust the pH = 7-8. The isolated mixtures were refluxed with continuous stirring for extra four hours, then collected and washed several times with hot ethanol until the filtrates become clear. The chelates were dried in desiccators over anhydrous calcium chloride. Obtained product is dried and stored in a sample glass bottle. The yields of the chelates were 47.60, 52.00 and 78.10%, respectively, and their melting points are above >300°C.

Physical measurements

The prepared Schiff base compound was subjected to CHN elemental analyses using Perkin-Elmer 2400 elemental analyzer, infrared spectra were obtained by KBr disc technique by using IFS-25DPUSRIR spectrometer (Bruker) in the range of 4000-400 cm⁻¹, proton nuclear magnetic resonance spectrum of the Schiff base was recorded on Varian Gemini 200-200MHz spectrometer using TMS as internal standard and D⁶ DMSO as a solvent. The electronic spectra of the Schiff base and its La(III), 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. 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 were done at Micro analytical center, Cairo University, Giza, Egypt.

Biological Assay

The *in vitro* antimicrobial screenings of the solvent, free ligand, metal precursors and the new La(III), Zr(IV) and Ce(IV) metal chelates were tested for their effect on certain human pathogenic bacteria and fungus by disc diffusion method. Antimicrobial activity measurements strains were obtained from the culture collection, Department of Microbiology, Faculty of Science, Sebha University, Sebha-Libya. The ligand, metal precursors and their La(III), Zr(IV) and Ce(IV) chelates were stored at room temperature and dissolved in dimethylsulphoxide (DMSO). The Gram -ve bacteria (*Escherichia coli*, *Salmonella kentucky*, *Lactobacillus fermentum* and *Streptococcus faecails*) was carried out. Bacteria were grown in Mueller Hinton agar medium and incubated at 37 °C for 40 hrs followed by frequent subculture to fresh medium and were used as test bacteria. Fungi; (*Asperigillus niger*, *Fusarinm*) was grown in Sabourard Dextrose Agar medium were incubated at 27 °C for 60 hrs followed by periodic subculturing to fresh medium and was used as test fungus. Then the petriplates were inoculated with a loop full of bacterial and fungal culture and spread throughout the petriplates uniformly with a sterile glass spreader. To each disc, the test samples and reference antibiotic (ciprofloxacin/miconazole) were added with a sterile micropipette. The plates were then incubated at 35 ± 2 °C for 18-20 hrs for bacteria and at 27±1 °C for 18-20 hrs for fungus, respectively. Plates with disc containing respective solvents served as control. Inhibition was recorded by measuring the diameter of the inhibitory zone after the period of incubation. [7] The diameter of the inhibition zone (mm) was measured and the activity index was also calculated by using the following Eq.1:

$$\text{*% Activity index} = C / T \times 100 \text{ ----- Eq.1}$$

Where, AI% = Activity index

C = diameter of zone inhibition of micro- organisms in check

T= diameter of the disc (The zone of inhibition was measured after 18-20 hr), ciprofloxacin(5µg/mL) and miconazole(25µg/mL) was used as positive standard.

RESULTS AND DISCUSSION

The reaction between *o*-hydroxyacetophenone and 2,2'.diaminodiethylene gives one compound in 2:1 [*o*-hydroxyacetophenone: 2,2'.diamino.diethylene] ratio which is a Schiff base as shown in the following chemical reaction:

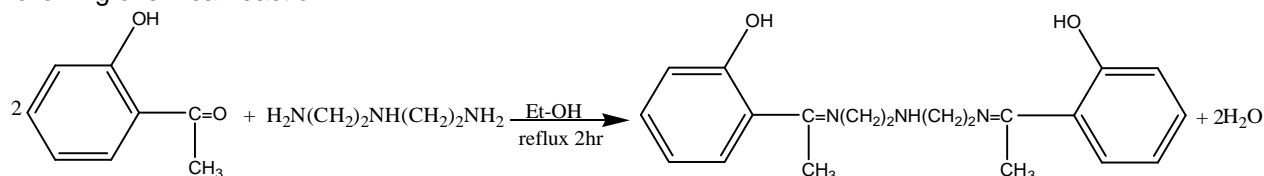


Fig. 1: Structure of Schiff base ligand (SB)

Elemental analyses and Molar conductivity

The CHN elemental analyses show that the calculated values are in a good agreement with found data (Table 1). The CHN elemental analysis data together with the non-electrolytic nature [8], in DMSO solvent suggest 1:1 [M:L] ratio.

Table 1: CHN analytical data and other physical properties of Schiff base ligand and its metal chelates

Comp. Empirical Formulae	Mol. Wt	Colour	m.p (°C)	Yield %	Elemental analysis%			Λm.	
					Cal	(Obs)			
						C	H	N	
SB C ₂₀ H ₂₅ N ₃ O ₂	339.44	Pale lemon-yellow	117.2	65.30	70.70 (67.90)	5.42 (5.72)	13.3 (13.1)	-	
[La(L)(OH)]2OH.2H ₂ O C ₂₀ H ₃₀ N ₃ O ₆ La	547.57	Pale White-creamy	>370	47.60	40.50 (41.00)	3.34 (3.37)	8.96 (8.84)	10.67	
[Zr(L)(OH) ₂]2OH. H ₂ O C ₂₀ H ₂₉ N ₃ O ₅ Zr	482.88	Light creamy	>370	52.00	42.00 (42.50)	1.85 (2.14)	4.15 (3.85)	7.26	
[Ce(L)(OH) ₂ .2H ₂ O] C ₂₀ H ₂₉ N ₃ O ₅ Ce	531.76	Pale brown-yellow	>370	78.10	40.20 (40.90)	3.93 (3.81)	10.6 (11.90)	1.94	

Λm=Ω-1 cm² Mol⁻¹, () Calculated values, and M.Wt = Molecular weight.

