matel complexes of schiff - base ligand; Synthesis, characterization and liquid crystalline properties

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Abstract:

In this work a Schiff base ester derived ligand [H_2L^1] were synthesized in three steps, first Synthesis of the pentanoiyl chloride from reaction thionyl chloride with pentanoic acid.

in the second step the precursosr (W1), 4-[3-(3-hydroxy-1-methyl-butylideneamino)- 4-methyl-phenylimino]-pentan-2-ol ,was prepared by the reaction of acetylaceton with tolylen2,4-diamin . In the theird step the ligands were synthesized by the reaction of precursor (W1)with pentanoiyl chloride to produce[H_2L^1] 1:2 mole ratio. The binuclear complexes with Cr^{3+}, Co^{2+} and Zn^{2+}, were synthesized by the reaction of the ligand with metal salts in 1:1 mole ratio. The compounds were characterized by spectroscopic methods [FT-IR, UV-Vis, CHN, ^{1}H-NMR] elemental analysis, along with conductivity, and melting point measurements. The structure of the complexes were obtained according to the previous studies. Finally the liquid crystalline properties of the prepared compounds were studied by hot stag and DCS.

Introduction

Schiff base have been widely used as ligand because of high stability of the coordinate compounds and their good solubility in common solvent. The system in a Schiff base often imposes a geometrical constriction and affects the electronic structure as well thermochemical properties of Schiff base have attracted much researcher attention in view of their ability to coordinate metal ions. (1-3)

Metallomesogens are transition metal complexes with ligands that exhibit liquid crystalline character(4). Currently there is much interest in the synthesis and characterization of liquid crystalline materials containing metal atoms because of the potential to modify many physical properties via the inclusion of a metal center (5)The introduction of an electron-dense metal center should influence properties such as birefringence and dielectric anisotropy. (6) Since mesophase formation depends on the intermolecular forces and the space around the metal occupied by the ligand, the properties of metallomesogens are dominated by the ligands and their arrangement, in other words by the overall shape of the molecule(7)

In the recent years ester derivatives of aromatic Schiff base have been reported to have liquid crystalline properties.(8) previously it was reported the synthesis ,characterization of some new Schiff base ester and their liquid crystalline properties due to immense pharmacological significance of the Schiff base and their derivatives (9) .In this study we attempt to charcteraization and study the L.C properties of two new ligand and their complexes with Cr, Co and Zn

Materials and methods

All reagents were obtained commercially and used without further purification. Solvents used in the synthesis were distilled from appropriate hot drying agent immediately prior to use.

Physical measurements

Elemental analyses (C , H , N) were carried out on a Heraeus instrument (Vario EL). IR spectra were recorded as KBr discs using a Shimadzu 8300 FTIR spectrophotometer from 4000-400 cm^{-1}. Melting points were obtained on a Buchi SMP-20 capillary melting point apparatus and are uncorrected. Electronic spectra were measured from 200-900 nm for 10^{-3} M solutions in ethanol at 25°C using a Shimadzu 160 spectrophotometer. ^1H NMR spectra were acquired in DMSO–d^6 solution using a Jeol 270 MHz spectrometers with tetramethylsilane (TMS) as an internal standard. Metals were determined using a Shimadzu (A.A) 680 G atomic absorption spectrophotometer. Conductivity measurements were made with ethanol solutions using a Jenway 4071 digital conductivity meter and room Synthesis. Al –Bayat University , Jordan. And Tharan University.

Synthesis of 4-[3-(3-hydroxy-1-methyl-butylideneamino)-4-methyl-phenylimino]-pentan-2-ol (W1)

To (1.00g,8.19mmol) of the tolylen2-4diamine dissolved in (20ml) of ethanol it was added with stirring (1.60g,16.38 mmol) of acetyl acetone in (20ml) of ethanol with a few drops of glacial acetic acid as a catalyst ,the mixture was refluxed for 3hrs, then left at room temperature ,the precipitate was recrystallized in hot ethanol (yield: 1.00g,92%)

Synthesis of 1-{3-[3-(1-Hydroxy-pentyloxy)-1-methyl-but-2-enylideneamino]-4methyl-phenylimino}-1-methyl-but-1-enyloxy)-pentan-1-ol [H_2L^1]

