Synthesis, Characterization and Theoretical Study of Some Metal Ions with Mixed ligands

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Abstract:-

A new mixed ligand complexes were prepared from 2-hydroxy benzylidene-N-(3-carboxyl phenyl) amine and 2-amino pyrimidine with Mn(II),Fe(II),Co(II),Ni(II) and Cu(II).The prepared complexes were characterized by element analysis, FTIR spectroscopy, Uv-vis spectroscopy, magnetic susceptibility and conductivity measurements. From the spectral measurements. From the above data ,the proposed molecular structure for the complexes are tetrahedral geometry. The Structure geometries of these compounds were also suggested in gas phase by using theo retical treatment , using Hyper chem.-6 program through the molecular mechanics and semi-empirical calculations .The heat of formation(ΔHf^o) and binding energy(ΔE_b) for the free ligands and its metal complexes were calculated by PM3 methods.

Key words:-Schiff base, Complexes of schiff base, Complexes of mixed ligands ,complexes of 2-amino pyrimidine.

Introduction:

Schiff bases have often been used as chelating ligands in the field of coordination chemistry and their metal complexes are of great interest for many years [1]. Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer and herbicidal applications [2-4]. They serve as models for biologically important species and find applications in biomimetic catalytic reactions [5]. Chelating ligands containing N, S and O donor atoms show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions [6]. The prepared complexes containing from different ligands were found to be quite stable. mixed-ligand complexes play key roles in some biological processes [7-8]. In this paper we describe the synthesis, physical properties and theoretical study of a new mixed-ligand complex of Mn(II),Fe(II),Co(II),Ni(II) and Cu(II) with 2-hydroxy benzylidene-N-(3-carboxyl phenyl) amine and 2-

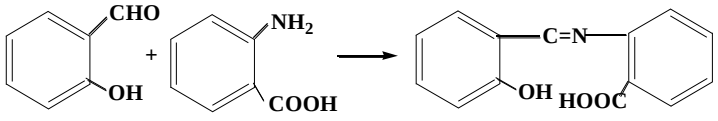
amino pyrimidine . This compound is the tetracoordinate

Materials and Methods

All chemicals used were of reagent grade and used without further purification manganese (II) chloride (Aldrich), iron (II) chloride(Aldrich), cobalt(II)chloride (Aldrich) ,nickel(II)chloride (4000-200)cm^{-1} and samples were measured as CsI discs. Electronic spectra were obtained using (Uv-160) Shimadzu Spectrophotometer at room temperature using ethanol as a solvent .The metal content was estimated using Atomic Absorption Shimadzu AA670 Spectrophotometer . Conductivity measurements were obtained using (WTW) conductometer, these measurements were obtained in DMSO using concentration 10^{-3} M at 25° C .Magnetic Susceptibility measurements was obtained at 25°C in the solid state, applying Faraday's method using Bruker BM6 instrument .

Synthesis of 2-hydroxy benzylidene-N-(3-carboxyl phenyl) amine

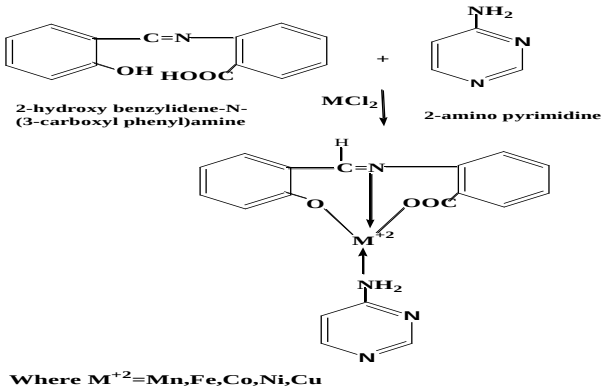
(0.2gm,2.mmol) of O-hydroxy benzaldehyed was added in ethanolic solution (15ml) of (0.87gm,2 mmol) O-amino benzoic acid and few drops of glacial acetic acid .The mixture was refluxed for 4 hrs., then cooled to room temperature, Yellow crystals were formed, the product was recrystallized from ethanol and dried under vacuum.