Infrared spectra

The infrared spectral data of the Schiff base and its La(III), Zr(IV) and Ce(IV) chelates were listed in table (2) and their spectra were shown in figures 2-5. The infrared spectral data of the Schiff base chelates exhibit broad bands in the range of 3424-3443 cm⁻¹ due to the existence of water molecules as hydrated and coordinated⁹. Whereas, the same spectra show three bands at 1630, 1616 and 1631 cm⁻¹, respectively, attributed to ν(C=N) vibration, the changing of these bands comparing to the Schiff base (1612 cm⁻¹) confirmed the involvement of this group in chelation through nitrogen atom¹⁰. The spectrum of the Zr(IV) chelate exhibits a band at 1028 cm⁻¹ indicating the existence of Zr=O group¹¹. New bands in the range of 537- 457 and 610-620 cm⁻¹ which are not present in the Schiff base are attributed to ν(M-N) and ν(M-O) vibrations¹², and the appearance of these vibrations support the participation of nitrogen and oxygen atoms of the OH and azomethine groups of the Schiff base in chelation process.

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

Comp.	IR spectral data, cm ⁻¹							Electronic spectral data, nm(cm ⁻¹)
	ν(OH)	ν(C=N)	ν(CH ₃)	ν(CH)	ν(CH ₂)	νM-O	ν M-N	
SB	3433	1612	1373	750	2905	-	-	265(37736), 322 (31056)
[La(L)(OH)]2OH.2H ₂ O	3443	1630	1331	843	2914	620	537	358 (27932)
[Zr(L)(OH) ₂].H ₂ O	3424	1616	1330	756	3043	610	468	320(31250),
[Ce(L)(OH) ₂].2H ₂ O	3432	1631	1429	794	2921	614	457	277(36101)

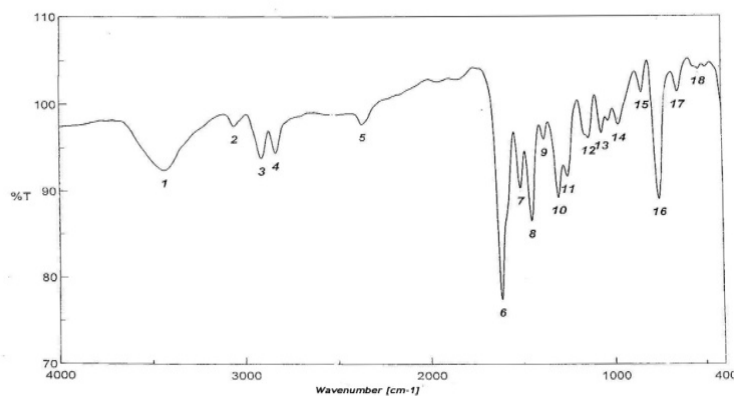


Fig. 2: Infrared spectrum of the Schiff base

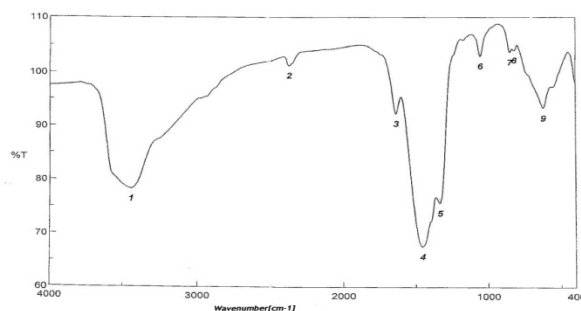


Fig. 3: Infrared spectrum of the La(III) chelate

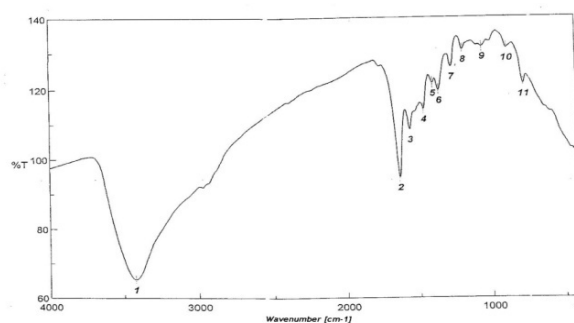


Fig. 4: Infrared spectrum of the Zr(IV) chelate

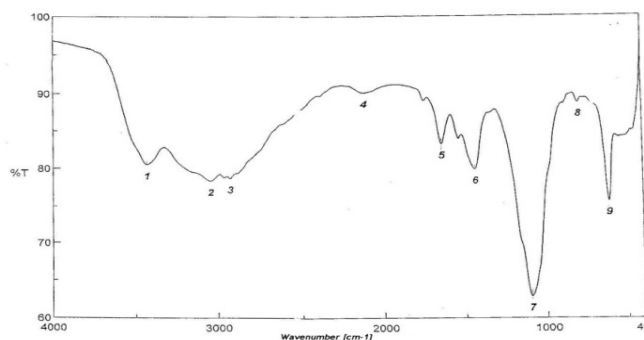


Fig. 5: Infrared spectrum of the Ce(IV) chelate

Electronic spectra of the Schiff base and its chelates

The electronic spectral assignments were listed in table 2 and their spectra were shown in figures 6-9. The electronic spectral results of the Schiff base show two bands at 265 nm (37736 cm^{-1}) and 322 nm (31056 cm^{-1}) due to $\pi \rightarrow \pi^*$ (Phenyl rings) and $n \rightarrow \pi^*$ ($-\text{C}=\text{N}$) transitions, respectively [13]. The electronic spectral data of La(III), Zr(IV) and Ce(IV) chelates were carried out in DMSO solvent. The octahedral chelates that contain a metal ion of d^0 electronic configuration are diamagnetic. The

spectrum of La(III), Zr(IV) and Ce(IV) chelates show bands (see table 2) attributed to charge transfer transitions [14,15]. The nature of the bands of the chelate confirms the existence of an octahedral geometry [16].

