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Mixed ligand chelates of some metal ions: Preparation and physicochemical characterizations

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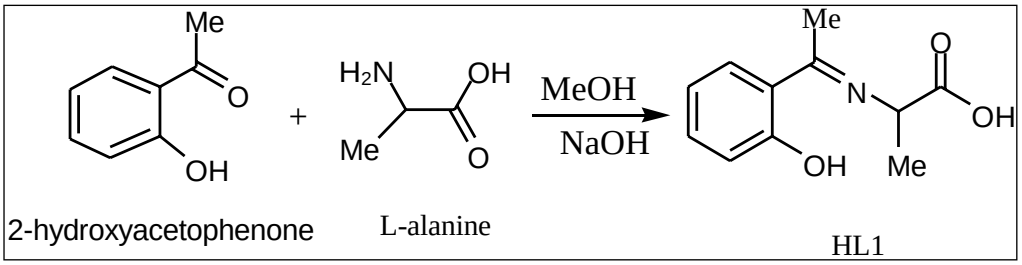
Abstract
In the present investigation, a Schiff base that produced by the condensation reaction of L-alanine with 2-hydroxyacetophenol as primary ligand (HL1) and 2-aminophenol as secondary ligand (L2) was synthesized and investigated. The synthesized Schiff base and 2-aminophenol ligands were used in the formation of three mixed ligand chelates with iron (III), cerium (IV) and thorium (IV) ions. The synthesized compounds were examined by applying analytical and physical tools. The bonding and electronic transitions confirmed the proper structures for Schiff base and mixed ligand chelates.

Keywords: Schiff base, L-alanine, 2-hydroxyaetophenone, 2-aminophenol, mixed ligand chelates

Introduction
The Schiff base moieties at the poly functional donor site were widely used in the analytical, biocidal, agrochemical, enzyme models, catalysis, food, chemical, and dye sectors [1, 2]. Schiff bases and their complexes were adaptable compounds made by precipitating an amino acid with a carbonyl group [3]. Some enzymes employ the amino group of an amino acid to react with carbonyl (C=O) to generate an azomethine linkage, the azomethine (-C=N) group of Schiff base compounds plays a significant role in many areas, including biological reactions [4].
Lakshmi and Geetha [5] Prepared four mixed ligand complexes of the formula [M–L(temn)], (where M=Cu(II), Ni(II), Zn(II) and Co(II) ions, L= Schiff base ligand formed by the condensation of L-tryptophan and 2-hydroxyacetophenone and temn- N,N, N, N-tetramethylethylenediamine. The Schiff base and its mixed ligand complexes were characterized by using analytical and spectral tools. All the compounds were examined for their biological activity against some pathogenic organisms (bacteria and fungi). Complexes of cerium(IV) and gadolinium(III) of the formula $[Ce(babh)_2](1)$and $[Gd(babh)(Hbabh)]\cdot H_2O(2\cdot H_2O)$ have been synthesized by the reactions of Ce(III) and Gd(III)ions with biacetylbis(benzoylhydrazone) (H2babh). The Schiff base and their complexes were studied using several spectral techniques [6].

Experimental Chemical Part
Material and Methods
All chemicals used in this investigation were of pure grade (BDH or Aldrich). Include; 2-hydroxyacetophenone L-anlanine, 2-aminophenol, DMF, DMSO, NaOH, methanol, ethanol, Fe $(Cl)_3$. $6H_2O$, $Ce(SO_4)_2$. $4H_2O$, Th $(NO_3)_4$. $4H_2O$, CH_3COOH and distilled water. The CHNS analyses for the prepared complexes were made on 2400-CHN elemental analyzer. The molar conductivity was determined in DMF on CMD-650 digital conductivity meter, Ajdabia University. The infrared spectra were carried out on IFS-25 DPUS/IR spectrometer. NMR spectra were recorded on Varian Gemini 200–200 MHz spectrometer using TMS as internal standard in d6-DMSO.
The electronic and mass spectra were recorded on Perkin-Elmer lambda-365 spectrophotometer, and Shimadzu QP-2010 Plus spectrometer, respectively.

Preparation of amino acid Schiff base
The present amino acid Schiff base was prepared as follows: NaOH (0.4g, 0.01 mol) was dissolved in 25mL methanol and L-alanine (0.90 g, 0.01 mol) was added to it. The mixture was stirred at room temperature for 5 minutes. When the mixture becomes homogeneous, 2-hydroxyacetophenone (1.36g, 0.01 mole) was added. After 2 minutes, the mixture was evaporated to 20% of its original volume and 1mL of acetic acid was added immediately.
After 2 hours, A yellow product was formed. The obtained product was filtered, washed, dried and recrystallized from hot methanol to give pure crystals in excellent yield of 85%, fig.1



Scheme 1: Preparation of amino acid Schiff base

Preparation of mixed ligand chelates

By adding 2.07g, 0.01 mole of the Schiff base (HL1) to a methanolic solution (25ml) of desired metal salts (0.01mole; 5.52, 4.04 and 2.70g) of Th(IV), Ce(IV) and Fe(III) ions, respectively, were prepared. In order to adjust the pH value at 8, few drops of 10% sodium hydroxide solution were added slowly until the chelates separated. the mixtures were refluxed for one hour and half, then added 1.10g, 0.01mol of 2-aminophenol in 25ml methanol as Co-ligand. The mixtures were again refluxed for extra 3hours. The formed products were filtered and washed several times with hot ethanol until the filtrates become clear. The obtained mixed ligand chelates were dried under calcium chloride in the desecrator.

Results and Discussion

Microanalysis and molar conductivity

The CHN elemental analysis data of the Schiff base and mixed ligand chelates offer a good agreement between the calculated and found values indicating the formation of the compounds under investigation (Table-1). Also, the molar conductivity values of the mixed ligand chelates display the existence of non-electrolytic nature [7] confirming the absence of any inorganic anions out the coordination sphere.