O-hydroxy benzaldehyed **O-amino benzoic acid** **(Fig 1)**

Preparation of Complexes:-

All complexes were prepared by dissolving (0.241g,1mmole) of 2-hydroxy benzylidene-N-(3-carboxyl phenyl) amine in ethanolic solution with few drops of the potassium hydroxide .The solution was added gradually with stirring to the ethanolic metal salt contains 0.196g,0.251g.0.236g,0.236g and 0.241g ($MnCl_2.4H_2O$,$FeCl_2.7H_2O$,$CoCl_2.6H_2O$,$NiCl_2.6H_2O$ and $CuCl_2.6H_2O$) ,an ethanolic solution of (0.95g,1mmole)2-amino pyrimidine was added to the mixture in each case, 1:1:1 molar ratio of these metal to ligands .After reflux for 2 hrs. , crystalline colored precipitates formed at room temperature, the resulting solids were filtered off, wahsed with cold ethanol and dried at room temperature. The physical properties and their metal complex was showed in Table(1).



(Fig 2)

Theoretical treatment

Computational chemistry

Today, advances in software have produced programs that are easily used by any chemist. Hyper Chem-6 program is known for its quality, flexibility and ease of use, it offers ten semi-empirical methods[9].Some of then have been devised specifically for the description of inorganic chemistry as well, and generally good for predicting molecular geometry and energetics.They can be used for predicting vibration modes and transition structures[10].

In the present work, parameterization method 3(PM3) was used for the calculation of heat of formation and binding energy for all metal complexes. PM3 is more popular than other Semi empirical methods due to the availability of algorithms and more accurate than with other methods.PM3\TM is an extension of the PM3 method to include d orbitals for use with transition metals[10]. It has been parameterized primarily for organic molecules and certain transition metals listed below: Ti,Cr,Mn,Co,Ni,Cu,Zn,Zr,Mo,Ru,Rh,Pd,Cd, Hf,Ta,W,Hg .

Table (1) Physical properties of the ligands and their complexes

Compound	Color	Melting point C^0	Yield %	C% Calc. (exp)	H% Calc. (Exp)	N% Calc. (Exp)	Metal %found (calculate)
L1	Yellow	188-190	86	69.70 (70.81)	4.56 (5.53)	5.80 (5.00)	-
L2	White	122-126	-	50.52 (49.30)	5.26 (6.00)	44.21 (45.21)	-
Mn(L1)(L2)]	Dark-green	223 d	55	55.54 (56.42)	3.59 (4.22)	14.39 (15.00)	6.83 (7.00)
[Fe(L1)(L2)]	Dark-Yellow	261 d	81	55.41 (54.43)	3.59 (4.27)	14.36 (14.06)	11.1 (12.0)
[Co(L1)(L2)]	Yellow –green	271 -273	51	54.97 (53.52)	3.56 (4.60)	14.25 (14.00)	11.2 (11.9)
[Ni(L1)(L2)]	Green	215 d	75	55.00 (54.30)	3.56 (3.82)	14.26 (15.31)	9.12 (10.3)

[Cu(L1)(L2)]	Dark-green	213 d	61	54.33 (55.01)	4.02 (3.25)	14.08 (15.09)	12.3 (13.2)

d=decomposite

Results and discussion:-

Electronic spectra of free ligands:-

The ultraviolet visible electronic spectra of the ligands (L1) and (L2) in DMSO solvent was recorded and shown in table(2). Bands at the wave lengths(30157,31427,38314,43630cm^{-1}) .These transitions attributed to ($\pi\rightarrow\pi^*$),($n\rightarrow\pi^*$) electronic transition .The electronic spectra of the complexes showed different absorptions from that of the free ligand. In the spectra of complexes the band were shifted to different wave length than the corresponding bands in the ligands as shown in the table (2).Which appeared in the wave length range between 32404-45249 cm^{-1}.