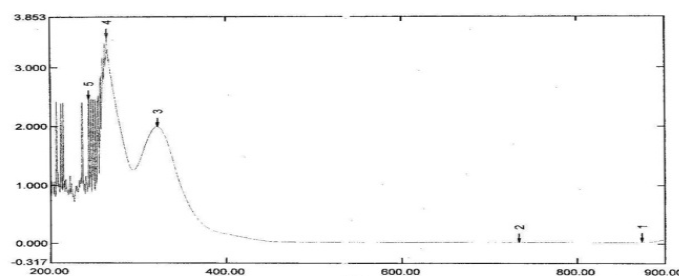


Fig. 6: Ultraviolet spectrum of the Schiff base

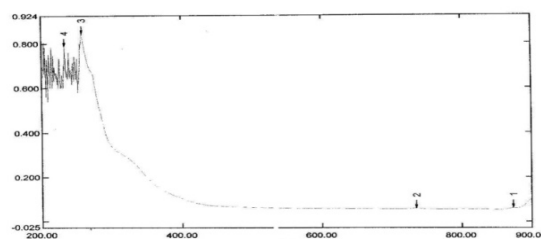


Fig. 7: Electronic spectrum of the La(III) chelate

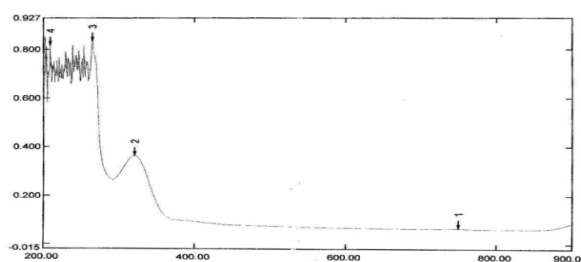


Fig. 8: Electronic spectrum of the Zr(IV) chelate

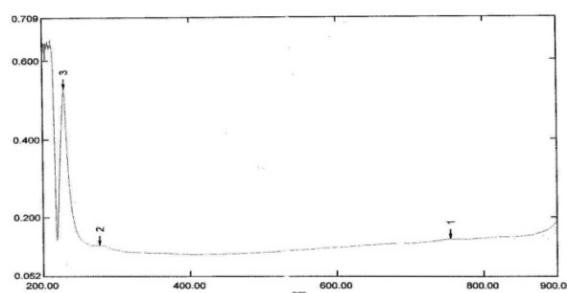


Fig. 9: Electronic spectrum of the Ce(IV) chelate

Mass spectra of Schiff base and its metal chelate

The mass spectral fragmentations of the Schiff base and its metal chelate are shown in schemes (1-4) and figures(10-14). The peak of Schiff base at $m/z = 339$ is attributed to loss of $C_{20}H_{25}N_3O_2$ from the original molecular weight. The peak at $m/z = 176$ which is in a good agreement with loss of $C_{10}H_{12}N_2O$ molecule from the original chemical structure. Whereas, the peak at $m/z = 119$ is analogous to the loss of methyl group from the compound. The loss of cyano group gives a peak at $m/z = 107$. The peak at $m/z = 91$ due to loss of hydroxyl group. The same spectrum shows a peak at $m/z = 71$ corresponding to loss of one carbon and eight hydrogen atoms. A peak at $m/z = 55$ is analogous to C_4H_7 ion. For Zr(IV) chelate, the spectrum exhibits a peak at $m/z = 480$ due to the original molecular

weight of the chelate. The peak at m/z 283 corresponding to the loss of two hydroxyl group and water molecular and the peak at m/z 191 due to the loss of Zr (IV) atom and oxy group from the chelate and peak at m/z 65 is assigned to the existence of a stable compound. Meanwhile second fragmentation which is C_5H_5 . The mass fragmentation of $[La(L)(OH)]_2OH \cdot H_2O$ chelate shows base peak at m/z 342 is analogous to the loss of water molecules, three hydroxyl group and $C_8H_{13}NO$ molecule from chemical formula of the chelate, La(III) ion, and other pack at m/z 65 analogous to C_5H_5 . For Ce(IV) chelate, The mass spectrum of cerium chelate exhibits peaks at m/z 314, 274, 69 and the final peak at m/z 55 is analogous to the appearance of C_4H_7 , these peaks attributed to loss of different atoms (see schemes 3). The above fragmentations illustrate the formation of the Schiff base and the formation of the chelates in 1:1 [M:L] ratio.

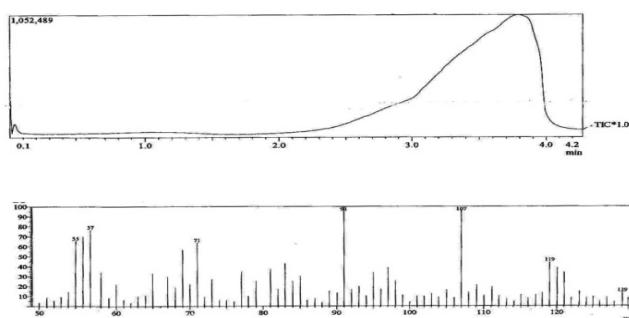
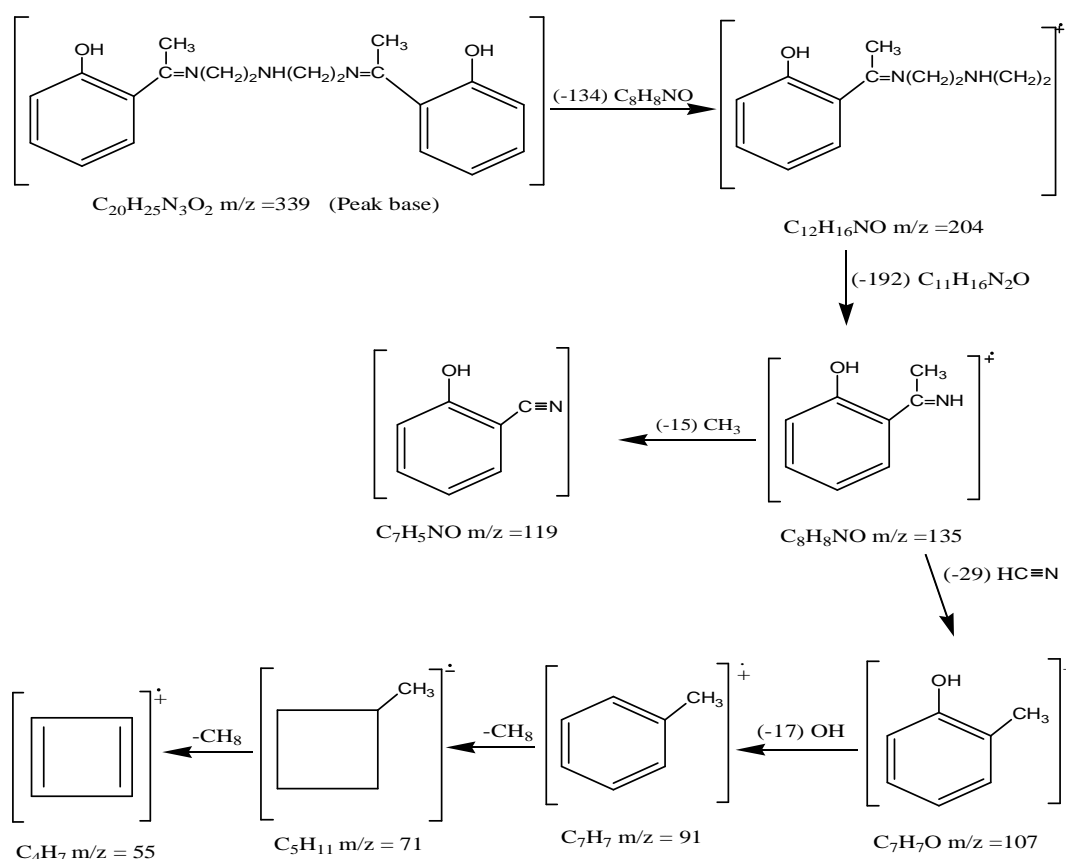