Table 1: Analytical and some related properties data of the Schiff base (HL1) and mixed ligand chelates

Ligand/chelates	M. wt	Color	Elemental analyses Calcd. Found				^m; $\Omega^{-1}cm^2mol^{-1}$	µ B.M
			C%	H%	N%	S%		
Schiff base HL1; ($C_{11}H_{13}NO_3$)	207	Daffodil	63.77 64.20	6.28 5.21	6.76 6.25	----	——	----
[Fe(L1)(L2)(OH)].H_2O	405	Black	50. 37 50.06	5.43 5.01	6.91 7.56	----	0.000582	6.33
[Ce((L1)(L2)(SO_4)(H_2O)].H_2O	586	Stone	34.81 34.88	3.92 3.04	4.78 5.35	5.46 6.00	0.00042	0.00
[Th(L1)(L2)(NO_3)(H_2O)].H_2O	644	Plum	34.81 34.02	3.58 3.95	6.52 6.03	----	0.00089	***0***0.0

Infrared spectra

The infrared spectral results of Schiff base compound HL1 is shown in table-2 and its spectrum is shown in figure-1, the strong broad band that appeared at 3441cm^{-1} is due to O-H vibration of the phenolic [8]. This band vanished due to complexation with metal ions. The spectrum shows a band at 1605cm^{-1} due to the formation of azomethine group (C=N) [9]. The same spectrum exhibits a band at 3094 cm^{-1} assigned to υCOOH vibration [10]. The infrared spectra of the L1L2 mixed ligand chelates of [Fe(L1)(L2)(OH)].(H_2O), [Ce(L1L2)(SO_4)(H_2O)].H_2O and [Th(L1)(L2)(NO_3)(H_2O)].H_2O are shown in the figures(2-4) and their band assignments are listed in table-2. The band corresponds to $–NH_2$ group of the co-ligand 2-aminophenol is overlapped with the bands of crystal water molecules present in the mixed ligand chelates [11]. Meanwhile, the same spectra display a band of azomethine group in the range of 1628-1528 cm^{-1}, the shifting of this group compared to the position of azomethine group in the free Schiff base (1605 cm^{-1}) indicating the involvement of -C=N nitrogen in coordination with the metal ions via a nitrogen atom [12]. In IR spectrum of the Schiff base, the strong broad band at 3441 cm^{-1} which is assigned to O-H stretching vibration is absent in the spectra of the mixed ligands indicating its involvement in chelation with the metal ions [13]. This evidence confirms the replacement of proton of hydroxyl group and bonding through oxygen atom to the metal ion. The band of υ-COOH in free ligand (3094cm^{-1}) is absent in the spectra of the mixed ligand chelates supporting the coordination of carboxylic acid group via oxygen atom with the metal ion. The spectra of Ce(IV) and Th(IV) mixed ligand chelates show a band at 840 cm^{-1} which is due to the existence of water molecule as coordinated molecule [14]. Also the other bands of Th(IV) mixed ligand chelate at 1034 and 756 cm^{-1} are assigned to the bidentate nitrate group [15, 16]. Whereas, the bands in the range of 1056-925 are assigned to the existence of O-SO_3 monodentate sulfate group in Ce(IV) mixed ligand chelate [17]. New bands in the range of 756-656 and 602-540 cm^{-1} attributed to υ(M-O) and υ(M-N) vibrations, respectively, were seen in IR spectra of the mixed ligand chelates [18].

