Synthesis and Spectroscopic Characterization of some Mixed Schiff Base Complexes

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Abstract: *Two different Schiff bases have been synthesized, the first Schiff base derived from the reaction of 2-hydroxyacetophenone and amino acid (tyrosine) as primary ligand (HL1) and the second Schiff base formed from the condensation of 4-dimethylaminobenzaldehyde and of 2-aminobenzoic acid as secondary ligand (HL2). These Schiff bases were used to form mixed Schiff base complexes with Co(II), Ni(II), Cu(II), Zn(II) and Fe(III) ions in the presence of alkaline media. The synthesized Schiff bases and their complexes have been investigated by using several techniques; in terms, CHN elemental analyses, molar conductivity, magnetic moment and spectroscopic studies [IR, UV-Vis, ^{1}HNMR, MS and EPR spectra]. The CHN elemental analysis data showed the formation of the mixed Schiff base complexes in 1:1:1[M:L1L2] ratio.The molar conductance measurements revealed that the mixed Schiff base complexes are electrolytes confirming the existence of sodium ions outside the frame of the complexes except Iron(III) complex which is non-electrolyte in nature. Room temperature magnetic moment values suggested that the complexes have six-coordinate geometry. Infrared spectral results exhibitedtheSchiff bases coordinated to the metal ion via the oxygen atom of -COOH and the nitrogen atom of azomethine and phenolic groups. The signals which obtained from The ^{1}HNMR spectra of the Schiff bases and their Zn(II)Schiff base complex supported the complexation between the Schiff bases and Zn(II) ion. Whereas, The UV spectral results of the Schiff bases showed π→π* (Phenyl ring) and n→π* (C=N, -COOH and –OH) transitions and the UV-Vis spectral data of the mixed Schiff base complexes suggested the geometrical structure which is an octahedral geometry around the metal ions. The mass spectral fragmentations of the Schiff bases and their Cu(II) complex were studied and confirming the formation of the Schiff bases and the iron(III) mixed Schiff base complex. The electron paramagnetic resonance spectral values confirmed the data which are obtained from UV-Vis study.*

Keywords: Schiff bases, Mixed Schiff base complexes, Transition metal ions

1. Introduction

The chemistry of Schiff bases is an important area of research with increasing interest due to their simple synthesis, versatility and the diverse range of applications for their complexes, *e.g.*, in the treatment of cancer, as antibactericidal agents, as antiviral agents, as fungicidal agents and for other biological properties[1]. Schiff bases have been studied as a class of ligands [2]and are known to coordinate with metal ionsvia the azomethine nitrogen atom. The synthesis of transition metal complexes with Schiff bases is reported due to sensitivity, selectivity and synthetic flexibility towards metal atoms [3]. Schiff bases are used as catalysts in medicine such as in antibiotics,anti-inflammatory agents and in industry as an anticorrosive. They are also used as analytical reagents for spectrophotometric metal analysis. Complexes of Schiff baseshave recently been used as precursors in the preparation of nano- structures of the respective metal oxides[4].

The present study aims to synthesis and characterize two different Schiff bases and their mixed Schiff base complexes with some transition metal ions.

2. Experimental

Chemicals and Reagents: All chemicals and reagents used in this study are of pure grade (BDH or Aldrich). Include; 4-dimethylaminobenzaldehyde, 2-aminobenzoic acid, 2-aminophenol, 2-hydroxyacetophenone, tyrosine, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $ZnCl_2$, $FeCl_3.6H_2O$, NaOH, acetic acid, DMSO, DMF, C_2H_5OH, CH_3OH and double distilled water.

Synthesis of {2-(2-hydroxy-1-phenylethylidene)amino)-3-(4- hydroxyphenyl) propanoic acid} (HL1): This Schiff basehas been synthesized [5]**.**