To a stirred solution of precursor compound (W1) (0.6g, 2.06mmol) triethylamine 4 drops in (5mL) of THF was added (0.5g, 4.1322mmol) penatanoic acid chloride at (0-4) C. After the addition had been completed the resulting suspension was stirred at the same temperature for 3hrs, the triethylamine hydrochloride salt was precipitate. it was filtered and the filtrate was poured with stirring into 100ml ice-water then the mixture was extracted by adding 50ml of diethyl ether. The ether solution was evaporated to give a residue which was recrystallized from hot ethanol (yield:(0.6) g, 67%, mp = (150-153)°C

Synthesis of[$Cr_2(L^1)_2 (H_2O)_2 Cl_2$] complex

To a solution of (0.10 g,0.21 mmole)of the ligand (H_2L^1) dissolved in (10 ml) ethanol with stirring and heating at (75) °C it was added (0.05g,0.21mmol) of chromium(III) chloride hexhydrate dissolved in 10 ml ethanol . The resulting mixture was refluxed for 2 hrs, filtered off washed with absolute ethanol and recrystallized from ethanol, (yield:0.1g, 87.93%, mp(132-135) °C

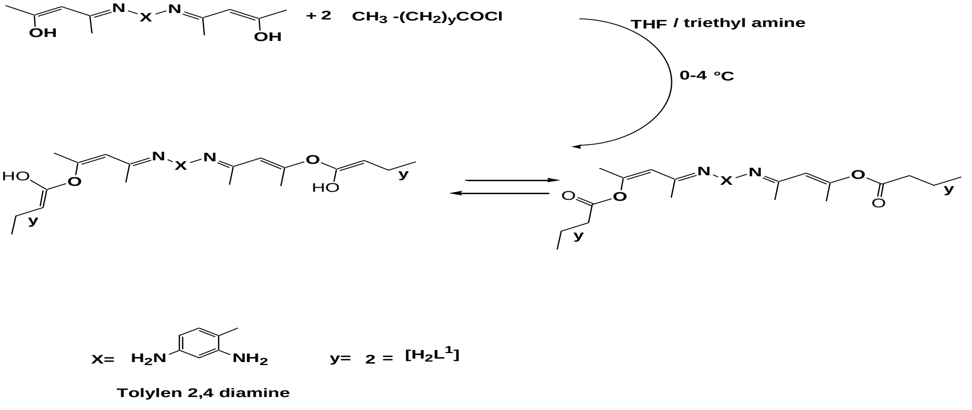
Synthesis of [$Co_2 (L^1)_2$] ,[$Zn_2 (L^1)_2$] Complexes

A similar method to that mentioned in the preparation of Cr^{III} complex was used to prepare the complexes of [H_2L^1] with $Co^{II}$and Zn^{II} ions, table (2) shows the physical properties of the complexes and their reactant quantity.