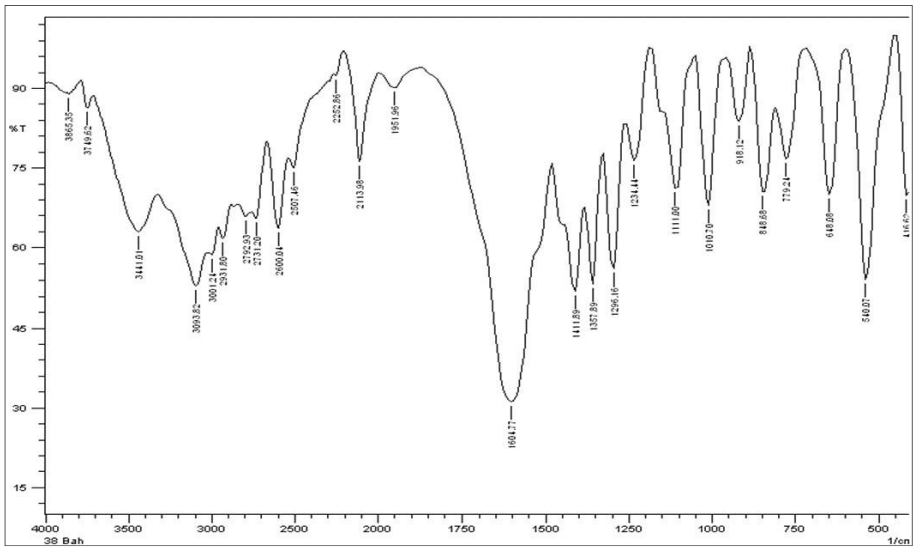


Fig 1: Infrared spectrum of the Schiff base HL1

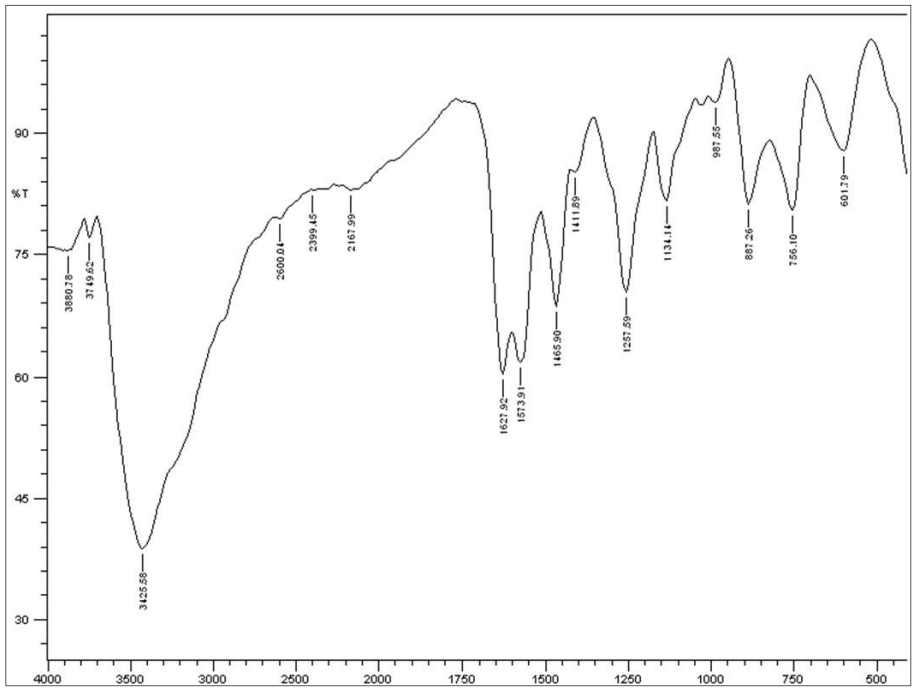


Fig 2: Infrared spectrum of [Fe (L1) (L2)(OH)].H_2O mixed ligand chelate

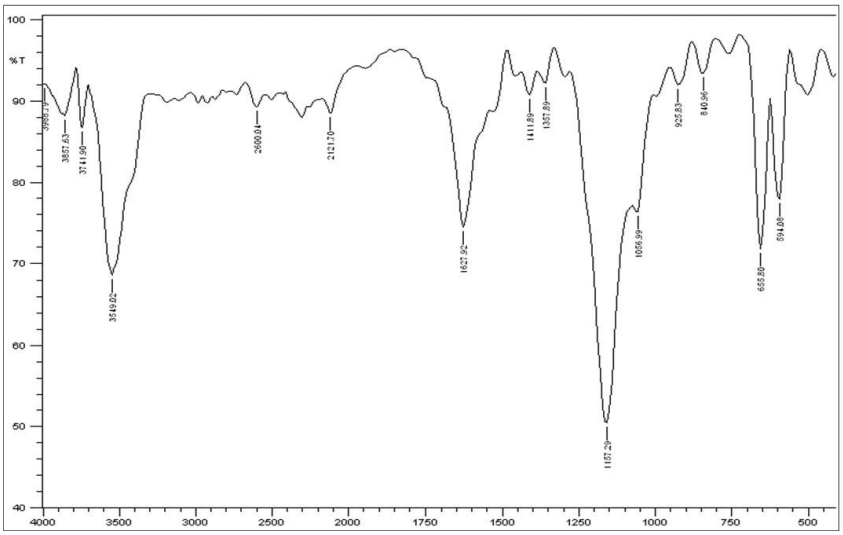


Fig 3: Infrared spectrum of [Ce(L1)(L2)(SO_4)(H_2O)].H_2O mixed ligand chelate

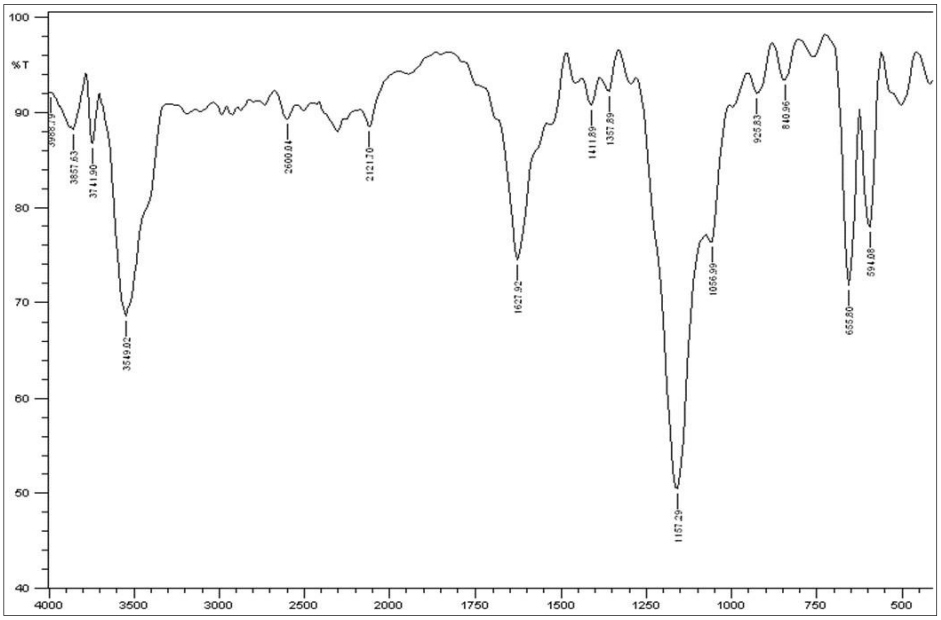


Fig 4: Infrared spectrum of [Th(L1)(L2)(NO_3)(H_2O)].H_2O mixed ligand chelate

Table 2: Characteristic infrared absorption frequencies ($cm^{-1)}$ of the Schiff base and mixed ligand complexes

Ligand/chelates	υ (OH) (H_2O) hydrate	ʊ (C=N)	ʊ (M-O)	ʊ (M-N)
Schiff base HL1; ($C_{11}H_{13}NO_3$)	3441	1605	---	---
[Fe (III)(L1)(L2)(OH)].H_2O	3426	1627	756	602
[Ce(IV)(L1)(L2)(SO_4)(H_2O)].H_2O	3549	1628	656	594
[Th(IV)(L1)(L2)(NO_3)(H_2O)].H_2O	3418	1582	671	540