Synthesis of 2-(4-(dimethylamino)benzylideneamino)benzoic acid (HL2): The following Schiff base(**Fig.1**) was synthesized by dissolving 4-dimethylaminobenzaldehyde (0.01 mol; 1.49 g) and same ratio of 2-aminobenzoic acid in ethanolic solution (30 cm^3). The resulting mixture was refluxed for 2 hrs. An orange crystals were formed upon cooling. The obtained product was filtered, washed with ethanol and allowed to dry in air. The product was recrystallized from hot ethanol to give an excellent yield of 87.30%.
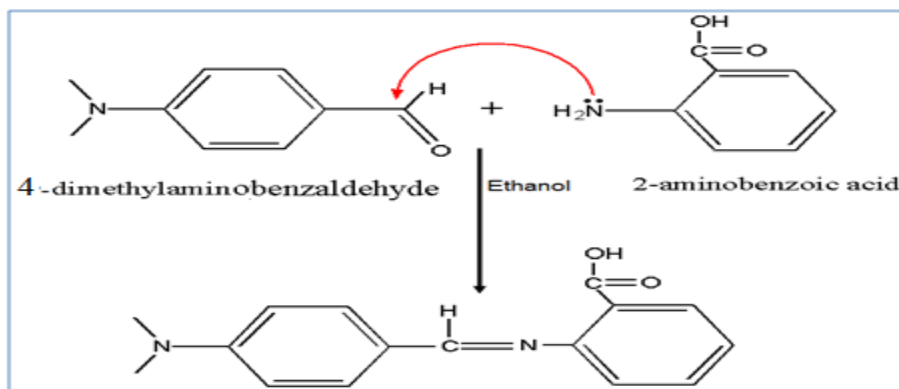
Figure 1: 2-(4-(dimethylamino)benzylideneamino)benzoic acid (HL2)

Synthesis of the mixed Schiff bases complexes: The present mixed Schiff base complexes of the Schiff bases under investigation with Co(II), Ni(II), Cu(II), Zn(II) and Fe(III) ions were synthesized by adding 0.01 mol, 3.31 g of the Schiff base (HL1) and 0.01 mol; 2.68 g of the Schiff base (HL2) in 25 cm^3 of the absolute ethanol to 0.01mol; 2.38, 2.37,1.70, 1.36 and 2.70 g) of the desired metal salts, respectively. Few drops of sodium hydroxide solution were added slowly to adjusted the P^H value at 8 until the complexes isolated, and then the mixtures were stirred and refluxed for four hours. The formed products were filtered, washed several times with hot ethanol until the filtrates become clear. and dried in desecrator under calcium chloride.

Physical Techniques

The Schiff bases and their mixed Schiff base complexes were subjected to CHN elemental analysis using 2400-CHN elemental analyzer. The molar conductivity of the mixed Schiff base complexes was measured in DMF solvent using digital conductivity meter CMD-650, at chemistry department, El-Baida University, El-Baida, Libya. The infrared spectra were carried out applying KBr disc technique using IFS-25 DPUS/IR spectrometer. Proton nuclear magnetic resonance spectra of the Schiff bases and their Zn(II) mixed Schiff base complexes were recorded on Varian Gemini200-200MHz spectrometer using TMS as internal standard and d^6-DMSO as a solvent. The electronic spectra were measured in DMF solvent by using a Perkin-Elmer lambda-4β spectrophotometer. The mass spectra also

carried out by using Shimadzu QP-2010 Plus. The electron paramagnetic resonance spectrum was recorded by using EMX ESR spectrometer (Bruker) 1998Y. All previous tools and analysis were done at micro-analytical centre, Assiut University, Assiut, Egypt.

3. Results and Discussion

Physical properties, Elemental analyses and molar conductivity: The Schiff bases and their mixed Schiff base complexesweresynthesizedinpowder formwithhighmeltingpoints(Table1). TheSchiff bases aresolubleinalcohols(methanol .ethanol),DMSOand DMF solvents, whereas, the mixed Schiff base complexes are not soluble in alcohols, but they arepartiallysolubleinDMFandDMSO solvents. All compounds are stable in air. The CHN elemental analysis data of the Schiff bases and their mixed Schiff base complexes agree with the suggested compositions. This means that the Schiff bases were formed and their mixed Schiff base complexes were also formed in 1:1:1[M:L1:L2] ratio. The molar conductivity values reveal the existence of electrolytic nature for Co(II), Ni(II), Cu(II) and Zn(II) mixed Schiff base complexes, because assigned to thepresenceof sodium ion outside the coordination sphere, whereas, the molar conductivity values for iron(III) mixed Schiff base complexes exhibit non-electrolytic nature, this means that there is nonegative or positive ions outside the complexes.[6]

Table 1: Some physical properties and CHN elemental analyses of Schiff bases and their mixed Schiff base complexes

