Iraqi Journal of Physics, 2018 *Vol.16, No.37, PP. 79-87*
DOI: 10.20723/ijp.16.37.79-87

Synthesis and characterization of ligands derived 2-hydroxy-1-naphthaldehyde and their complexes with divalent metal ions (Mn^{+2}, Fe^{+2}, Ni^{+2})

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Abstract

In this work, Schiff base ligands L1: N, N-bis (2-hydroxy-1-naphthaldehyde) hydrazine, L2: N, N-bis (salicylidene) hydrazine, and L3:N –salicylidene- hydrazine were synthesized by condensation reaction. The prepared ligands were reacted with specific divalent metal ions such as (Mn^{2+}, Fe^{2+}, Ni^{2+}) to prepare their complexes. The ligands and complexes were characterized by C.H.N, FT-IR, UV-Vis, solubility, melting point and magnetic susceptibility measurements. The results show that the ligands of complexes (Mn^{2+}, Fe^{2+}) have octahedral geometry while the ligands of complexes (Ni^{2+}) have tetrahedral geometry.

Key words
2-hydroxy-1-naphthaldehy, hydrazine hydrate, metal complexes.

Article info.
Received: Nov. 2017
Accepted: Nov. 2017
Published: Jun. 2018

تحضير وتشخيص ليكاندات المشتقة من 2-هيدروكسي نفثالديهايد ومعقداتها مع الايونات الثنائية $Ni^{(II)}$,$Fe^{(II)}$,$Mn^{(II)}$

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الخلاصة

في هذا البحث حضرت ليكندات قواعد شف
L1:N,N-bis(2-hydroxy-1-naphthaldehyde)hydrazineL2:N,N-bis(salicylidene) ethylenediamineL3:N –salicylidene- hydrazine
بواسطة تفاعل التكاثف. حضرت معقدات تناسقية من خلال تفاعل الليكندات المحضرة مع ايونات الفلزات (Mn^{2+}, Fe^{2+}, Ni^{2+}). تم تشخيص المركبات المحضرة باستخدام قياسات جهاز تحليل العناصر C.H.N ومطياف الأشعة تحت الحمراء ومطياف الأشعة فوق البنفسجية والمرئية وقابلية الذوبان ونقطة الانصهار و القابلية المغناطيسية. بينت النتائج إن روابط المعقدات (Mn^{2+}, Fe^{2+}) هي ذات شكل هندسي ثمانية السطوح بينما روابط المعقدات (Ni^{2+}) هي ذات شكل هندسي رباعية السطوح.

Introduction

In the last decade, there has been a dramatic growth of the interest inorganic complex based material that exhibit unusual properties [1-5]. The chemical organic compound containing azomethin group (-HC=N-) and anils derived from an amines and aldehyde or keton. The coordination of these ligands and metals are an important class of ligands coordinate to metal ion are very important in the development of coordination chemistry. These complexes have a lot of uses such as, applications of medical and pharmaceutical, biology, industrial [6-11]. In this work, metal ions like (Mn^{2+}, Fe^{2+}, Ni^{2+}) complexes were synthesized and characterized by elemental analyses, IR, UV, and magnetic susceptibilities. The Schiff bases were also synthesized and their structures investigated by elemental analyses, FT-IR, and UV spectra then compared with their complexes.

Experiments

Preparation of ligand: N, N-bis (2-hydroxy-1-naphthaldehyde) hydrazine: a mixture of hydrazine (0.6g, 0.01mmol) in (15 ml) ethanol with (0.72 g, 0.02 mmol) aldehyde in ethanol refluxed for the chemical equation of 2h then concentrated of the solution. The precipitate was separated by filtration, washed with ethanol and then air-dried. Fig. 1 shows the ligand preparation.

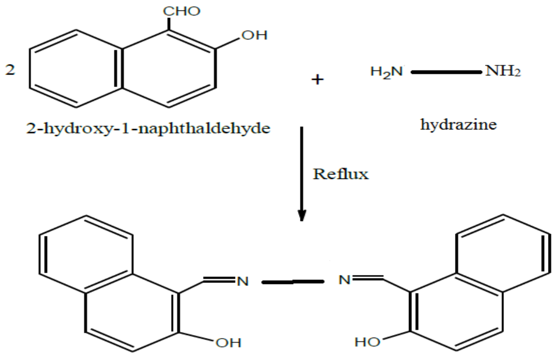

Fig. 1: The chemical equation of ligand preparation.