Results and discussion

Synthesis and characterization of ligands [H_2L^1] ,

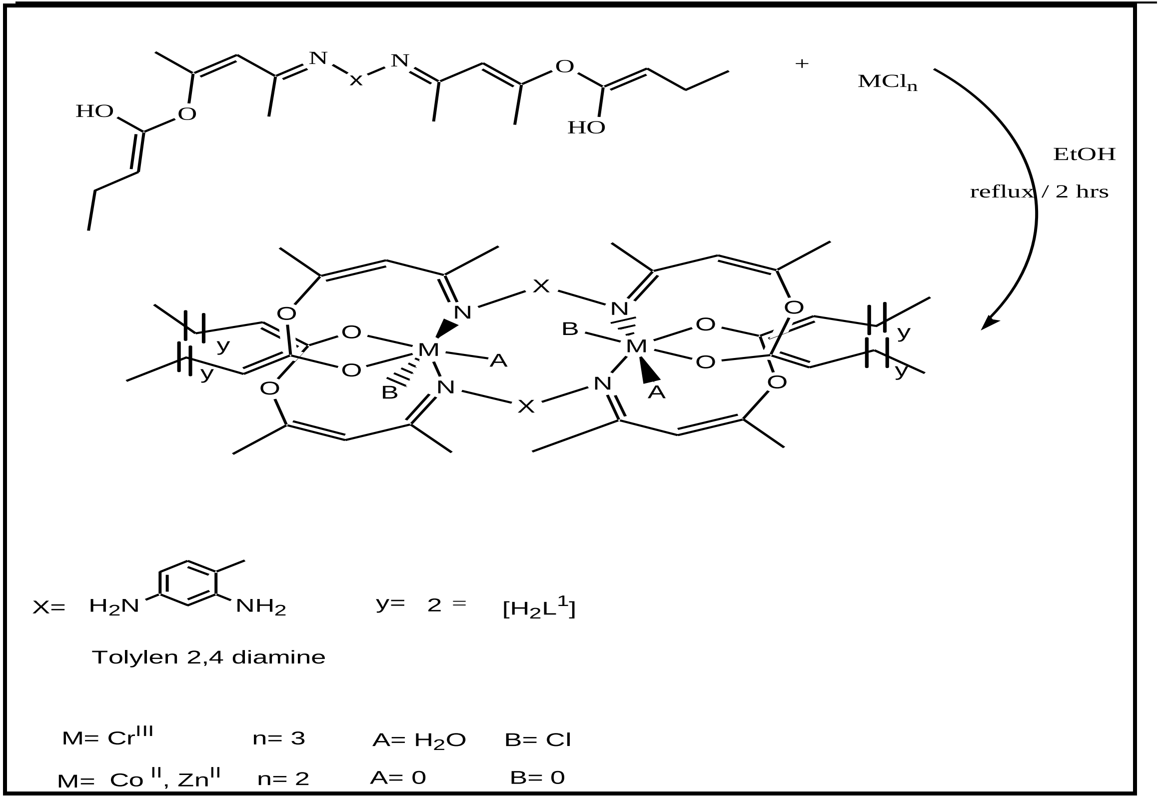
Potentially four tetradenate new ligands type N O donor atoms have been synthesized. The ligand contains two labile protons [H_2L^1], by removing these protons an anionic (-2) tetradentate system is formed. The ligands [H_2L^1] synthesized by the condensation reaction of precursor [W1] with penatanoyl chloride in 1:2 mole ratio using THF as a solvent and TEA as catalyects according to the general route shown in scheme(1)



Scheme(1):Synthesis route of the ligands

Synthesis and characterization of the complexes

All complexes were prepared by a similar method shown in scheme (2). The complexes were prepared from the reaction of the ligand with metal chloride salt in 1:1 mole ratio at reflux in ethanol and pure complexes were formed. In scheme (2)



Scheme (2): Synthesis route of complexes

FT-IR spectral data for the ligand [H$_2$L^1]

FT-IR spectrum for ligand [H$_2$L^1] show band at rang (3238) cm^{-1} refers to υ(N-H) of tautomarized schiff base(10-11). The spectrum show two new bands of weak intensity at (3200) cm^{-1} and (3053) cm^{-1} may attributed to (OH) and (=CH)$_{olif}$. respictivley, resulting from tautomerisation of ester group(10-12), the bands at rang (2957) cm^{-1}and at (2929) cm^{-1} can be refer to (C-H)$_{aro}$, and (C-H)$_{alip}$ respectivly(10). The spectrum shows another band at rang (1653) cm^{-1} can be attributed to azomethen υ(C=N). The spectrum shows new band at rang (1421) may be attributed to υ(CH_2) stretching(13). Finally the appearance of υ ((C=O)O-C) ester group at (1275) cm^{-1} and disappearance of(C–O-H) group indicates the formation of the ligand(14). The assignment of characteristic bands are summarized

FT-IR spectral data of [Cr$_2$(L^1)$_2$ (H$_2$O)$_2$ Cl$_2$] (1), [Co$_2$(L^1)$_2$] (2) and [Zn$_2$ (L^1)$_2$](3) complexes

The FT-IR spectra for complexes are shown in Figs. (5), (6) and (7). The FT-IR spectrum of Cr(III) complex revealed two bands at rang (3431) cm^{-1} and (927) cm^{-1} can be attributed to (OH) group of the coordinated water molecules(13). The infrared spectra shows band at (3498) cm^{-1},which can be attributed to(O–H) group of the hydrate water molecules in complexes (14). A strong band at [(3236) cm^{-1} can be attributed to υ(N-H) group resulted from tautomarization in complexes. The FT-IR spectra of complexes were compared with that of the free ligand in order to determine the coordination sites involved in chelation. There were some guide peaks in the spectrum of ligand, the position of these peaks were expected to change upon chelation. The detected band at (1661) cm^{-} which assigned to the stretching vibration of the azomethine group υ(C=N) of the free ligand, this band is shifted to [(1647)-(1656)] cm^{-1} in complexes,

In the spectrum of the metal complexes the υ(C-O) band underwent a shift towards 1ower frequencies and appeared at (1126) cm^{-1} in complexes, and this shift confirms the participation of ester oxygen in the (C-O-M) bond$^{(10)}$. On the other hand, in the infrared spectra of the complexes, new absorption bands at (598) cm^{-1},and (478) cm^{-1} cm^{-1} were observed indicating the υ(M–O) and υ(M–N) bonds, in complexes $^{(10)}$.