Schiff bases/Chelates	M.wt	Colour	Yield%	C% Calc. (Exp.)	H% Calc. (Exp.)	N% Calc. (Exp.).	^*
$C_{18}H_{21}NO_5$. (L1)	331.00	Pale yellow	90.32	68.22 (69.01)	5.69 (6.20)	4.68 (5.45.)	_
$C_{16}H16N_2O_2$ (L2)	268.00	Orange	87.30	71.64 (72.54)	5.97(6.15)	10.45 (10.57)	_
$Na[Co(L1)(L2)(H_2O)]3H_2O$	749.90	Burnt Umber	78.34	54.40 (54.56)	5.06 (6.31.)	5.90 (6.72)	77
$Na[Ni(L1)(L2)(H_2O)]3H_2O$	749.60	Raw Umber	89.98	52.82 (53.21)	5.60 (6.45.)	5.60 (6.76)	74
$Na[Cu(L1)(L2)(H_2O)]4H_2O$	772.50	Light green	75.00	52.1 3 (52.71)	5.68 (6.23.)	5.42 (6.04.)	70
$Na[Zn(L1)(L2)(H_2O)]3H_2O$	756.40	Dark yellow	68.87	52.35 (52.98.)	5.55 (6.38)	5.55 (6.68.)	80
$[Fe(L1)(L2)(H_2O)]2H_2O$	707.00	Light brown	71.09	56.02 (57.33)	5. 65 (6.17.)	5.94 (6.90.)	23

^*= molar conductivity

Table 2: Infrared spectral data (cm^{-1}) and electronic spectral data (nm, cm^{-1}) of mixed Schiff base complexes

Schiff bases/ Chelates	υ OH (H$_2$O)	υ (COO)	υ RC=N HL1, (HL2)	υ M-O	υ M-N	nm (cm^{-1})
C$_{18}$H$_{21}$NO$_5$(L1)	3422	1591	1609	–	–	**265** (37736) **290**(34483)
C$_{15}$H$_{16}$N$_2$O(L2)	-	1678	1535	–	–	**260**(38462) **275** (36364)
Na[Co(L1)(L2)(H$_2$O)]2H$_2$O	3206	1042	**1543**,(1538)	576	528	**733** (13643)
Na[Ni(L1)(L2)(H$_2$O)]H$_2$O	3408	1044	**1446**,(1517)	575	528	**410** (24390) **626** (15974) **733** (13643)
Na[Cu(L1)(L2)(H$_2$O)]H$_2$O	3421	1041	**1554**,(1517)	675	528	**734** (13624)
Na[Zn(L1)(L2)(H$_2$O)]H$_2$O	3305	1045	**1591**,(1541)	674	486	**733** (13643)
[Fe(L1)(L2)(H$_2$O)]2H$_2$O	3206	1040	**1588**,(1514)	578	490	**733** (13643)

R= CH$_3$ for L1, (R= H for L2)

Infraredspectra

The infrared spectra of themixed Schiff base complexes show bands in the range of 1593–1611 cm^{-1} due to the υC=O stretching frequency of –COOH which is shifted to a lower frequency ranging from 67 to 85 cm^{-1} in all of the L1 L3 mixed Schiff base complexes. The shifting of these bands to a lower region support the entering of oxygen atom from the hydroxyl group of COOH in chelation with the metal ions.[7]The water molecules were indicated by the presence of broad bands in the range of 3408-3427 cm^{-1}[8]. Whereas, the OH group of the Schiff base L1 is overlapped with the position of water molecules indicating the participation of oxygen atom of hydroxyl group in complexation with the metal ions.[9]The IR spectra of the complexes (Table 2) reveal changes in the bands in comparison to the free Schiff bases(1609 cm^{-1} for L1 and 1535 cm^{-1} for L2) which are due to azomethine group suggesting the involvement of the imine group via nitrogen atom.[10]The new bands in the range of 486-529 and 649-756 cm^{-1} assigned to υ (M-N) and υ (M-O) vibrations, respectively.[11]The appearance of υ (M-N) and υ (M-O) bands which are not present in the free Schiff bases confirms the involvement of oxygen and nitrogen atoms in chelation with metal ions.