Electronic spectra and magnetic moments

The spectrum of the Schiff base (HL1) exhibits absorption bands at 260nm (38711cm^{-1}) and 313 nm (31949cm^{-1}) corresponding to $\pi \rightarrow \pi^*$ (phenyl ring) and $n \rightarrow \pi^*$ transition, respectively [19]. The electronic absorption spectrum of Iron(III) chelate shows four bands at 354 nm(28249cm^{-1}), 427(23419 cm^{-1}), 576(17361 cm^{-1}) and 681 nm(14681cm^{-1}), the first band owing to charge transfer and the other three bands corresponding to $^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$, $^6A_{1g}(S) \rightarrow {}^4T_{2g}(G)$ and $^6A_{1g}(S) \rightarrow {}^4E_g$, $^4A_{1g}(G)$, respectively [20-22]. The magnetic moment value of this chelate is (6.33 B. M) indicates the presence of paramagnetic character. Based on these data, an octahedral geometry was suggested for the chelate [23]. The electronic spectra of the cerium (IV) and thorium (IV) mixed ligand chelates display absorption bands in the range of 411-440(24330-22727) and 407-431nm (24570-23202cm^{-1}), respectively, These bands may be related to the charge transfer transitions [24, 25]. whereas, in the same spectra, the bands in the region at 500-700 nm(20000-14286cm^{-1}) are not clear, because they due to f-f transition [26].

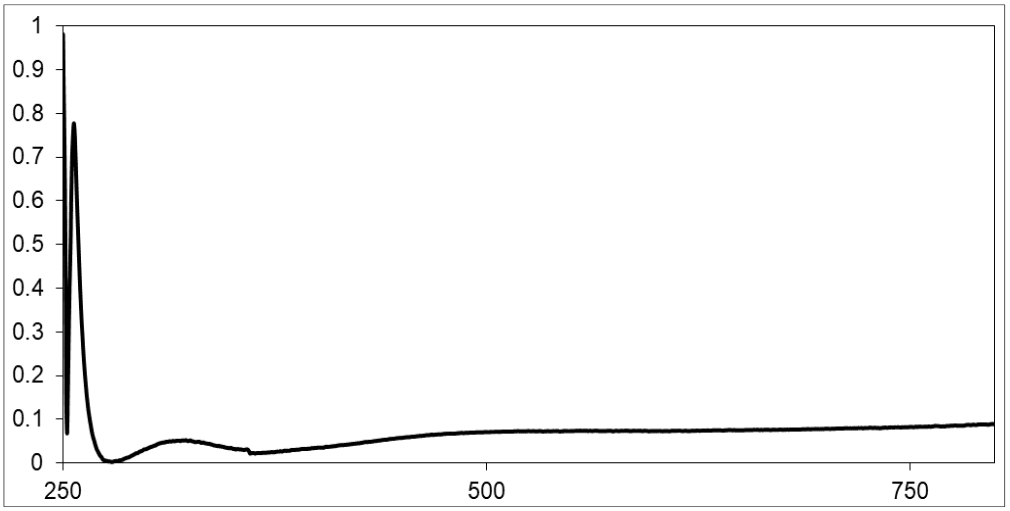


Fig 5: Electronic spectrum of Schiff base (HL1)