-Electronic spectra of the complexes:-

1-[Mn(L1)(L2)]:-

The dark –green complexe showed a strong bands at (44504.9),(32467)cm^{-1} attributed to($n\rightarrow\pi^*$) and charge transfer band (C.T) [11,12].

2-[Fe(L1)(L2)]

The dark –yellow complexe showed band at (27701)cm^{-1} belong to (C.T) and another band at (23753)cm^{-1} caused by the electronic transition $^5E\rightarrow{}^5T_2$ [15].

3- [Co(L1)(L2)]

The Yellow –green complex of cobalt (II) showed band at (34224)cm^{-1} ,(15602)cm^{-1} attributed to $^4A_2\rightarrow{}^4T_2$, $^4A_2\rightarrow{}^4T_{1\ (F)}$ respectively [12] .

4-[Ni(L1)(L2)]

The electronic spectrum of green complexes of Ni(II)(44247),(31948) cm^{-1} attributed to($n\rightarrow\pi^*$) and (C.T) bands.[12-14

5-[Cu(L1)(L2)]

The spectrum of the dark - green complexe of Cu(II) gave two bands at (45249)cm^{-1} and(29499) which assigned(C.T) and $^2T_2\rightarrow{}^2E$ [15].

According to spectral data as well as those obtained to spectral from elemental analysis ,the chemical structure of complexes may be suggested as a tetrahedral for [M(L1)(L2)] were M=(Mn^{+2}, Fe^{+2}, Co^{+2},Ni^{+2},Cu^{+2}),L1=2-hydroxy benzylidene-N-(3-carboxyl phenyl) amine ,L2=2-amino pyrimidine.

Table(2) Electronic spectra ,conductance in DMSO solvent and magnetic moment (B.M)for the present prepared metal complexes of ligands

Compounds	Absorption Bands(cm-1)	Assignments	B	10Dq	Dq	B^-	B	μeff B.M	Molar Conductance $\Lambda m(\Omega^{-1} cm^2 mol^{-1})$	Suggested geometry
L1	43630 31427,38314	π→π* n→π*								
L2	30308 30157	n→π* n→π*								
[Mn(L1)(L2)]	44504 32467	n→π* C.T						4.72	16.30	T.d
[Fe(L1)(L2)]	27701 23753	(CT) $^5E \rightarrow {}^5T_2$						4.7	17.88	T.d
[Co(L1)(L2)]	34224 56127.9)Cal(15602	$^4A_2 \rightarrow {}^4T_2$ $^4A_2 \rightarrow {}^4T_{1(P)}$ $^4A_2 \rightarrow {}^4T_{1\,(F)}$	1128	3602	360.2	716.2	0.639	3.8	20	T.d
[Ni(L1)(L2)]	44247 31949	n→π* CT						2.72	15.15	T.d
[Cu(L1)(L2)]	45249 29499,	(CT) $^2T_2 \rightarrow {}^2E$						1.37	13.14	T.d