^{1}HNMR spectra

The[1]HNMR spectra of the Schiff base HL2 and Zn(II complex are shown in figures 2,3. The resonance of protons has been assigned on the basis of their integration and multiplicity pattern. The spectrum of Schiff base HL1(Published)[5]. The ^{1}HNMR spectrum of the Schiff base HL2 displays a range of signals between 2.51-9.69 ppm, the signals at 9.69, 3.21, 3.05 and 2.51 ppm due to HC=N, COOH, CH$_3$ and DMSO solvent, respectively. The spectrum of the Schiff base exhibits two signal's at 6.49 and 8.05 ppm assigned to phenyl protons of the Schiff base.[12]The ^{1}HNMR spectrum of Zn(II) complex shows the azomethine proton signal at 9.69 ppm which is shifted to lower field 7.67 ppm on complexation process supporting the bonding of this group with Zn(II) ion through azomethine nitrogen. The aromatic protons have been resonated in the region δ 6.02-7.20 as multiple. The DMSO solvent and methyl group appear as signals at 2.5 and 3.18 ppm, respectively. The same spectrum exhibits the disappearance of proton of phenolic –OH group indicating its participation in coordination with Zn(II) ion via carboxylic oxygen moiety.
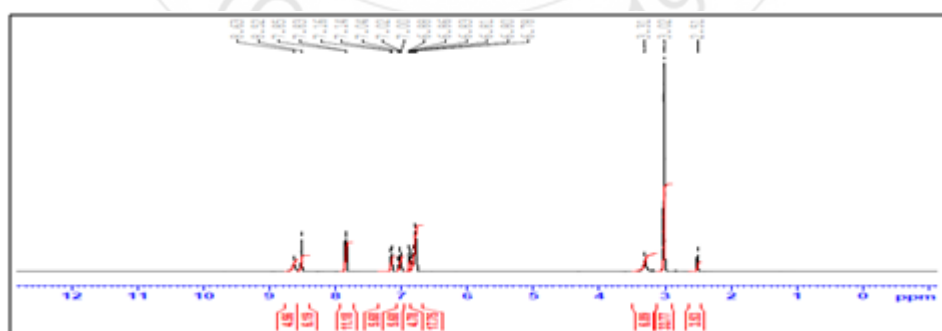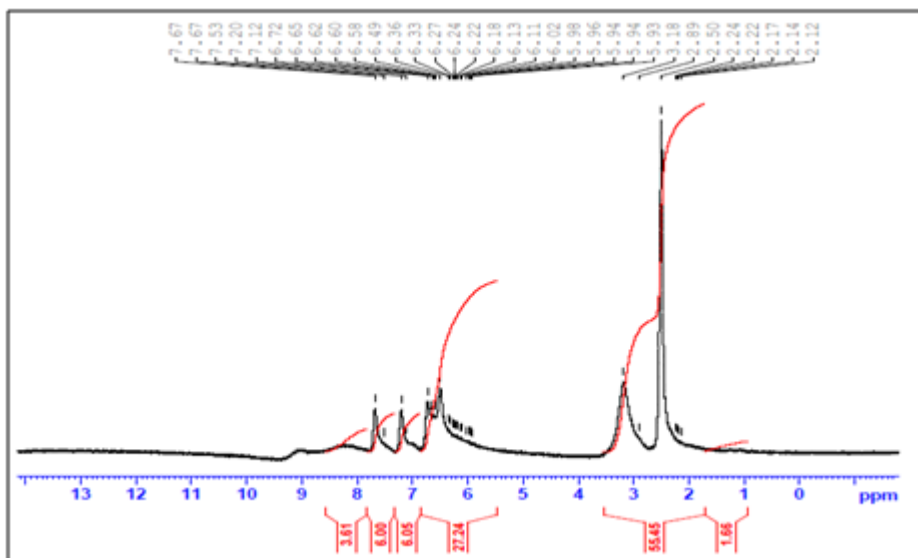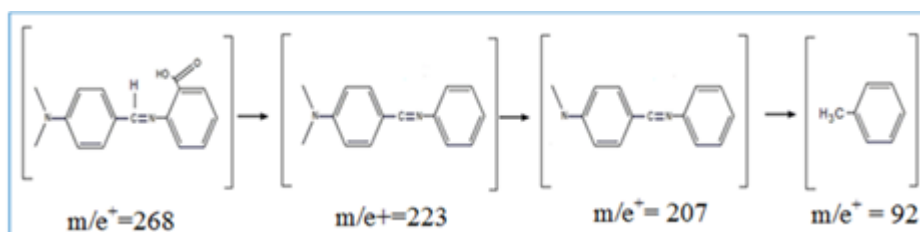