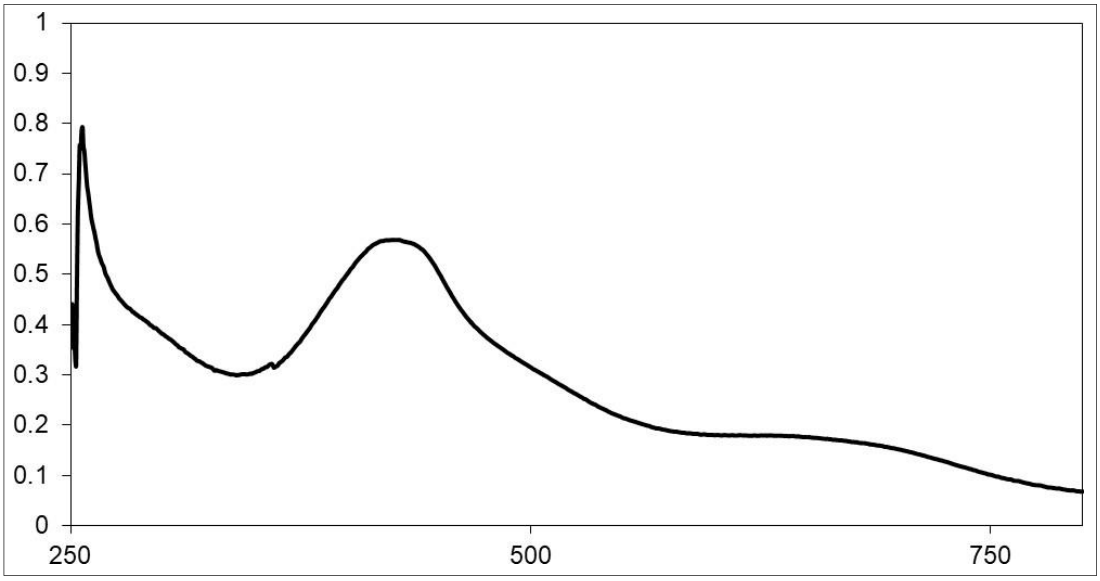


Fig 6: Electronic spectrum of [Fe (L1) (L2) (OH)]. H_2O mixed ligand chelate

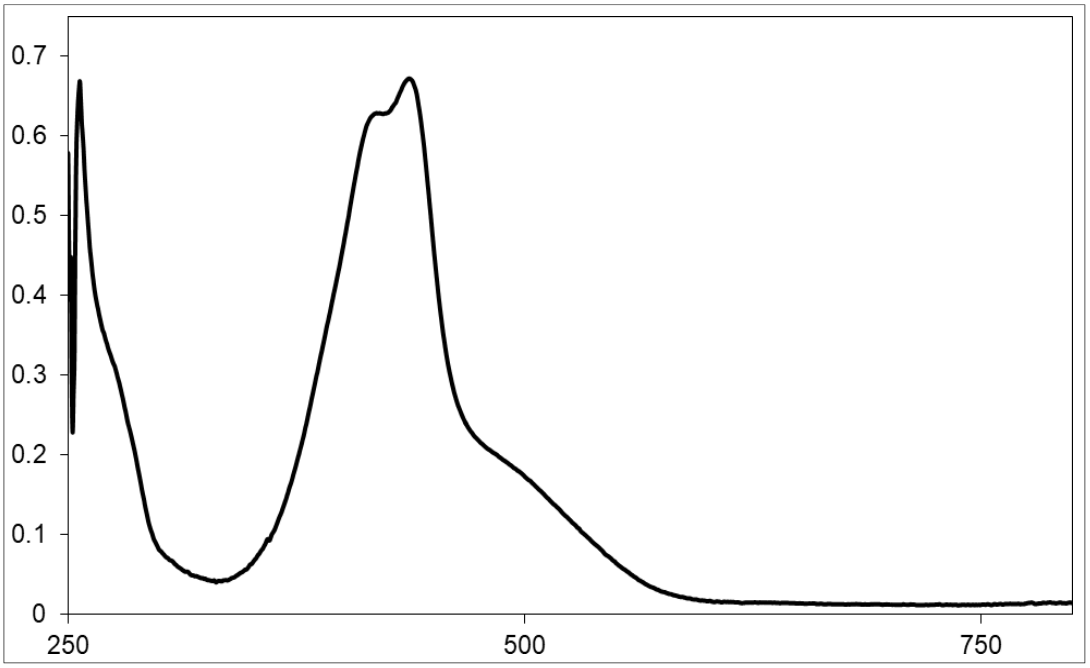


Fig 7: Electronic spectrum $[Ce(L1)(L2)(SO_4)(H_2O)].H_2O$ mixed ligand chelate

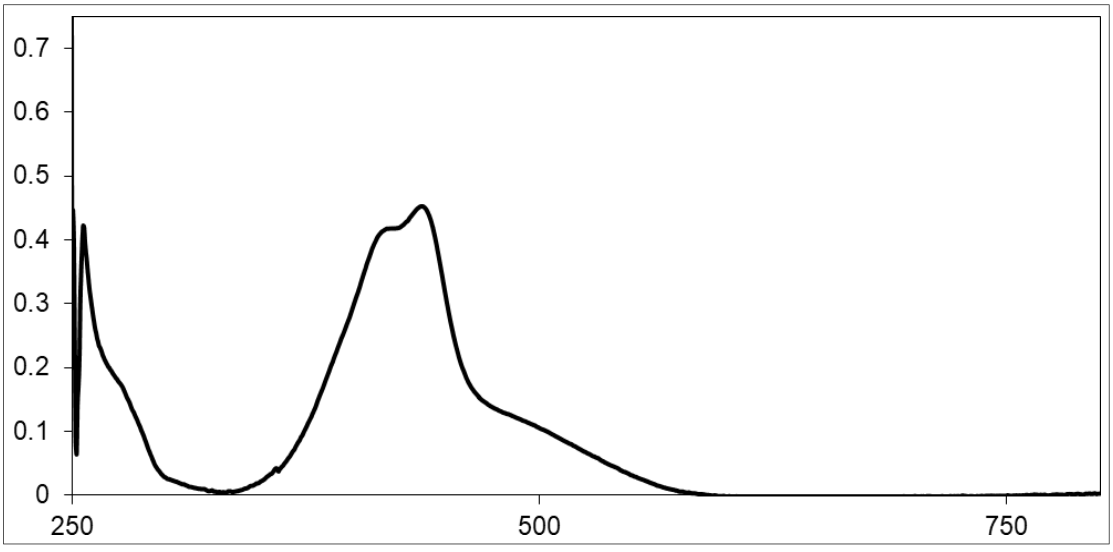


Fig 8: Electronic spectrum of $[Th(L1)(L2)(NO_3)(H_2O)].H_2O$ mixed ligand chelate

Table 3: Electronic spectral data (nm, cm^{-1}) of the Schiff base and mixed ligand chelates

Compounds	λ nm (cm^{-1})	Assignment
HL1; ($C_{11}H_{13}NO_3$)	260nm(38711cm^{-1}) 313 nm(31949 cm^{-1}	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$
[Fe (L1)(L2)(OH)].H_2O	354 nm(28249cm^{1-}) 427nm(23419 cm^{1-}) 576nm(1736 cm^{1-}) 681nm(14681$cm^{-1)}$	CT $^6A_1g(S) \rightarrow {}^4T_1g(G)$ $^6A_1g(S) \rightarrow {}^4T_2g(G)$ $^6A_1g(S) \rightarrow {}^4Eg, {}^4A_1g(G)$
[Ce(L1)(L2)(SO_4)(H_2O)].H_2O	411-440nm (24330 -22727cm^{-1}) 500-700nm (16667-14286cm^{-1})	MLTC f-f transitions
[Th(L1)(L2)(NO_3)(H_2O)].H_2O	407-431nm (24570-23202cm^{-1}) 500- 700 nm (16667-14286cm^{-1})	MLTC f-f transitions