Tetrahedral :T.d

FT.IR Spectra

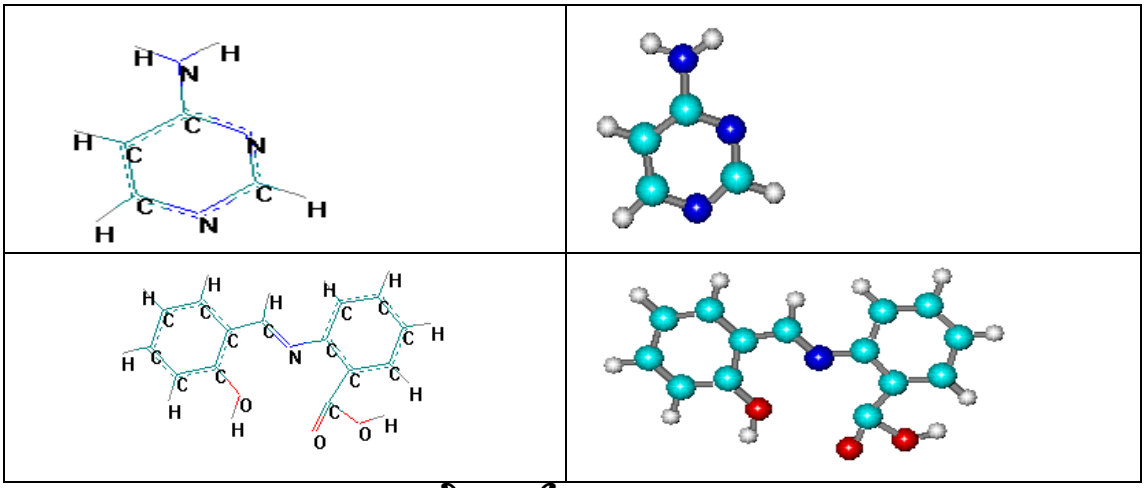
All complexes were readily soluble in DMSO and were found to be stable toward air and moisture. The spectrum of ligand (L1) showed absorption bands at 3017,1657,1651,1222 cm^{-1} assigned to hydroxyl ,isomethane ,acetate group ν(COO)asym. and ν(COO)sym.respectivly [16,18].In the spectrum of ligand($C_4H_5N_3$) there was noticed broad band at 3329 cm^{-1} attributed to stretching (NH_2)[18].The infrared spectra of the prepared complexes exhibited stretching (C=N) in the range (1589-1597)cm^{-1} show shifting to lower frequencies in comparsion with ligand(L1) ,but with ligand $C_4H_5N_3$ shifting to higher frequencies which indicated the coordination of these ligands with metal ions through nitrogen atoms[18].The spectra bands of complexes at (1222)cm^{-1} was characteristic for the lower frequencies suggesting that the oxygen atom of acetate group is coordinated to the metal ion[19,20]. The infrared of prepared complexes showed bands in the range (503-520)cm^{-1} and (433-450)cm^{-1} was attributed to the stretching vibration of (M-O) and (M-N) respectively these result are tabulated in table(3).

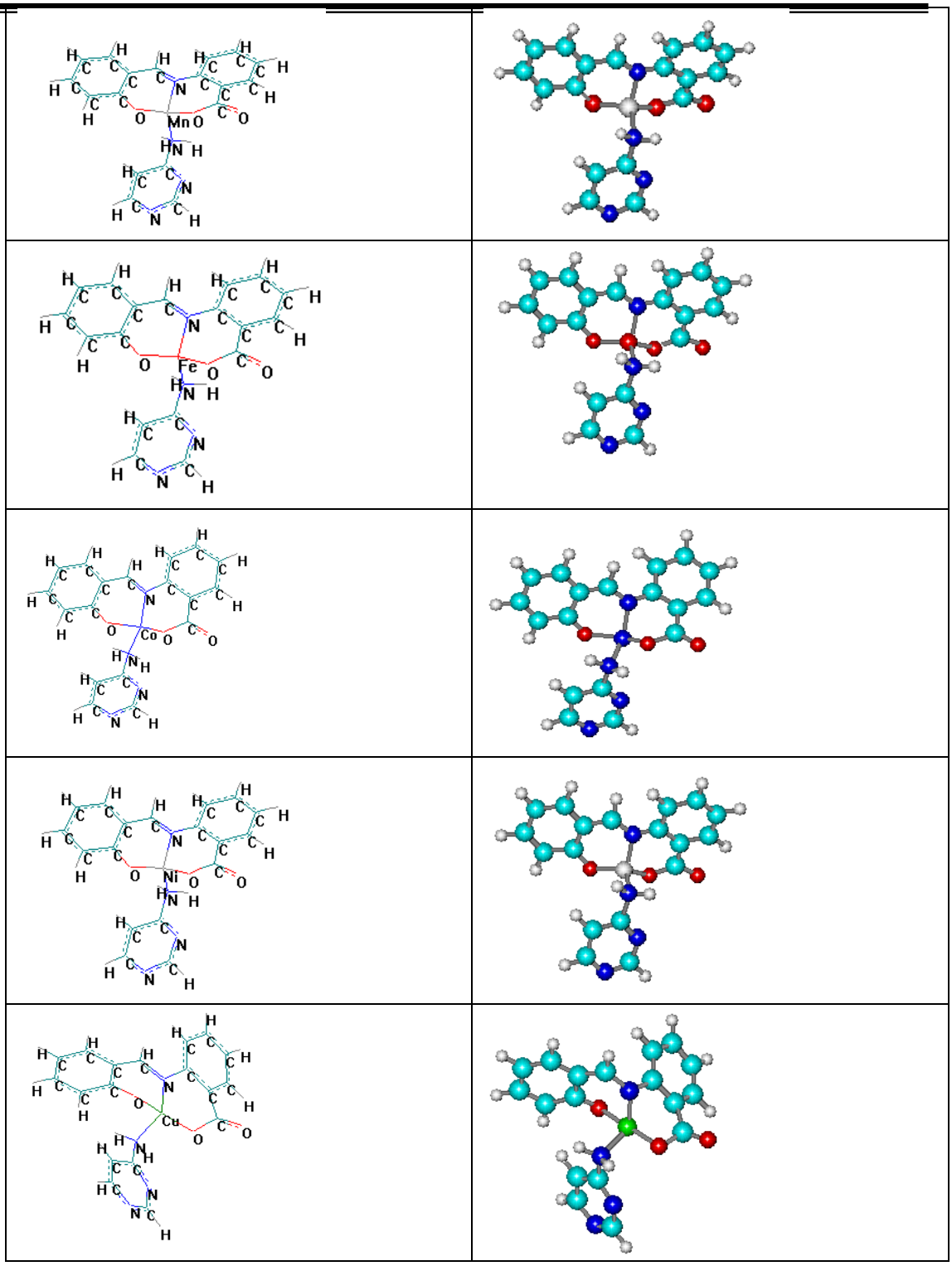
Table(3) The most diagnostic FTIR bands of ligands and their metal complexes(cm^{-1})