(U.V–Vis) spectral data of ligands [H_2L^1]

Spectral data of ligands show peaks of shortness wave length presenting at rang (218nm) (45871cm^{-1}) (ε_{max}=903molar^{-1}cm^{-1}) may be assigned to $\pi\rightarrow\pi^*$ transition of the aromatic rings of Schiff' s base ligands [H_2L^1] $^{(15)}$. The peaks at rang (310nm) (32258cm^{-1}) (ε_{max}=136 molar^{-1} cm^{-1}) may be assigned to the $n\rightarrow\pi^*$ transition of imine group in ligand [H_2L^1]$^{(16)}$.

(U.V–Vis) spectral data of [$Cr_2(L^1)(H_2O)_2Cl2$], [$Co_2(L^1)2$] and [Zn_2 (L^1)2]complexes

The peaks at the rang (318nm) (31446cm^{-1}) (ε_{max}=1708molar^{-1} cm^{-1}), may be assigned to M→L charge transfer transition for the complexes$^{(17)}$.

The peaks in the visible region can be associated with d-d transitions. The Cr (III) complexes shows a peak at (584nm) (17123cm^{-1}) (ε_{max}=71-15molar^{-1}cm^{-1}) assignable to $^4A_2g(F)\rightarrow{}^4T_2g(F)$ transition suggesting distorted octahedral geometry around Cr (III) ion. The result was in agood accordance with results reported $^{(18)}$..

The Co (II) complex shows a peak at (551 nm) (18148cm^{-1}) (ε_{max}=13 molar^{-1} cm^{-1}) assignable to $^4A_2(F)\rightarrow{}^4T_2(F)$ transition suggesting tetrahedral geometry around Co (II) ion. The result was in a good accordance with results reported$^{(19)}$. .

The Zn (II) metal ion of complex (3) belong to d^{10} system and these metal do not show (d–d) transition. Tetrahedral geometry was proposed around Zn (II) ion$^{(20)}$..

Nuclear magnetic resonance (^{1}H-NMR) spectral data of ligand [H_2L^1]

The ^{1}H-NMR spectrum of prepared ester Schiff baseligand [H_2L^1] in DMSO–d^6 shown in Fig.(3-38). A single chemical shift of the OH proton in the ester resulted from tautomarization was observed at (δ=9.80 ppm s,1H) because of intramolecular hydrogen bonding with the nitrogen atom on the imine group.(21) The spectrum of ligand showed chemical shift at range (δ=2.11-2.50 ppm m,21H) can be attributed to the (CH_3) methyl group protons. While the multiple chemical shift between (δ=1.23-1.56 ppm m,12H) was assigned to the methylene protons of the long alkyl chain ($-CH_2-$) . The multiple chemical shifts around (δ=7.07-7.61 ppm m,3H) may assigned to aromatic protons(22) . Finally the spectrum showed a chemical shift due to the (-N-H-) proton at (δ= 9.22 ppm,s,1H) for free ligand

Liquid crystalline properties of synthesized compounds:

Currently there is much interest in the synthesis and characterization of liquid crystalline materials containing metal atoms because of the potential to modify many physical properties via the inclusion of a metal center (23).

Liquid crystalline physical properties of prepared compounds was studied using differential scanning calorimetry (DSC) and hot- stage polarizing microscopy.

In this study it is found that ligand has an effect on the liquid crystalline properties of the prepared ligand. Some of the prepared compounds showed liquid crystalline properties, $[H_2L^1]$,

Liquid crystalline properties of $[H_2L^1]$

$[H_2L^1]$ exhibited asmectic A (SmA) at 172 **ºC** and the ligand was ternd isotropic liquid at 293 **ºC**

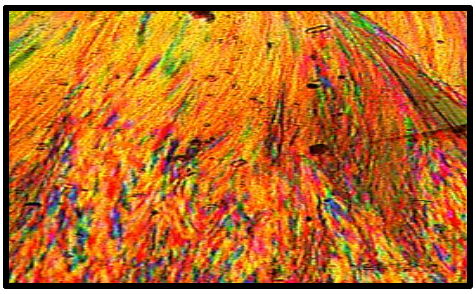


Fig (1): Sm mesophase (SmA) at (172 ºC)