Preparation of the complex: Bis N,N-bis (2-hydroxy-1-naphthaldehyd) hydrazine manganese(∏): A mixture of $MnSO_4$(0.01 mmol) in ethanol with (0.02 mmol) in ethanol were refluxed for 2h then concentrated of the solution. The precipitate was separated by filtration, washed with ethanol and then air-dried.

Preparation of the complex: Bis N,N-bis (2-hydroxy-1-naphthaldehyd) hydrazin Iron (∏): A mixture of $FeSO_4$. $7H_2O$(0.01 mmol) in ethanol with (0.02mmol) in ethanol were refluxed for 2h then concentrated of the solution, the precipitate was separated by filtration, washed with ethanol and then air-dried.

Preparation of the complex: Bis N,N-bis (2-hydroxy-1-naphthaldehyde) hydrazine nickel (∏): A mixture of NiCl. $6H_2O$(0.01 mmol) in ethanol with (0.02 mmol) in ethanol were refluxed for 2h then concentrated of the solution, the precipitate was separated by filtration, washed with ethanol and then air-dried.

The IR spectra of ligands and its complexes are obtained by Fourier transform infrared spectroscopy (FTIR) Japan- Shimadzu uses KBr substrates. In order to study the optical properties of prepared samples, the absorbance measurements were carried out by using UV/Visible Shimadzu - Japan spectrophotometer. The elemental micro analysis of C,H,N was carried out by EuroEA 3000 system.

Results and discussion

The prepared ligands were studied and characterized by using the following techniques:

Elemental microanalysis (C,H,N)

The results obtained from Elemental Microanalysis (C.H.N) for show high agreement with calculated theoretical weight percentage as shown in Table 1.

Table 1: The comparison between the results of (C.H.N) and theoretical calculations.

Experimental			**Molecule weight gm\ mole**	**Compounds**
theoretical calculations				
N%	**H%**	**C%**		
8.32 9.13	4.7 (5.63)	77.64 (78.72)	340	$L_1(C_{22}H_{16}N_2O_2)$
7.62 (6.91)	4.35 (4.22)	71.93 (70.52)	734	$[Mn(L_1)_2]$ $(Mn\ C_{44}H_{32}N_4O_4)$
7.60 (6.94)	4.34 (4.15)	71.73 (70.25)	736	$[Fe(L_1)_2]$ $(Fe\ C_{44}H_{32}N_4O_4)$
7.57 (6.65)	4.33 (4.71)	71.44 (70. 53)	739	$[Ni(L_1)_2]$ $(Ni\ C_{44}H_{32}N_4O_4)$
20.58 (19.973)	5.88 (4.812)	61.76 (62.233)	136	$L_2\ (C_7H_8N_2O)$
14.14 (13.841)	4 (3.927)	42.42 (41.471)	396	$[Mn(L_2)_2]\ Cl_2$ $(Mn\ C_{14}H_{16}N_4O_2\ Cl_2)$
14 (13.589)	4 (4.042)	42.21 (44.244)	398	$[Fe(L_2)_2]\ Cl_2$ $(Fe\ C_{14}H_{16}N_4O_2\ Cl_2)$
16.91 (15.94)	4.83 (4.64)	50.75 (51.843)	331	$[Ni(L_2)_2]$ $(Ni\ C_{14}H_{16}N_4O_2)$
10.44 (10.267)	5.96 (5.95)	71.56 (69.792)	268.32	$L_3\ (C_{16}H_{16}N_2O_2)$
7.1 (8.084)	4. (4.602)	48.69 (47.104)	392.253	$[Mn(L_3)]\ Cl_2$ $(Mn\ C_{16}H_{16}N_2O_2\ Cl_2)$
7 (6.946)	3 (4.381)	48.587 (49.555)	395.167	$[Fe(L_3)]\ Cl_2$ $(Fe\ C_{16}H_{16}N_2O_2\ Cl_2)$
8.5 (8.562)	4,8 (4.56)	58.65 (57.869)	327. 32	$[Ni(L_3)]$ $(Ni\ C_{16}H_{16}N_2O_2)$

Solubility

The solubility of prepared compounds were experimented in organic solvents and distilled water which shown in Table 2:

Table 2: Solubility of prepared compounds.