Fig. 10: Infrared spectrum of the Schiff base



Schemes. 1: mass spectral fragmentations of the Schiff base

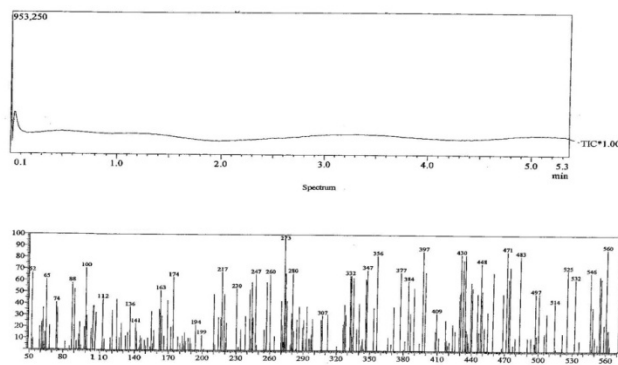
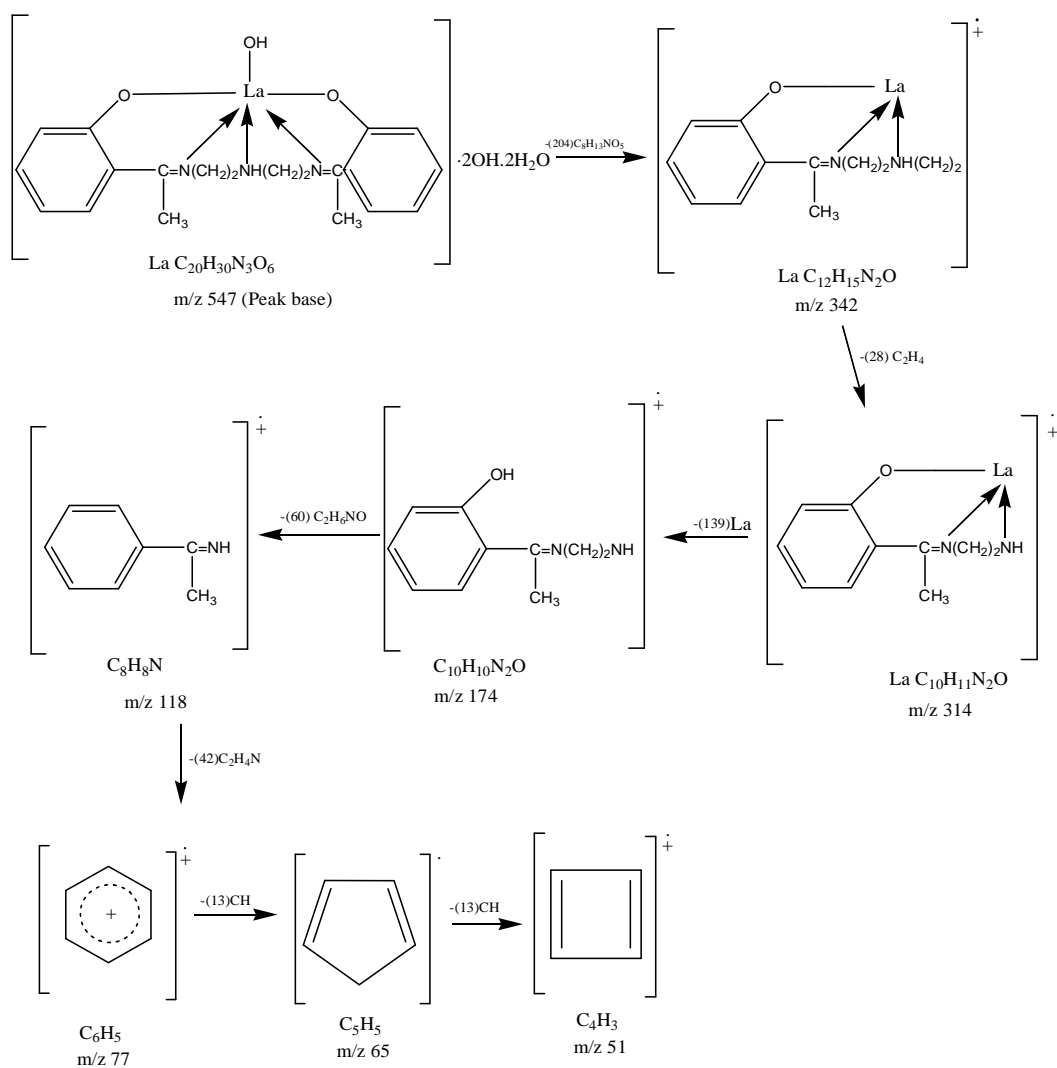