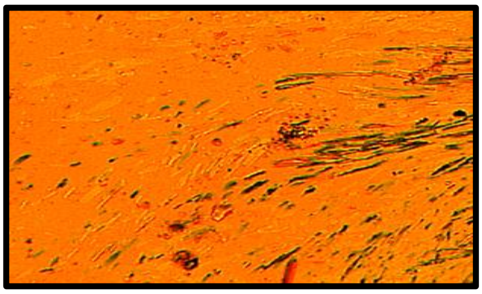


Fig (2): isotropi (SmA) at(293 ºC)

DSC thermograph showed medium transition peak indicated that $[H_2L^1]$ exhibited smectic A phase at 161.9 **ºC** and it was tern to isotropic liquid at 293 **ºC**. Fig(3).

Fig (3) DSC thermogram the compound $[H_2L^1]$

Compound	Empirical formula	M.wt	Yield %	M.p. C°	Colour	Found (calc.) %		
						C	H	N
W_1	$C_{17}H_{26}N_2O_2$	290.20	92.91	_	Darck Brown	_	_	_
$[H_2L^1]$	$C_{27}H_{46}N_2O_4$	462.67	67.74	160-163	Yelow	(70.02) 70,20	(9.94) 9.53	(6.05) 6.24

Table (1) Microanalysis and physical properties for the precursors W_1 and ligand $[H_2L^1]$

Empirical formula	**M.wt**	**Yield %**	**Colour**	**M.p.C°**	**Found, (Calc)%**	
					M	**Cl**
$[Cr_2(L^1)_2(H_2O)_2Cl_2]$	1068.06	87.93	Dark green	132-135	(4.86) 3.77	(6.63) 7.52
$[Co_2(L^1)_2]$	521.06	86.98	Green	110-112	(11.29) 10.10	Nil
$[Zn_2(L^1)_2]$	528.06	91.99	Pal Brown	120-122	(12.38) 13.25	Nil

Table (2) Physical properties and elemental analysis of complexes $[H_2L^1]$.

Table (3) Infrared spectral data (wave number ύ) cm^{-1} of the starting materials, precursor [W1], ligand $[H_2L^1]$

Mpound	**υ(O-H)**	**υ(NH2)**	**υ(N-H)**	**υ(C=O)**	**υ(C=N)**	**υ(CH2)**	**υ(C-O)**	**C-Cl**	**Additional peaks**
Tolylen2-4diamine	_	3381(asy) 3354(sy) (s)		_	_		_		υ(C-H)aro.(3020) , υ (C-H)alip(2926), υ(C=C)aro.(1581),
Acetylacetone	3003(b)	_	_	1728(m)	_	1417(m)	1244 (s)		υ(=CH)olif.(2970) υ(C-H)alip.(2922) υ(C=C)olif.(1604), υ(C=C)aro.(1543)
Pentanoic acidchloride	_	_	_	1797(s)	_	1413(m)	_	682(m)	υ(C-H)alip.(2956)
Precursor[W1]	3361(w)	_	3232(m)	1668 (w)	1602(s)		1286(s)		υ(=CH)olif.(2970) υ(C-H)aro.(2924) υ(C-H)alip.(2860), υ(C=C)olif(1564) υ(C-H)aro(1516),
$[H_2L^1]$	3300(b)	_	3238(m)	_	1653(s)	1421(m)	1275(m)		υ(=CH)olif.(3053) υ(C=H)aro.(2957) υ(C-H)alip (2869), υ(C=C)olif.(1600), υ(C=C)olif.(1537)

br=broad s=strong alip=aliphatic υ=stretching sy=symmetric w=weak m=medium aro=aromatic asy=asymmetric olif=olifenic

Table (4) Infrared spectral data (wave number ύ) cm^{-1} of the ligands $[H_2L^1]$ and $[H_2L^2]$and their metal complexes

Compound	**υ(O-H)**	**υ(N-H)**	**υ(C=N)imini**	**υ(C-O)**	**υ(M-O)**	**υ(M-N)**
$[H_2L^1]$	3120(br)	3238 (m)	(1653 s)	1275 (m)	_	_
$[Cr_2(L^1)2(H_2O)_2Cl2]$	3388 (br)	3240(m)	1649 (s)	1134(w)	570(w)	450(w)
$[Co_2(L^1)2]$	3398(br)	3240(m)	1647(s)	1126(w)	586(w)	459 (w)
$[Zn_2(L^1)2]$	3367 (br)	(3236 m)	1647 (s)	1126 (w)	567 (w)	486 (w)