Melting point ^oC	**Colors**	**Compounds**
260-263	Dark yellow	$L_1\ (C_{22}H_{16}N_2O_2)$
163-166	Dark red	$[Mn(L_1)_2]$ $(Mn\ C_{44}H_{32}N_4O_4)$
170-173	Dark red	$[Fe(L_1)_2]$ $(Fe\ C_{44}H_{32}N_4O_4)$
217-220	red	$[Ni(L_1)_2]\ Cl_2$ $(Ni\ C_{44}H_{32}N_4O_4)$
210-213	light pink	$L_2(C_7H_8N_2O)$
243-246	Dark Brown	$[Mn(L_2)_2]\ Cl_2$ $(Mn\ C_{14}H_{16}N_4O_2\ Cl_2)$
245-248	Dark red	$[Fe(L_2)_2]\ Cl_2$ $(Fe\ C_{14}H_{16}N_4O_2\ Cl_2)$
247-250	red	$[Ni(L_2)_2]$ $(Ni\ C_{14}H_{16}N_4O_2)$
126-128	Light yellow	$L_3(C_{16}H_{16}N_2O_2)$
125-127	Brown	$[Mn(L_3)]\ Cl_2$ $(Mn\ C_{16}H_{16}N_2O_2\ Cl_2)$
247-250	Dark Brown	$[Fe(L_3)]\ Cl_2$ $(Fe\ C_{16}H_{16}N_2O_2\ Cl_2)$
245-247	Dark red	$[Ni(L_3)]$ $(Ni\ C_{16}H_{16}N_2O_2)$

Magnetic susceptibility measurements

The magnetic sensitivity of prepared compounds were measured by using device of Auto magnetic susceptibility Balance sherwood scientific as shown in Table 3.

Table 3: The magnetic sensitivity measurements of prepared compounds.

Effective magnetic torque B.M(μ_{eff})	**Number of individual electrons**	**Atomic sensitivity $X_A x10^{-6}$**	**Molecular sensitivity $X_M x10^{-6}$**	**Weight sensitivity $X_g x10^{-6}$**	**Compounds**
1.6	1	200.875	2.715	3.7	$[Mn(L_1)_2]$
0.0	0.0	0.0	0.0	0.0	$[Fe(L_1)_2]$
2.11	2	4598.15	4479.01	10.28	$[Ni(L_1)_2]$
1.7	1	83.966	1.346	3.4	$[Mn(L_2)_2]$
0.0	0.0	0.0	0.0	0.0	$[Fe(L_2)_2]$
3.8	2	4594.12	4485.01	9.29	$[Ni(L_2)_2]$
2.3	1	1.140	980.632	2.5	$[Mn(L_3)]$
0.0	0.0	0.0	0.0	0.0	$[Fe(L_3)]$
3.31	2	4598.14	4485.01	10.27	$[Ni(L_3)]$

(L_1) Correlation factor D= -160.24
(L_2) Correlation factor D= -172.38
(L_3) Correlation factor D= -82.62

The magnetic susceptibility measurements show that the complexes have magnetic torque values which range from 1.6-3.31 B.M., indicating the presence of four unpaired electrons per Mn(III) ion. These magnetic moments are in good agreement with Mn(III) in an octahedral configuration and the same observations for other ligands [2, 7, 11].

Infrared spectral studies

The prepared ligands and complexes were studied by FTIR spectroscopy. The results show that the main bands are related to: absorption bands at 1324-1340 cm^{-1} which attributed to the vibrations of (C-O) while the (C=N) group appears in 1610 -1637 cm^{-1} .Also the (C-H) group observed at 750-460 cm^{-1} which attributed to (M-O) and (M-N) vibration. (O-H) group is clear appeared at 3400 cm^{-1}. The FTIR spectra of prepared compounds are shown in Figs. 2-7 and Table 4 shows the summarized results of all compounds.