Compounds	νC=Niso	ν(COO)asy	ν(COO)sym.	Noh	νM-N	νM-O	ν NH_2
L1	1651	1657	1222	3017	-	-	
L2				-			3329
[Mn(L1)(L2)]	1589	1611	1315	-	520	433	-
[Fe(L1)(L2)]	1597	1653	1441	-	508	452	-
[Co(L1)(L2)]	1592	1656	1422		503	453	-
[Ni(L1)(L2)]	1590	1633	1423	-	504	442	-
[Cu(L1)(L2)]	1593	1642	1435	-	510	450	-

Optimized geometries energies and vibrational for starting materials and free ligands Schiff bases (L1 and L2)

All theoretically probable structures of metal complexes with Schiff bases and 2-amino pyrimde have been calculated to search for the most probable model building stable structure, which shown in figure(1) .The results of semi-empirical method of calculation in gas phase for the heat of formation and binding energies of Schiff bases were tabulated in table (5), which shows that the L1 was more stable than L2. This difference in stability might be related to the present of OH,COOH groups in the ortho position of the L2. The vibration spectra of the free ligands have been calculated. As shown in table (6). The theoretically calculated wave number for these ligands shows that some deviations from the experimental values. These deviations are generally acceptable in theoretical calculations. The most diagnostic calculated vibrational frequencies were chosen for the assignment of ligands, which are included in table (6), fig's (5).





Fig(3): conformation structure of L1, L2 and its complexes

Electrostatic potential

The electron distribution governs the electrostatic potential of molecules.

The electrostatic potential (E.P) describes the interaction of energy of the molecular system with a positive point charge. (E.P) of the ligands were calculated and plotted as 2D&3D contours to investigate the reactive sites of the molecules, see fig (2),. Also, one can interpret the stereochemistry and rates of many reactions involving soft electrophiles and nuclephiles in terms of the properties of frontier orbitals (HOMO and LUMO). Overlap between the HOMO and LUMO is a governing factor in many reactions[21] . The HOMO and LUMO values were plotted as 3D contour to get more information about these molecules, see fig (2). The results of calculation shows that the LUMO of transition metal ion prefers to react with the HOMO of oxygen and nitrogen atoms of Schiff base and NH_2 compounds.