Table (5) Electronic spectral data of ligands $[H_2L^1]$

Compound	**λ (nm)**	**υ^{-} cm^{-1}**	**ε_{ma}molar^{-1} cm^{-1}**	**Assignments**
$[H_2L^1]$	218	45871	903	$\pi\rightarrow\pi^*$
	310	32258	136	$n\rightarrow\pi^*$

Table (6) Electronic spectral data of $[H_2L^1]$ and$[H_2L^2]$ complexes

Compound	**Wave number**		**ε_{max} molar^1.cm^1**	**Assignment**	**Suggested Structure**
	nm	**cm^{-1}**			
$[Cr_2(L^1)_2(H_2O)_2Cl_2]$					Octahedral
	318	31446	1708	Ligand field	
	412	24271	114	Charge transfer	
	584	17123	71	$^4A_2g(F)\rightarrow{}^4T_2g(F)$	
$[Co_2(L^1)_2]$	233	42918	1881	Ligand field	Tetrahedral
	318	31446	192		
	343	29154	112	Charge transfer	
	672	14880	4	$^4A_2(F)\rightarrow{}^4T_2(F)$	
$[Zn_2(L^1)_2]$	260	38461	3995	Ligand filed	Tetrahedral
	312	32051	2100		
	318	31446	1708	Charge transfer	

Table (7) ^{1}H-NMR spectral data for $[H_2L^1]$measured in DMSO–d^6 and chemical shift in ppm (δ)

Compound	**Funct. Group**	**δ (ppm)**
$[H_2L^1]$	O-H	(9.80) (1H, S)
	N-H	(9.22) (1H,S)
	CH_3	(2.11-2.50) (21H,m)
	Ar-H	(7.07.-7.61) (3H,m)
	CH_2	(1.23-1.56) (12H,m)

Table(8) The molar conductivity of the $[H_2L^1]$

No. Compound	**Compound**	**Λ_m S.cm^2 molar^{-1}**	**Ratio**
1	$[Cr_2(L^1)_2(H_2O)_2Cl_2]$	18.80	Non
2	$[Co_2(L^1)_2]$	10.65	Non
3	$[Zn_2(L^1)_2]$	3.40	Non
4	$[Cr_2(L^1)_2(H_2O)_2Cl_2]$	18.25	Non

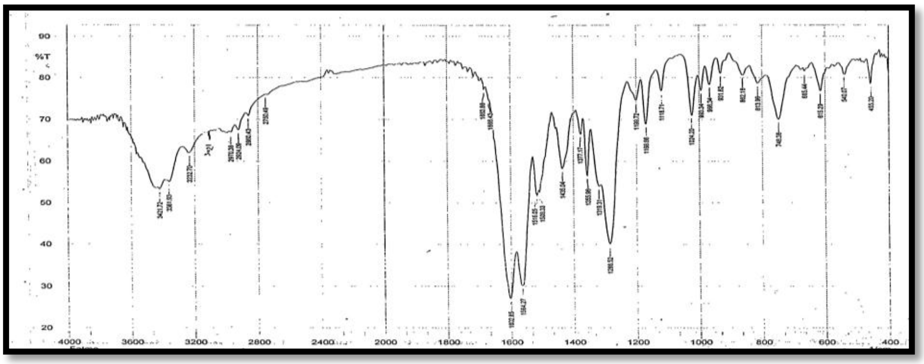


Fig.(4):FT-IR spectrum of the ligand [H_2L^1]