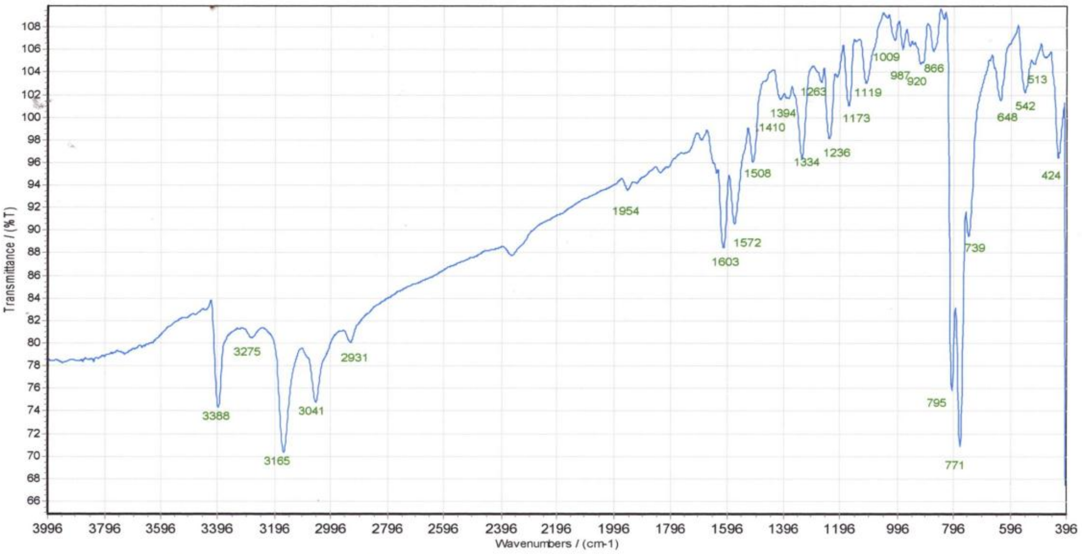

Fig. 2: IR spectrum of ligand L1.

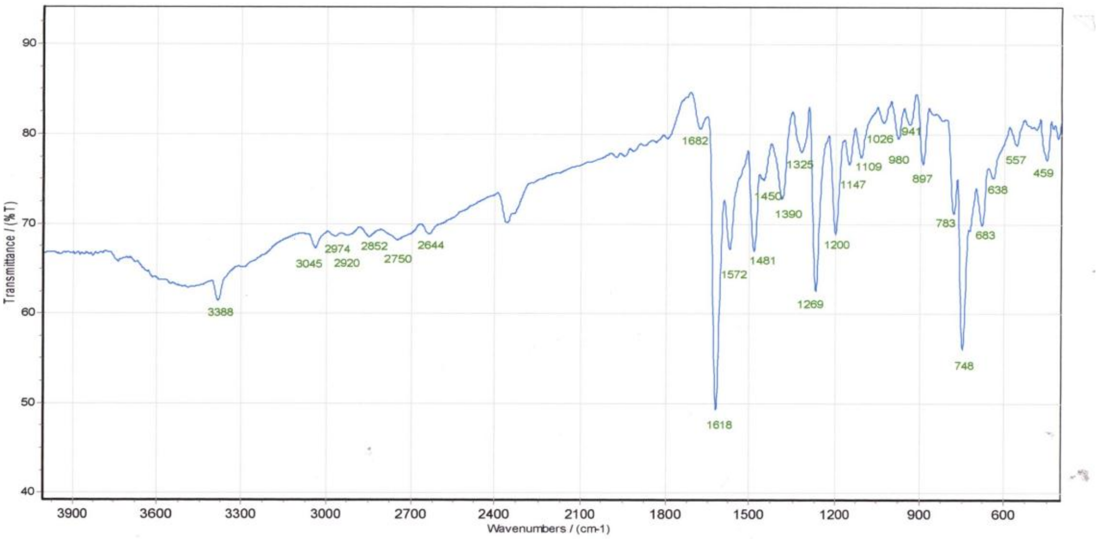

Fig. 3: IR spectrum of ligand L2.