Fig. 11: Mass spectrum of the La(III) chelate



Schemes. 2: mass spectral fragmentations of the La(III) chelate

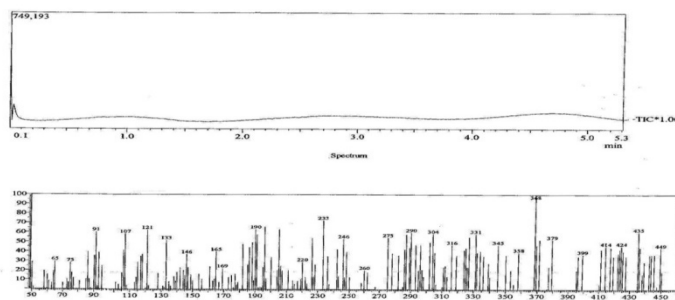
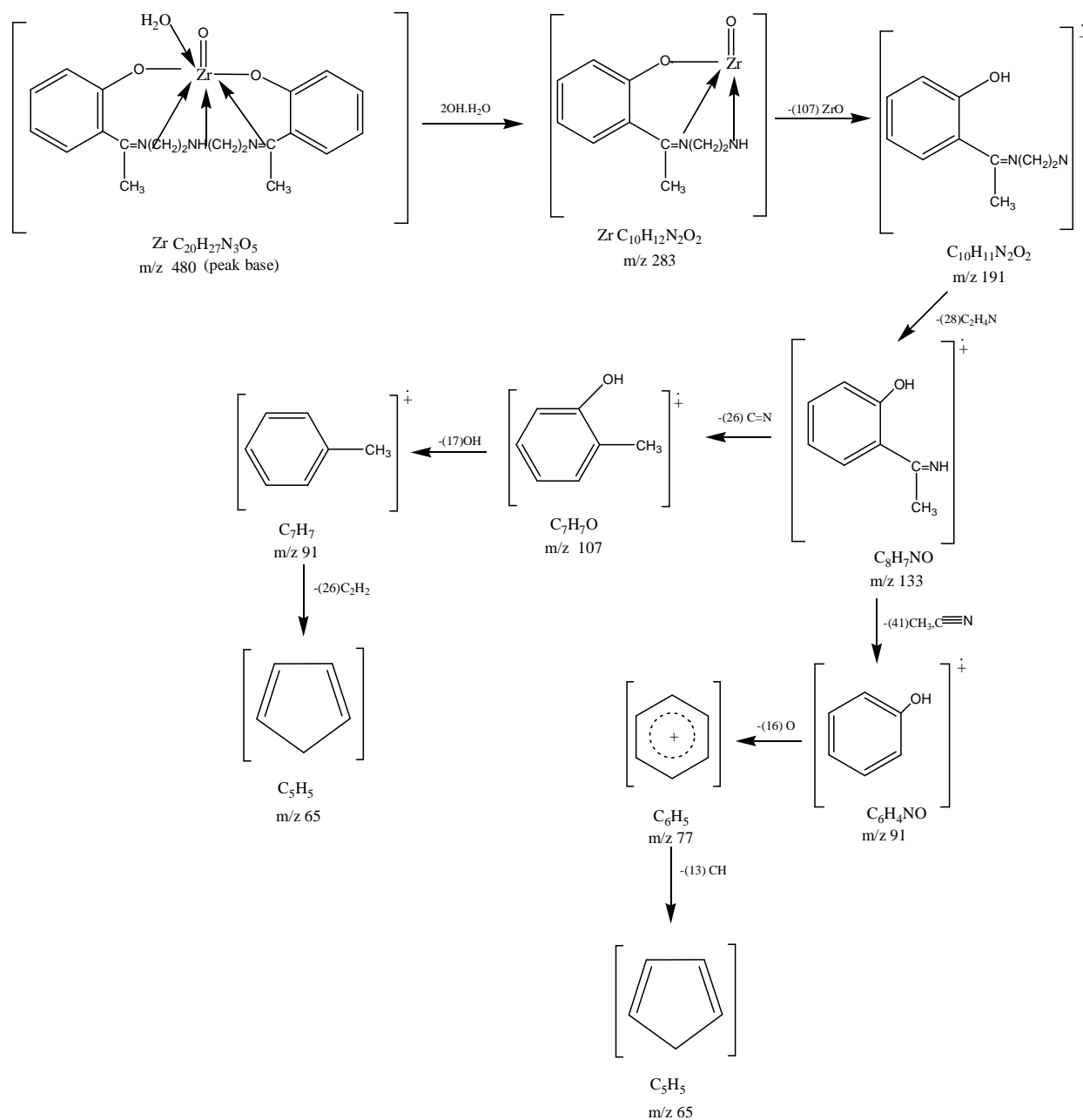