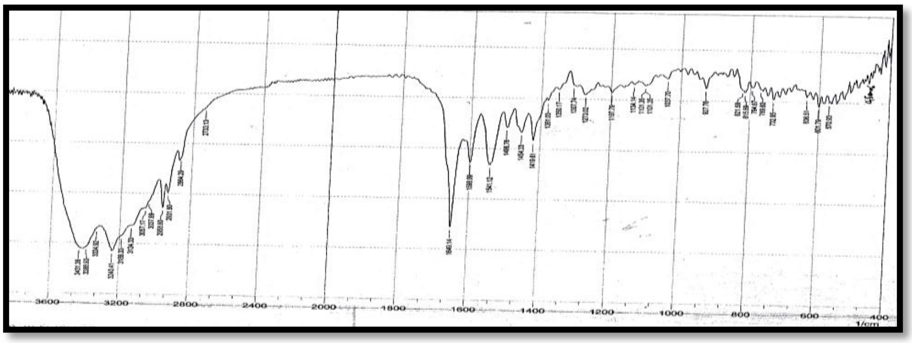


Fig.(5): FT-IR specrum of [Cr_2 $(L^1)_2$ (H2O) $_2$Cl2]Complex

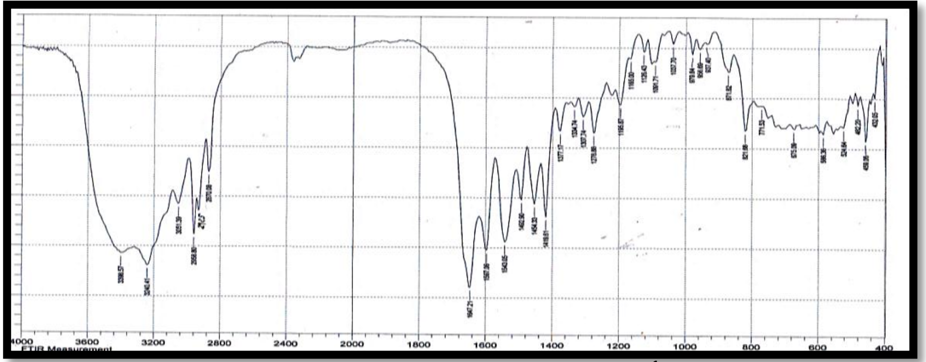


Fig.(6): FT-IR specrum of [Co_2 $(L^1)_2$] Complex

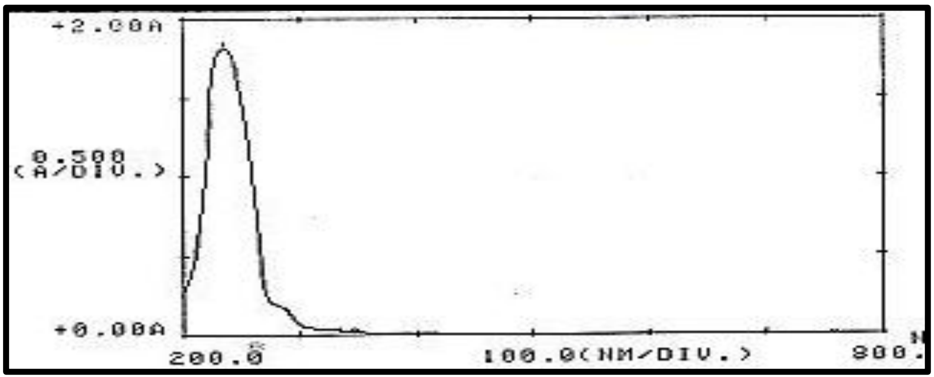


Fig.(7): FT-IR specrum of [Zn_2 $(L^1)_2$] Complex

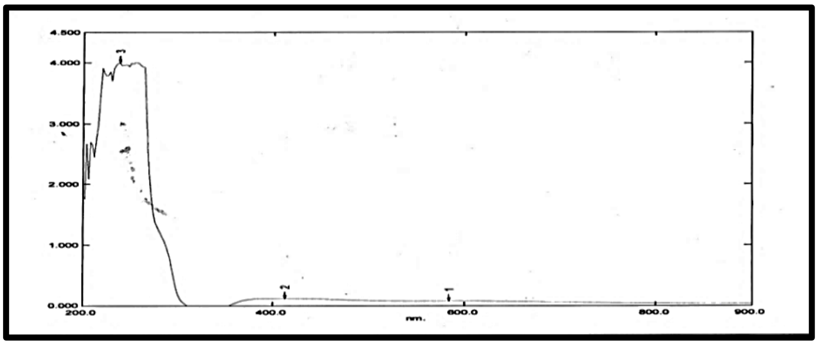


Fig.(8):Electronic spectrum of the ligand [H_2L^1]