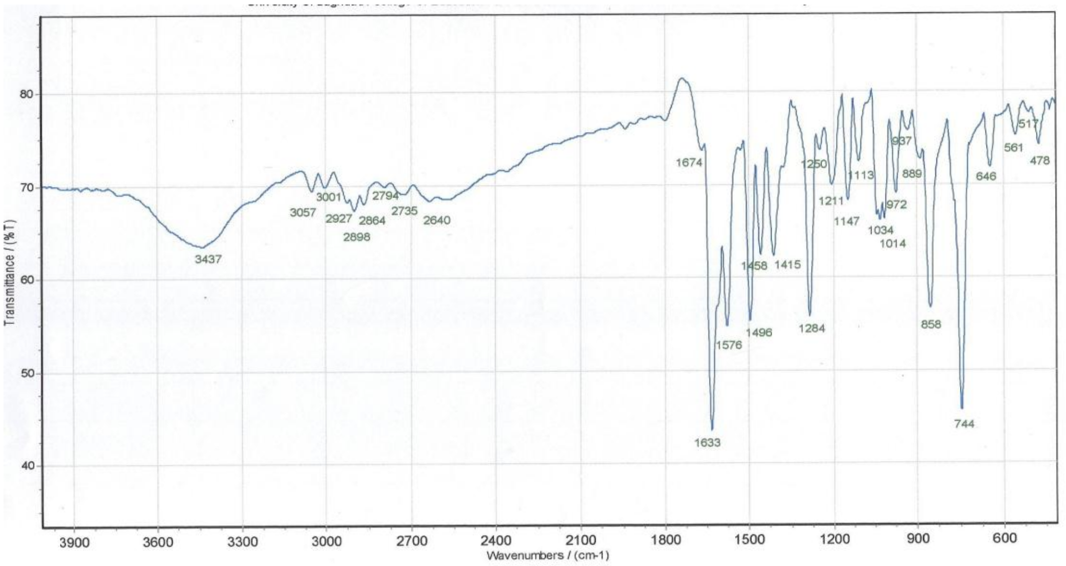

Fig. 4: IR spectrum of ligand L3.

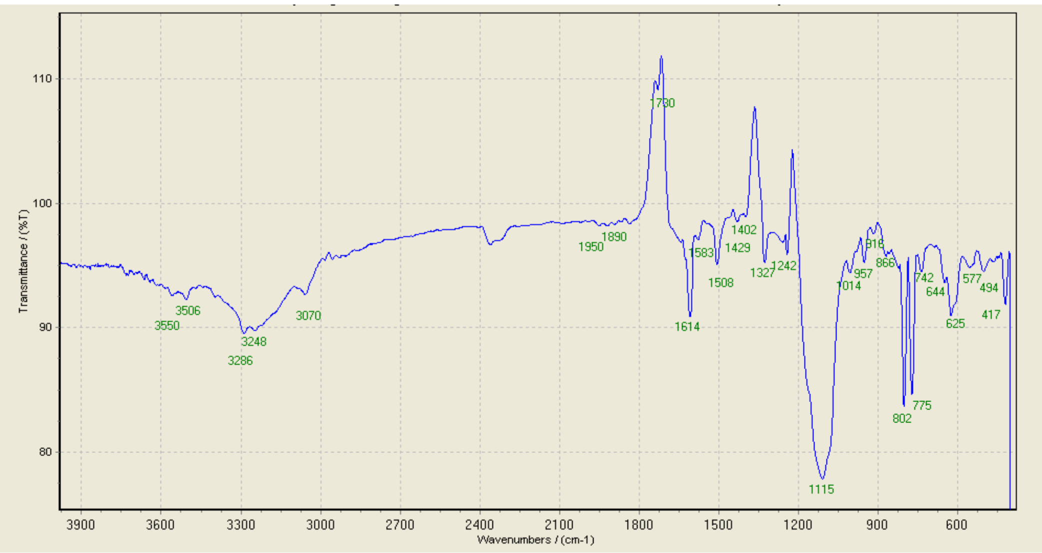

Fig. 5: IR spectrum of ligand [Mn-L_1].