Fig. 13: Mass spectrum of the Zr(IV) chelate



Schemes. 3: mass spectral fragmentations of the Zr(IV) chelate

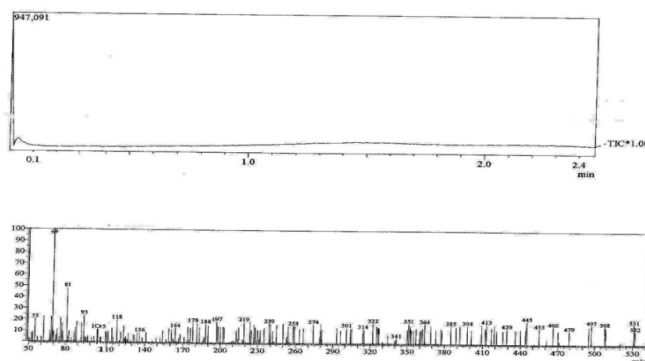
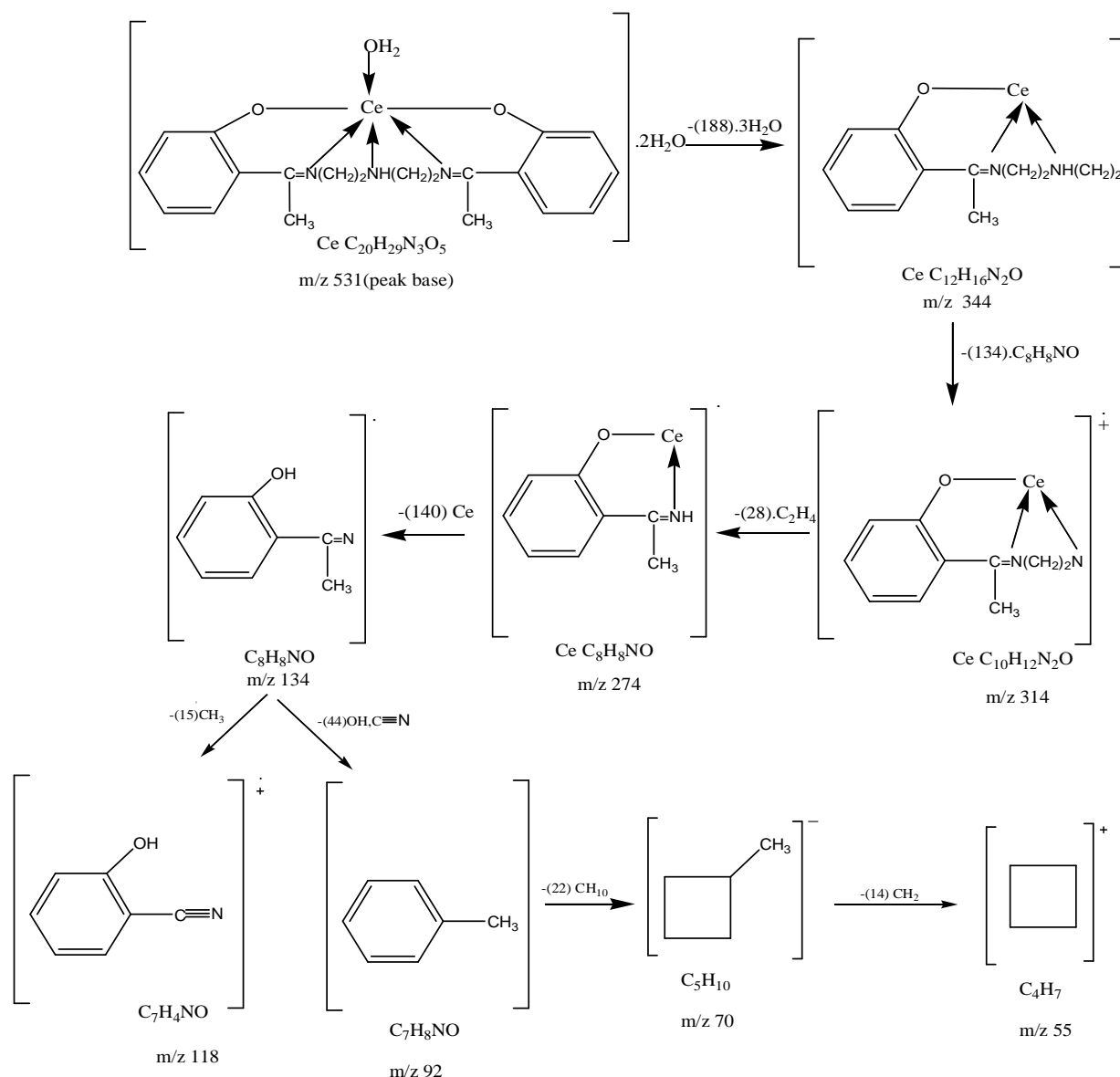


Fig. 14: Mass spectrum of the Ce(IV) chelate



Schemes. 4: mass spectral fragmentations of the Ce(IV) chelate

Biological activity of the Schiff base and its metal chelates

Bacteria

The data in tables (3-4); the antibacterial screening results indicates that compounds **B2**, **B3** and **B5** have significant inhibitory activity and compounds **B1**, **B4**, **B6** and **B7** have poor activity against the majority of strains comparing to activity results. (SB) **C1** ligand is found to have no biological activity against all tested bacteria and moderately effective against *Lactobacillus fermentum*. All the metal chelates exhibit higher resistive antibacterial activity than the free ligand. Lanthanum (III) **C2**,

Zirconium (IV) **C3** and Cerium (IV) **C4** chelates have higher sensitive bacterial activity and La(III) metal chelate is slightly effective against *Escherichia coli* than the other chelates. The bioactivity of the ligand and its chelates is found to be order La(III) >SB(II) >Zr(IV) ~Ce(IV).

Fungus

Compounds **B1-B7** showed medium activity against *Aspergillus niger* and slightly effective against *Fusarium solani*. SB ligand shows antifungal activity against *F. solani* and *A. niger*. From Table (3), (SB) **C1** is found to have slightly effective against *F. solani* than *A. niger*. Metal chelates have no antifungal biological activity and follow the order SB > La(III) ~Zr(IV) ~Ce(IV). Chelates are found to have no antifungal activity more than the parent SB ligand. However, all the other results were weak, small or no activity against most of strains. The higher resistive inhibition zone of metal chelates than those of the ligands can be explained on the basis of Overtone's concept and Chelation theory. On chelation, the polarity of the metal ion will be reduced to greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further, it increases the delocalization of π -electrons over the whole chelating ring and enhances the penetration of the complexes into lipid membranes and blocking of the metal binding sites in the enzymes of microorganisms. There are other factors which also increase the activity are solubility, conductivity and bond length between the metal and ligand [18, 19].