^{1}HNMR spectra of Schiff base (HL1) and its mixed ligand chelate

The ^{1}HNMR spectra of the compounds were obtained in d^6 DMSO solution as a solvent at room temperature using TMS as an internal reference. In the present study, the ^{1}HNMR spectral signals are depicted in figs. (9,10). The resonance of protons has been assigned on the basis of their integration and multiplicity pattern. The ^{1}HNMR spectrum of Schiff base HL1; ($C_{11}H_{13}NO_3$) shows two signals at 7.73 and 4.1 ppm which are attributed to the presence of OH proton in phenyl ring and COOH group in amino acid, also the signals at 1.2, 2.3, 3.2 and 2.5 ppm are due to the existence of methyl groups and DMSO solvent, respectively [27, 28]. The aromatic protons have been resonated in the region at 6.4-7.5ppm [29]. The ^{1}HNMR spectrum of [Ce(L1)(L2)(OH)].($H_2O)_2$] mixed ligand chelate displays the absence of signals due to the OH proton and COOH indicating their replacement by the metal ion during chelation formation. The low intensity singlet peak at 6.3 ppm attributable to water protons [30]. Also the signals at 6.8–7.4 ppm are corresponding to aromatic protons resonate. Whereas, the signals at 1.25 and 2.5 ppm are attributed to the methyl group and DMSO solvent. The singlet at 5.14 ppm is assigned to NH_2 group of the 2-aminophenol (L2). The shifting of this group during the chelation process indicates its participation in bonding with metal ions [31].