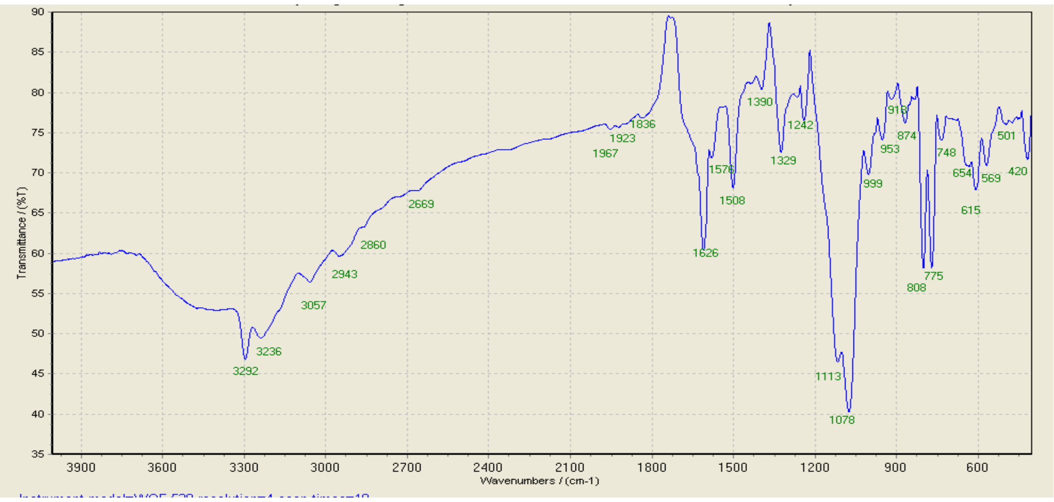

Fig. 6: IR spectrum of ligand [Fe-L_1].

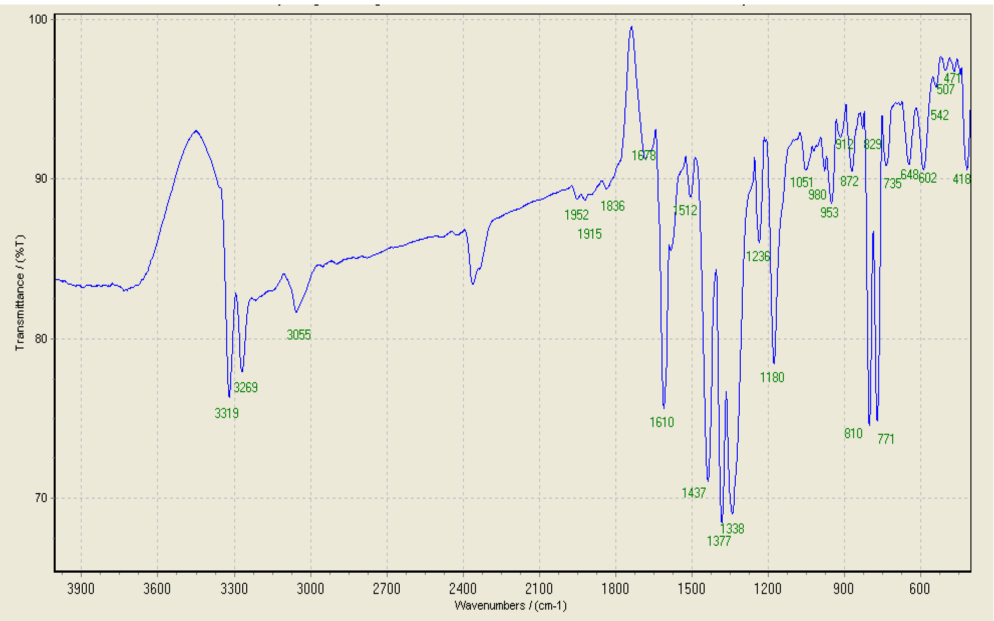

Fig. 7: IR spectrum of ligand [Ni-L_1].

Table 4: Summarized results of all compounds.