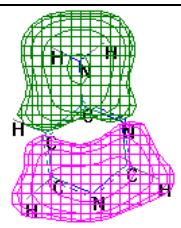
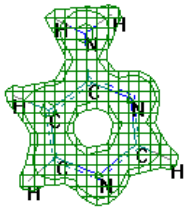
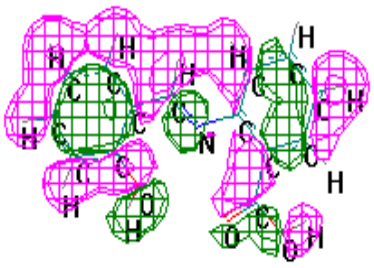
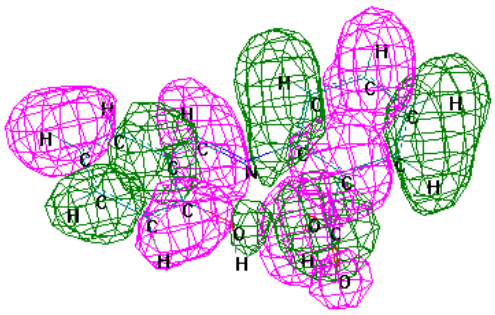
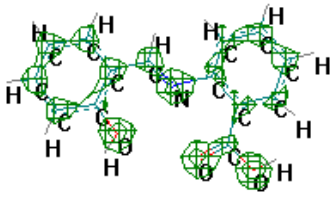
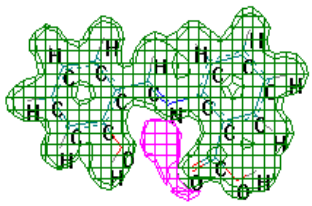
	