Figure 2: ^{1}HNMR spectrum of Schiff base   (HL2)

Figure 3: ^{1}HNMR spectrum of Zn(II)-L1L2 mixed Schiff base complex

Electronic spectra and magnetic moment

The UV spectra of Schiff bases were recorded at room temperature in DMF solvent and their data were recorded in table 2. The spectrum of Schiff base HL1(Published)[5] The spectrum of the Schiff base (HL2) shows two bands at 260 nm (38462 cm^{-1}) and 275 nm (36364cm[1]) assigned to and $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.[13] The electronic spectrum of the Co(II) mixed Schiff base complex exhibits a band at 733 nm (13643 cm^{-1}) which is assigned to $^4T_1g(F) \rightarrow ^4A_2g(F)$ transition, The intensity of the band and the magnetic moment value of the complex (4.82B.M) suggesting the existence of an octahedral geometry around Co(II) ion.[14] The electronic spectral data of the Ni(II) Schiff base complex reveal three bands at 410 nm (24390 cm^{-1}),626 nm (15974 cm^{-1}) and 733 nm (13643cm^{-1}) attributed to $^3A_2g(F) \rightarrow ^3T_2g(F), ^3A_2g(F) \rightarrow ^3T_1g(F)$ and $^3A_2g(F) \rightarrow ^3T_1g(P)$ transitions, respectively. Based on the nature of the bands and magnetic moment value (4.50 B.M), an octahedral structure was proposed for Ni(II) mixed Schiff base complex.[15] Copper (II) has a d[9] configuration showing absorption band at 734 nm (13624 cm^{-1}) which is due to $^2E_g \rightarrow ^2T_{2g}$ transition suggesting a distorted octahedral geometry around the Cu(II) ion which is confirmed from the obtained value of the magnetic moment (1.95 B.M)that belongs to the existence of unpaired electron in d orbital of Cu(II) ion.[16]The electronic spectral data of the Zn(II) complex show band at 733 nm (13643 cm^{-1}) due to charge transfer transition. The intensity of the band and a diamagnetic phenomena confirm the presence of an octahedral geometry for this complex.[17] Meanwhile, The electronic spectrum of Iron(III) mixed Schiff base complex exhibits a band at 733nm (13643cm^{-1}) which is attributed to d-d transition. The nature of the band and the existence of weak field (high spin complex)lead the complex to has an octahedral geometry.[18]

Mass spectra: The mass spectral fragmentations of the Schiff base HL2 and C(II) complex are shown infigures4,5and Schemes 1,2.Whereas, the mass spectral studies of HL1 is published[5].The mass spectrum of Schiff base HL2 shows a base peak at m/e[+]=268 which is corresponding to the original molecular weight. The peak at m/e+=223 is analogous to $C_{15}H_{15}N_2$. Meanwhile, another peak at m/e[+]= 207 is equal to the formula of $C_{14}H_{11}N_2$. The last peak at m/e[+] = 92 is attributed to C_7H_8. The mass spectrum of the copper (II) mixed Schiff base complex shows a molecular ion peak atm/e[+]= 256 which is corresponding to [$C_{15}H_{16}N_2O_2$]. The peak at m/e[+] = 137 is analogues toantthranlic acid [$C_7H_7 O_2N$] and the final peak appeared at m/e[+] = 92 due to C_6H_6N.