No	complex	ν(C=C)	ν(C-N)	ν(C=N)	ν(C-O)	ν (M-N)	ν(M-O)
1	**(L_1)**	15 72	1173	1603	1236	542	424
2	**(L_2)**	15 72	1147	1618	1269	557	458
3	**(L_3)**	1576	1147	1633	1284	517	478
4	**[Mn(L_1)$_2$]**	1579	1119	1626	1259	577	417
5	**[Fe(L_1)$_2$]**	1576	1132	1610	1273	569	420
6	**[Ni(L_1)$_2$]**	1579	1173	1626	1232	542	418
7	**[Mn(L_2)$_2$]**	1576	1144	1622	1277	561	459
8	**[Fe(L_2)$_2$]**	1579	1113	1614	1269	565	459
9	**[Ni(L_2)$_2$]**	1576	1151	1618	1273	592	467
10	**[Mn(L_3)]**	15 76	1136	1637	1246	557	424
11	**[Fe(L_3)]**	1535	1146	1630	1188	542	482
12	**[Ni(L_3)]**	1539	1138	1633	1240	521	432

UV-VIS spectroscopy

UV-Vis spectra of ligands were studied using dimethyl sulfoxide (DMSO) at 10^{-3} mol at room temperature. The spectrum of ligand (L_1) shows two absorption bands at 284 nm wavelength and the molar absorptivity ϵmax=1716 L.mol $^{-1}$.cm^{-1}. This result attributed to the electronic transitions ($\pi - \pi^*$), while the molar absorptivity ∊max at 357 nm equals to 983 L. mol^{-1}.cm^{-1} attributed to n $\rightarrow \pi^*$ electronic transitions [2].

UV-VIS spectrum of ligand [Mn-L_1] shows the absorption bands at 236 nm with ∊max = 1556 L.mol^{-1}.cm^{-1} attributed to charge transitions while at 345 nm the ∊max=2343 L.mol^{-1}.cm^{-1} result of electronic transitions ^{6}A1g → ^{4}Eg(G). Also the molar absorptivity ∊max = 1345 L.mol^{-1}.cm^{-1} of ^{6}A1g → ^{4}T$_2$g(G) appeared at 360 nm. The result of ligand [Fe-L_1] shows that the absorption bands at 246 nm with ∊max = 1058 L.mol^{-1}.cm^{-1} which attributed to electronic transitions of ^{6}A1g→ ^{4}Eg(G) ∊max = 60 L.mol^{-1}.cm^{-1} at 871nm result of ^{6}A1g → ^{4}T$_2$g(G) transitions. The last ligand [Ni-L_1] shows the absorption bands located at 236 nm with ∊max = 1523 L.mol^{-1}.cm^{-1} result of charge transitions while at 345 nm the ∊max= 2337 L.mol^{-1}.cm^{-1} attributed to electronic transitions of ^{6}A1g → ^{4}Eg(G). Table 5 shows the absorption parameters of, UV-Vis spectra, and the results discern out the orthorhombic geometry [2, 5].

UV-VIS spectrum of ligand L_2 shows that the absorption bands release at 288 nm with ∊max= 2271 L.mol^{-1}.cm^{-1} result of electronic transitions ($\pi - \pi^*$), while at 361 nm the ∊max = 1379 L.mol^{-1}.cm^{-1} attributed n $\rightarrow \pi^*$. For ligand [Mn-L_2] the absorption bands at 292nm with ∊max = 1598 L.mol^{-1}.cm^{-1} result of electronic transitions ^{6}A1g → ^{4}T$_2$g(G). The ligand [Fe-L_2] appears the absorption bands at 229 nm with ∊max = 1853 L.mol^{-1}.cm^{-1} attributed to charge transitions at 361 nm the ∊max = 185 L.mol^{-1}.cm^{-1} result of electronic transitions ^{6}A1g → ^{4}Eg(G) and at 825 nm with ∊max = 160 L.mol^{-1}.cm^{-1} result of ^{6}A1g → ^{4}T$_2$g(G). The ligand [Ni-L_2] spectra become clear, that the absorption bands located at 292 nm with ∊max = 1702 L.mol^{-1}.cm^{-1} attributed to charge transitions, while at 360 nm the ∊max=1251L.mol^{-1}.cm^{-1} result of electronic transitions ^{6}A1g → ^{4}Eg(G) and at 830 nm with ∊max = 90 L.mol^{-1}.cm^{-1} result of ^{6}A1g → ^{4}T$_2$g(G). From these result we suggested the tetrahedral geometry for prepared ligand L_2 [5].