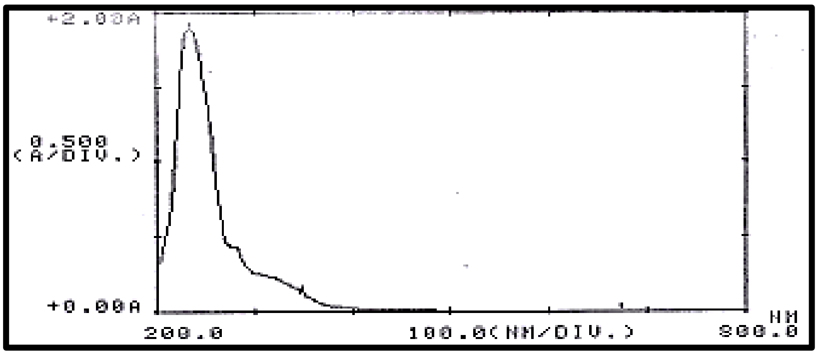


Fig.(9):Electronic spectrum of [$Cr_2(L^1)_2(H_2O)_2Cl_2$] Complex

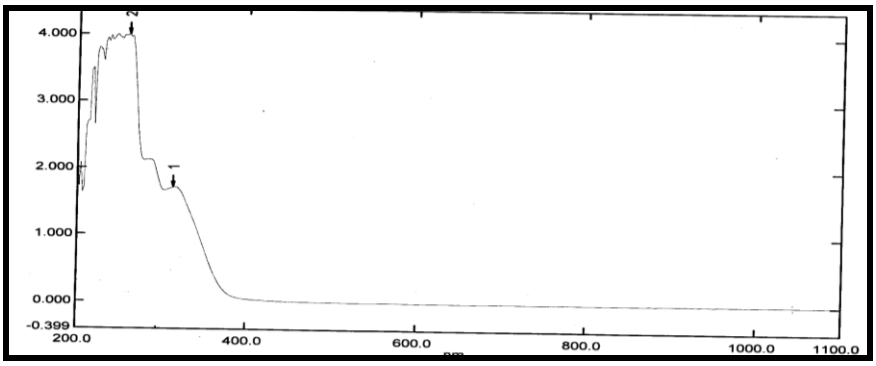


Fig.(10):Electronic spectrum of [$Co_2(L^1)_2$]complex

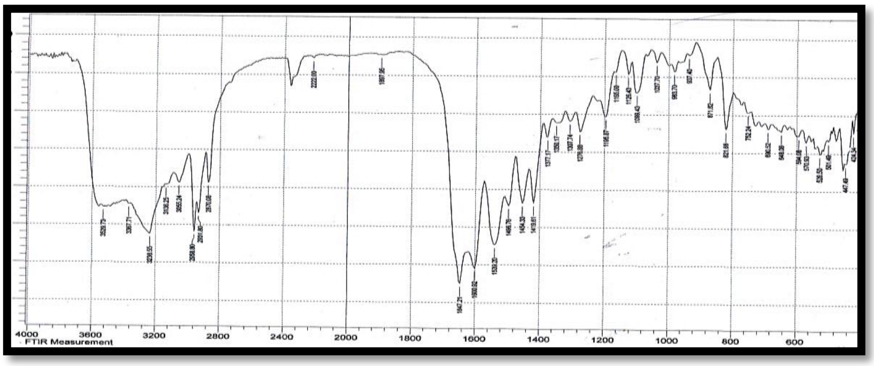


Fig.(11):Electronic spectrum of [$Zn_2(L^1)_2$]complex

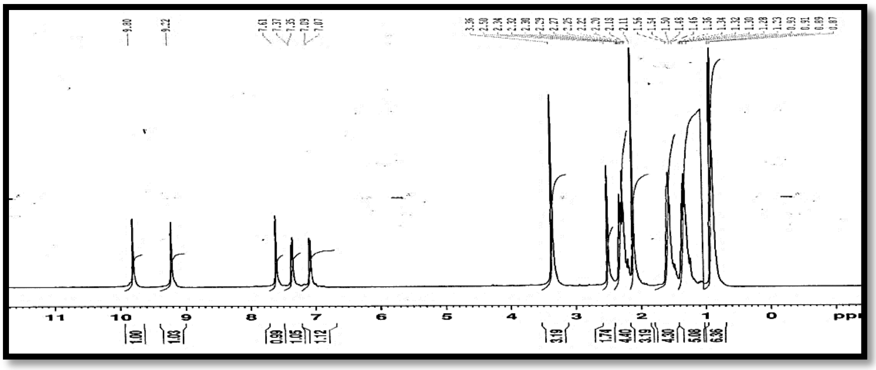


Fig.(12): ^{1}H-NMR spectrum of the ligand [H_2L^1]

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