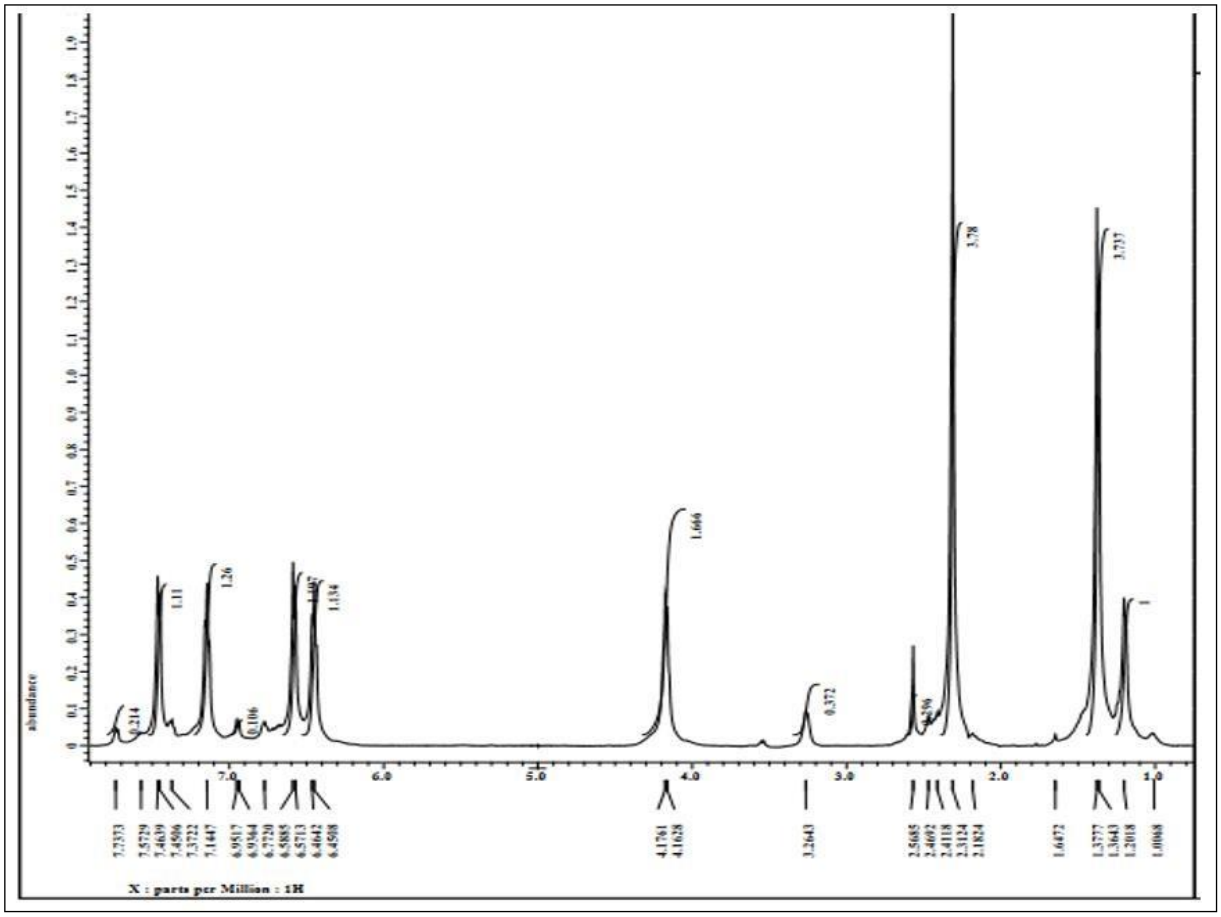


Fig 9: ^{1}HNMR spectrum of Schiff base HL1

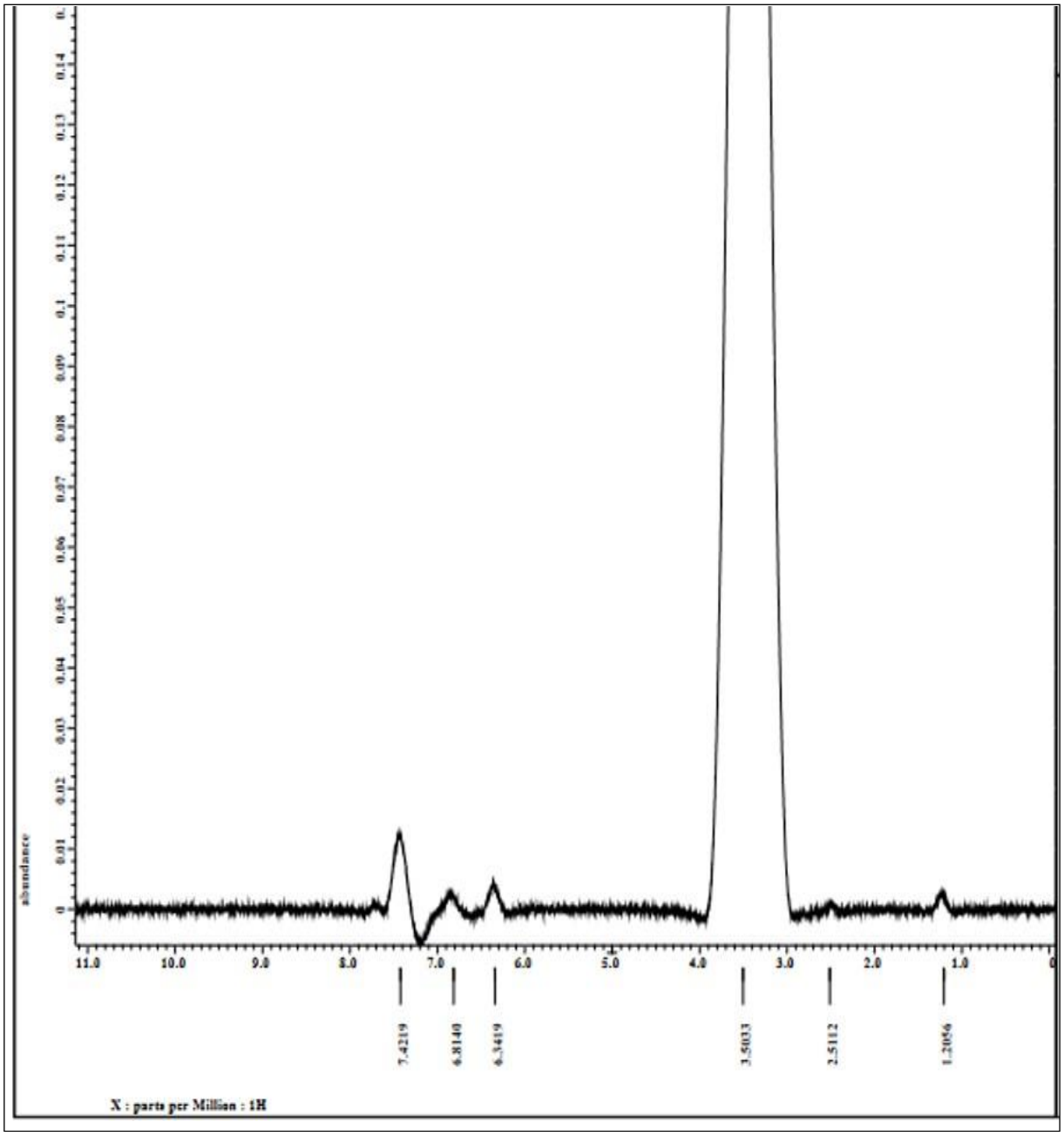


Fig 10: ^{1}HNMR spectrum of [Ce((L1)(L2)(SO_4)(H_2O)].H_2O mixed ligand chelate

Mass spectra

The mass spectral results of Schiff base compound HL1 and [Th(L1)(L2)$(NO)_3$(H_2O)].H_2O mixed ligand chelate are shown in figs.11,12 and their fragmentations are listed in table-4.

Table 4: Mass spectral data of the Schiff base and [Th(L1)(L2)$(NO)_3$(H_2O)].H_2O mixed ligand chelate

Compound	Fragmented ion	m\e$^+$ Value
HL1; ($C_{11}H_{13}NO_3$)	$C_{11}H_{10}NO_2^-$	188
	$C_8H_9NO_2$	151
	C_7H_9O	109
	C_7H_7	91
[Th(L1)(L2)(NO_3)(H_2O)].H_2O	$C_{17}H_{21}N_3O_9Th$	643
	$C_{15}H_{14}N_2O_3Th$	502
	$C_{14}H_{14}N_2O_2Th$	474
	C_7H_7NOTh	353
	$VC_5H_3Th^+$	294
	$C_4H_2^-$	51

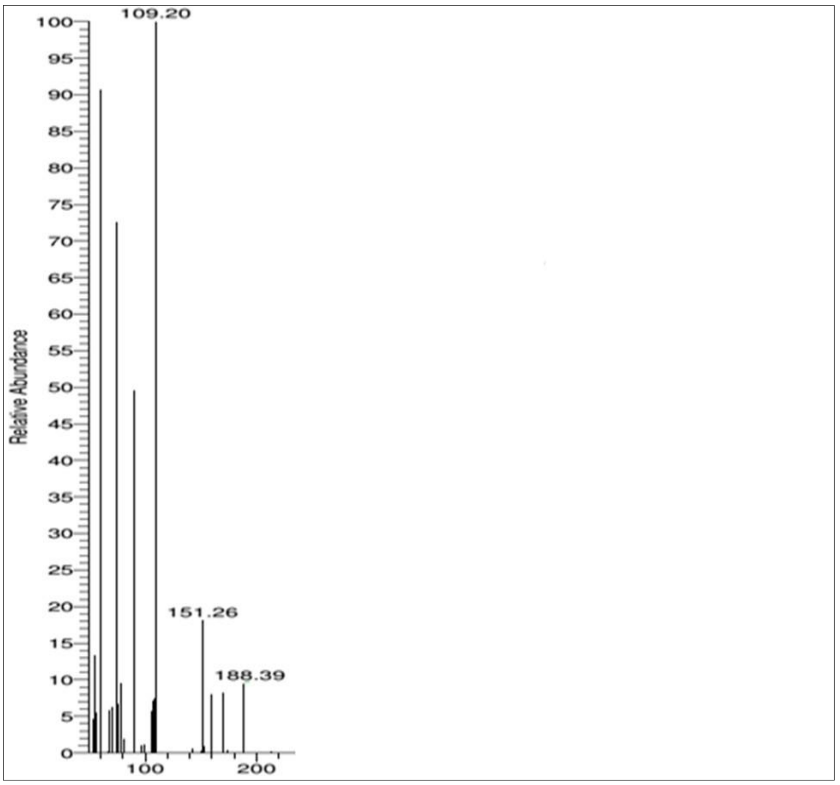


Fig 11: Mass spectrum of the Schiff base (HL1)