Table 3: Antimicrobial activities of compounds, Schiff bases and its chelates on growth of microorganisms

		Gram negative organisms											
		<i>Escherichia coli</i>					<i>Salmonella Kentucky</i>						
		% Activity index					% Activity index						
		5	50	500	5	50	500	5	50	500	5	50	500
B-1	HAPH	0	0	0	0	0	0	0	0	0	0	0	0
B-2	BD	0	10	14	0	25	35	7	11	19	20	31	48
B-3	DETA	0	12	17	0	30	43	8	10	20	20	25	50
B-4	OPD	0	0	17	0	0	43	0	0	11	0	0	32
B-5	La(III)	8	13	18	20	33	45	8	11	16	23	31	46
B-6	Zr(IV)	0	0	0	0	0	0	0	0	0	0	0	0
B-7	Ce(IV)	0	0	8	0	0	0	8	10	13	23	29	37
C-1	SB	0	0	0	0	0	0	0	0	0	0	0	0
C-2	La(III)	0	8	10	0	20	25	0	0	0	0	0	0
C-3	Zr(IV)	0	0	11	0	0	28	0	0	0	0	0	0
C-4	Ce(IV)	0	0	10	0	0	25	0	0	0	0	0	0
C	DMSO	0	0	0	0	0	0	0	0	0	0	0	0

HAPH (*o*-hydroxyacetophenone), BD(1,4-Butanediamine),DETA(2,2'-diaminodiethylamine),OPD (1,2-diaminobenzene) *microgram per mL

Table 4: Antimicrobial activities of compounds, Schiff bases and its chelates on growth of microorganisms

S.N	Comp.	Diameter of inhibition zone (mm); Concentration in $\mu\text{g/ml}$													
		Gram positive organisms													
		<i>Aspergillus niger</i>					<i>Fusarium solani</i>								
		% Activity index					% Activity index								
		5	50	500	5	50	500	5	50	500	5	50	500		
B-1	HAPH	0	0	19	0	0	73	0	0	0	0	0	0		
B-2	BD	11	17	23	53	81	109	0	0	0	0	0	0		
B-3	DETA	2	4	8	10	48	38	0	0	0	0	0	0		
B-4	OPD	0	0	11	0	0	52	0	0	11	0	0	85		
B-5	La(III)	0	0	3	0	0	14	0	0	0	0	0	0		
B-6	Zr(IV)	0	0	4	0	0	19	0	0	0	0	0	0		
B-7	Ce(IV)	0	0	19	0	0	90	0	0	0	0	0	0		
C-1	SB	0	0	3	0	0	14	0	0	0	0	0	0		
C-2	La(III)	0	0	0	0	0	0	0	0	0	0	0	0		
C-3	Zr(IV)	0	0	0	0	0	0	0	0	0	0	0	0		
C-4	Ce(IV)	0	0	0	0	0	0	0	0	0	0	0	0		
C	DMSO (Control)	0	0	0	0	0	0	0	0	0	0	0	0		

HAPH (*o*-hydroxyacetophenone), BD(1,4-Butanediamine),DETA(2,2'-diaminodiethylamine),OPD(1,2-diaminobenzene).

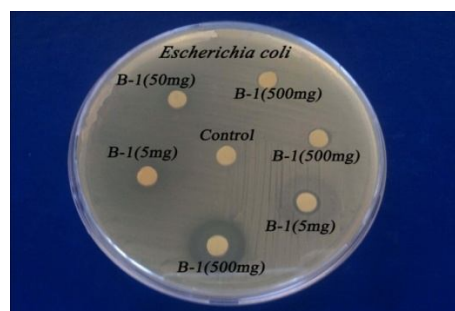


Plate. 1: Effect of O-hydroxyacetophene and 1,4- Butanediamine. On *Escherichia coli*
Plate. 2: Effect of O-hydroxyacetophene and 1,4-Butanediamine. On *Salmonella kentucky*

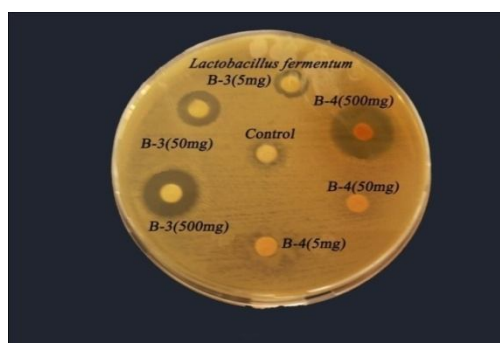


Plate. 3: Effect of 2,2'-diaminodiethylamine and 1,2-diaminobenzene. On *Lactobacillus fermentum*

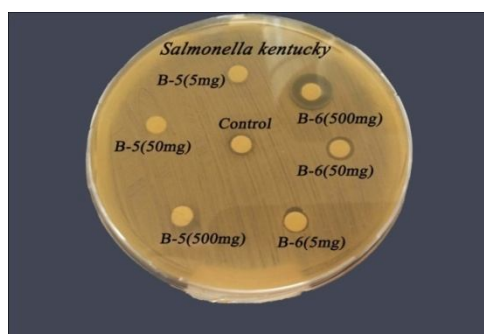


Plate. 4: Effect of $ZrOCl_2 \cdot 8H_2O$ and $La(NO_3)_3 \cdot 6H_2O$. On *Salmonella Kentucky*

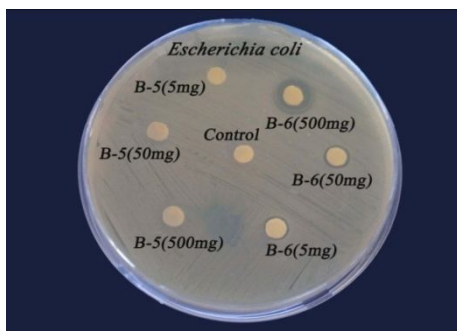


Plate. 5: Effect of $ZrOCl_2 \cdot 8H_2O$ and $La(NO_3)_3 \cdot 6H_2O$ On *Escherichia coli*