(HOMO and LUMO) of L2 as 3D	(E.P) as 3D of L2
	
-19.17 ev(HOMO and LUMO) of L1as 3D	-20.43 ev(HOMO & LUMO)of L1as 3D
	
(E.P) as 3D of L1	(E.P) as 3D of L1

Fig (4): HOMO & Electrostatic potential as 2D Contours for L1&L2

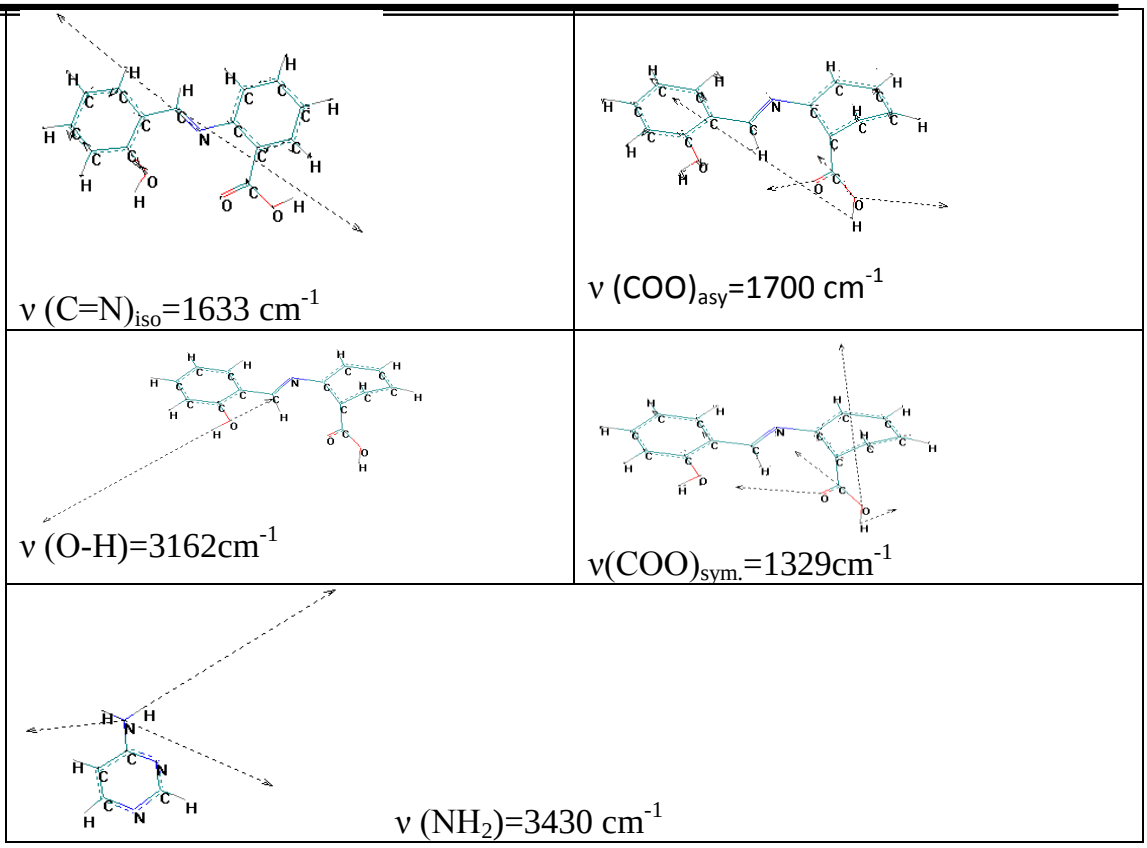


Fig (5): Calculated vibrational frequencies of L1&L2

Table (5): Conformation energetic (in kJ.mol^{-1}) for (L1 &L2) and their metal complexes.

Conformation	PM3	
	ΔH_f°	ΔE_b
L1	-53.2604310	-3310.5194310
L2	34.9830384	-1248.0869616
[MnL1L2]	-22.6018287	-4871.6458287
[FeL1L2]	-9.4087415	-5658.8527415
[CoL1L2]	-34.5727319	-7589.7712681
[NiL1L2]	-432.9087654	-6762.6984320
[CuL1L2]	-35.9770126	-4608.9669863

Table (6): Comparison of experimental and theoretical vibrational frequencies(cm^{-1}) for Ligand(L1&L2).

COMP.	ν COO_{asy}	νCOO_{sym}	**C**=N_{iso} ν	νOH	ν NH_2
L1	(1657)* (1700)** (-2.59)***	(1222)* (1329)** (-8.75)***	1651)*((1633)** (1.09)***	(3070)* (3162)** (-2.99)***	
L2					(3329)* (3430)** (-3.03)***

***: Experimental frequency, **: Theoretical frequency, ***: Error % due to main difference in the experimental measurements and theoretical treatments of vibrational spectrum.**

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تحضيروتشخيص ودراسة نظرية لبعض أيونات الفلزات مع ليكاندات مختلطة

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الخلاصة:-

تم تحضير معقدات جديدة من ليكاندات مختلطة بتفاعل2-هيدروكسي بنزلدين-N-(3-كاربوكسيل فنيل) أمين و2-امينو بايرمايدين مع الايونات الثنائية للمنغنيز،الحديد،الكوبلت،النيكل والنحاس. شخصت المعقدات المحضرة بأستخدام تحليل العناصر، طيف الاشعة تحت الحمراء ، طيف الاشعة فوق البنفسجية ، الحساسية المغناطيسية والتوصيلية الكهربائية. من القياسات الطيفية أعلاه ، أقتراح الشكل رباعي السطوح للمعقدات .تم أقتراح الاشكال الهندسية للمركبات في الحالة الغازية أيضاً بأستخدام المعالجة النظرية بأستخدام برنامج Hyper Chem-6 بتطبيق الميكانيك الجزيئي والشبه التقريبي في الحساب. تم حساب حرارة التكوين القياسية وطاقة الترابط لليكاندات والمعقدات المحضرة بأستخدام طريقة الـ PM3في الحساب.