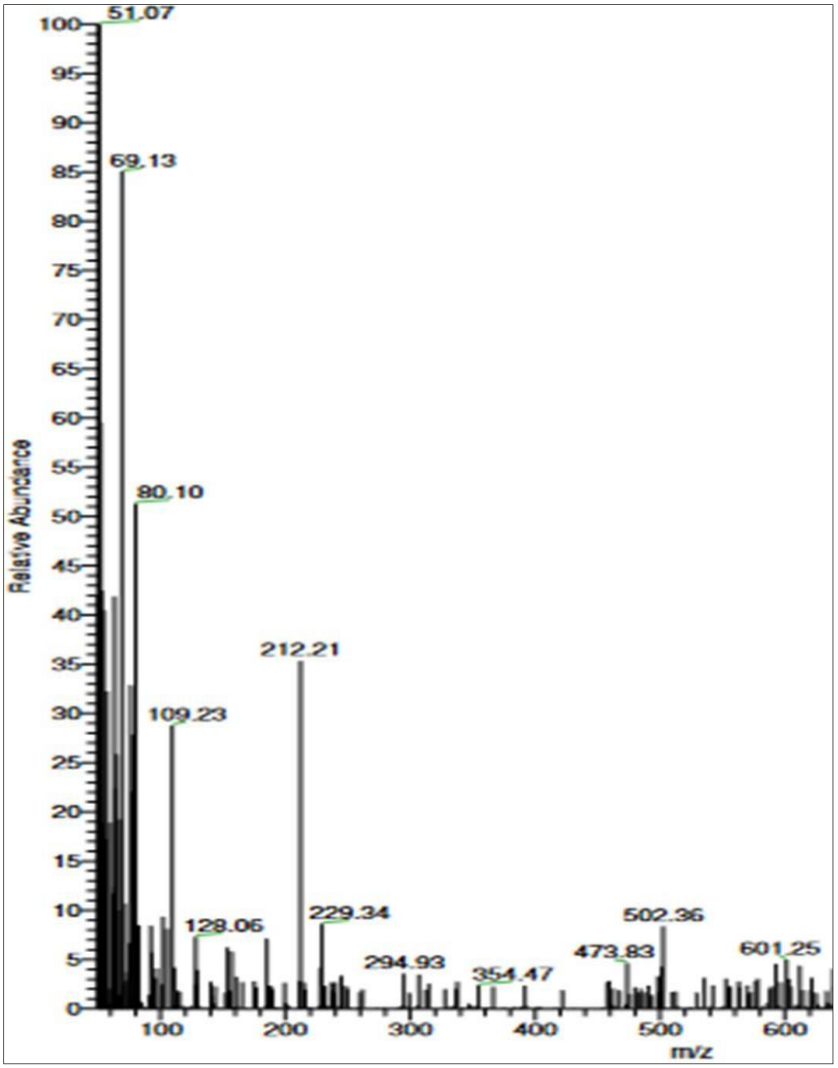


Fig 12: Mass spectrum of [Th(L1)(L2)(NO_3)(H_2O)].H_2O mixed ligand chelate

Conclusion

The physicochemical techniques showed the formation of the mixed ligand chelates in 1:1:1[M: L1L2] ratio and the prepared mixed ligand chelates were non-electrolytic in nature. Also their electronic transitions were reported. The chemical structures of the chelates were listed below

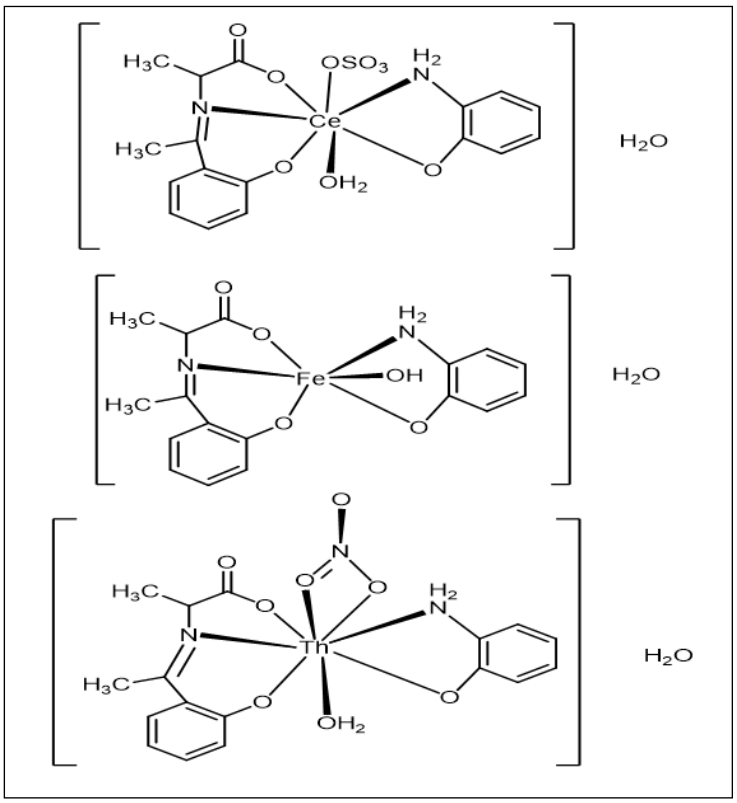


Fig 13: Suggested chemical formula of mixed ligand chelates

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