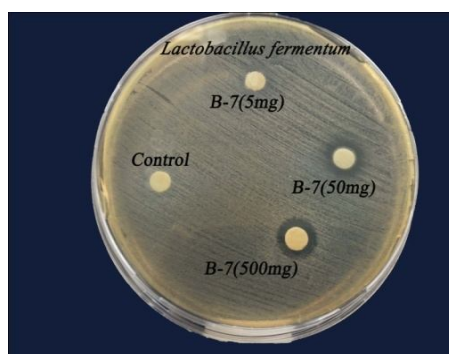


Plate. 6: Effect of Effect of $Ce(SO_4)_2 \cdot 4H_2O$. On *Lactobacillus fermentum*

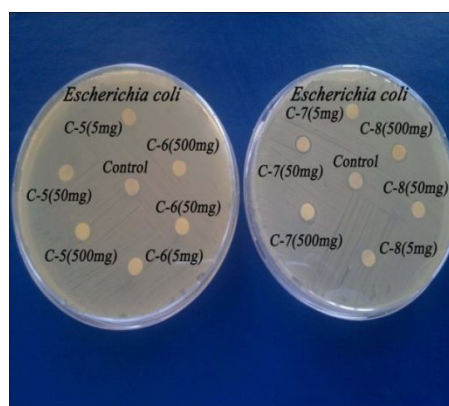


Plate (7): Effect of Schiff base-Zr(IV), La(III) and Ce(IV) chelates. On *Escherichia coli*

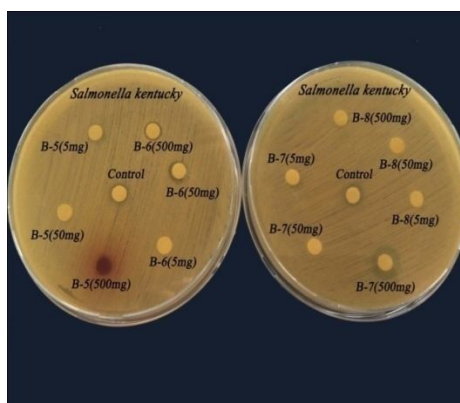


Plate (8): Effect of Schiff base- Zr(IV), La(III) and Ce(IV) chelates. On *Salmonella Kentucky*

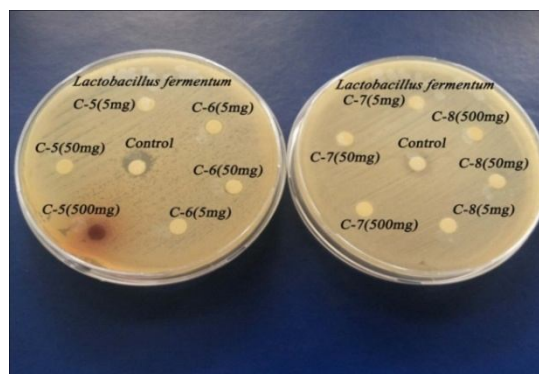
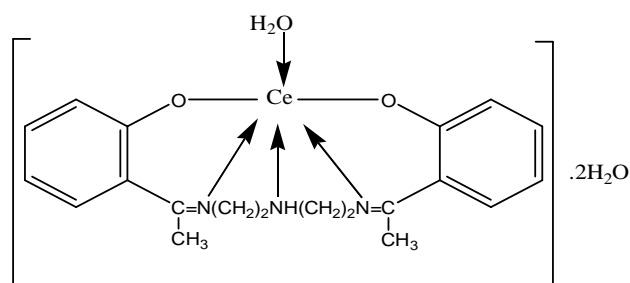
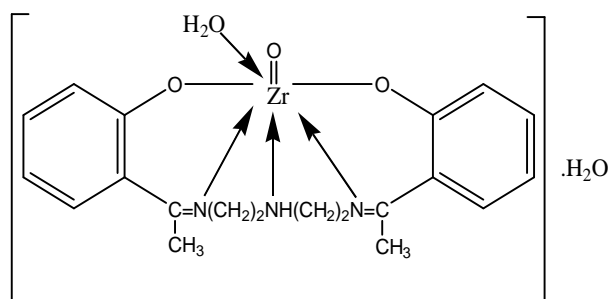
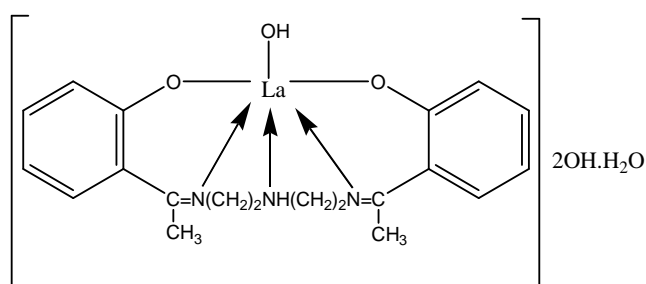


Plate (9): Effect of Schiff base and Zr(IV), La(III) and Ce(IV) chelates on *Lactobaci*

CONCLUSION

The obtained analytical data suggest the octahedral geometry for all chelates. From the previous analyses, we can display the following geometrical structures:



Antibacterial and antifungal activity of the synthesized compounds were done in comparison with ciprofloxacin and miconazole as standard drugs to reveal the potency of synthesized compounds. The results of this investigation support the suggested structures of the metal chelates. Meanwhile, the

Schiff base and its metal chelates, La(III), Zr(IV) and Ce(IV) showed moderately effect on all pathogenic bacteria except fungi tested. The effect was higher concentrations of metal chelates. It is obvious from this study that only mononuclear chelates are obtained. La(III) Zr(IV) and Ce(IV) chelates have trivalent and tetravalent ion. The metal ion were tested alone, the trivalent ions showed a good effect, then the metal ions were fungi tested, did not have any effect then the tetravalent ion have showed moderately effect for all bacteria, but except fungi no have activity. The biological activities of the Schiff base under investigation and their chelates against bacterial and fungal organisms are promising which need further and deep studies on animals and humans.

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