The UV-VIS spectrum of ligand L$_3$ shows, that the absorption bands at 287nm with $\in$max = 4040 L.mol^{-1}.cm^{-1} which result of the electronic transitions ($\pi - \pi^*$) and at 360 nm the $\in$max = 2258 L.mol^{-1}.cm^{-1} of electronic transitions n $\rightarrow \pi^*$ the absorption bands of ligand [Mn-L$_3$] at 238 nm the $\in$max = 2385 L.mol $^{-1}$.cm^{-1} attributed to charge transitions at 305 nm with $\in$max = 2208 L.mol $^{-1}$.cm^{-1} result of ^{6}A1g → ^{4}Eg(G) and at 403 nm the $\in$max = 264 L.mol^{-1}.cm^{-1} attributed ^{6}A1g → ^{4}T$_2$g(G) electronic transitions [9].

The UV-VIS spectrum of ligand [Fe-L$_3$] shows that the absorption bands appears at 241 nm with $\in$max = 1925 L.mol $^{-1}$.cm^{-1} which attributed to charge transitions at 740 nm the $\in$max= 80 L.mol $^{-1}$.cm^{-1} attributed to the electronic transitions of ^{6}A1g → ^{4}Eg(G) and at 887 nm with $\in$max = 70 L.mol^{-1}.cm^{-1} attributed ^{6}A1g → ^{4}T$_2$g(G) according to above result and analysis we can suggested that the ligand with orthorhombic geometry. On other hand, the ligand [Ni-L$_3$] spectra appears that the absorption bands located at 245 nm with $\in$max = 2350 L.mol^{-1}.cm^{-1} result of charge transitions while at 326 nm the $\in$max= 689 L.mol^{-1}.cm^{-1} attributed to electronic transitions of ^{6}A1g → ^{4}T$_2$g(G) these spectra absorption result that the suggestion of the ligand with tetrahedral [11, 12]. Table 5 refers absorption locations of prepared ligand from UV-VIs spectra.

Table 5: UV-Vis spectra results.

No	Compound	λ (nm)	Abs.	$\in$max (mole^{-1}, cm^{-1})	Effective magnetic torque μ_{eff} (B.M)
1	(L$_1$)	284 357	1.716 0.983	1716 983	-
2	(L$_2$)	288 361	2.271 1.379	2271 1379	-
3	(L$_3$)	287 360	4.040 2.258	4040 2258	-
4	[Mn(L$_1$)$_2$]	236 345 360	1.716 2.343 1.345	1716 2343 1345	1.6
5	[Fe(L$_1$)$_2$]	246 360 871	1.058 1.203 0.60	1058 1203 60	0.0
6	[Ni(L$_1$)$_2$]	236 345 805	1.553 2.337 0. 180	1553 2337 180	2.11
7	[Mn(L$_2$)$_2$]	292 360 848	1.598 1.213 0.170	1598 1213 170	1.7
8	[Fe(L$_2$)$_2$]	229 361 825	1.853 0.185 160	1853 185 160	0.0
9	[Ni(L$_2$)$_2$]	292 360 830	1.702 1.251 0.90	1702 1251 90	3.8
10	[Mn(L$_3$)]	238 305 403	2.385 2.208 0.264	2385 2208 264	2.3
11	[Fe(L$_3$)]	241 740 887	1.925 0.008 0.007	1925 80 70	0.0
12	[Ni(L$_3$)]	245 326	2.350 0.360	2350 360	3.31

Conclusions

The (Mn^{+2}, Fe^{+2}, Ni^{+2}) complexes are coloured, insoluble in most of the organic solvent but soluble in DMF and DMSO. C.H.N, FT-IR, UV-VIS, and N.M.R analysis were carried out to characterize the prepared ligands. The infrared spectral data indicate that all the ligands act as mononegative bidentate species towards (Mn^{+2}, Fe^{+2}, Ni^{+2}) complexes. Electronic spectra supported by magnetic moment revealed orthorhombic geometry for ligand L1 and tetrahedral geometry for ligand L2 and L3.

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