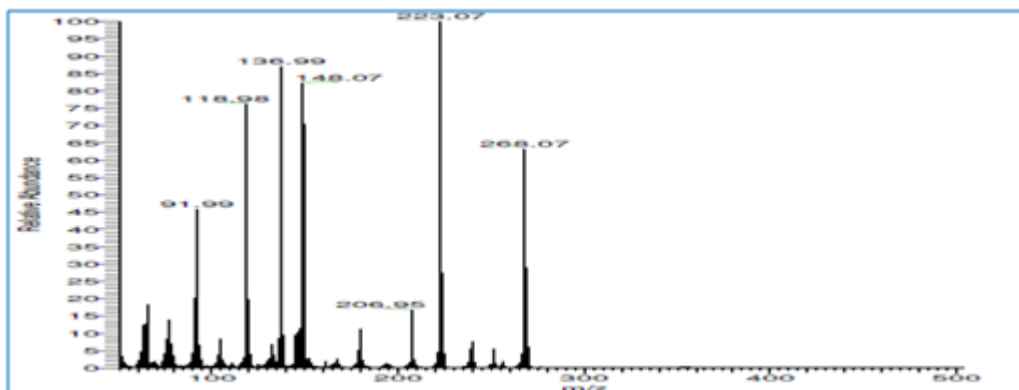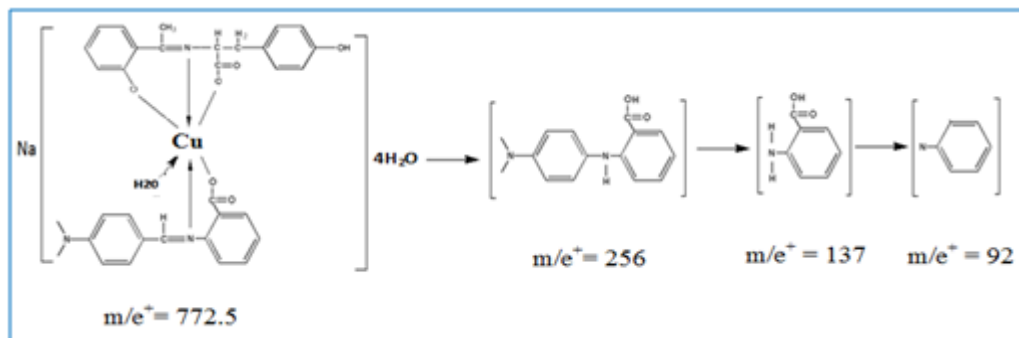**Scheme 1:** Mass spectral fragmentations of Schiff base (HL2)

Figure 4: Mass spectrum of Schiff base (HL2)

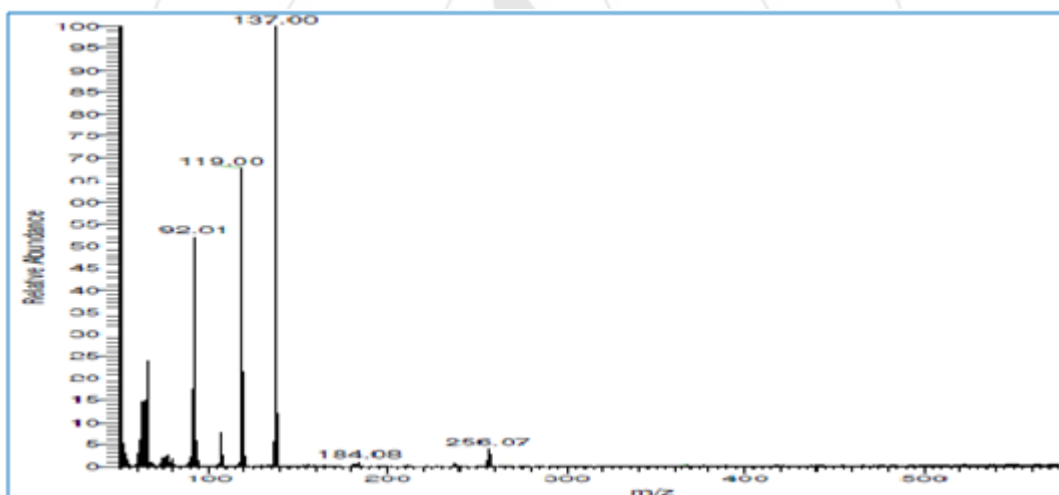**Scheme 2:** Mass spectral fragmentations of Cu(II) mixed Schiff base complex

Figure 5: Mass spectrum of Cu(II)-L1L3 mixed Schiff base complex

Fig.(3): Mass spectrum of Cu(II) mixed Schiff base complex

Electron paramagnetic resonance spectra:

The electron paramagnetic resonance spectral results of the mixed Schiff base complexes of L1L2 display g values lied in the range of 2.174-2.230. The deviation of these values from the ideal value (2.0023) is due to the formation of the covalent bonds between the metal ions and the Schiff bases under investigation. The experimental values confirm the presence of an octahedral structure for all the complexes.[19], Fig.6.
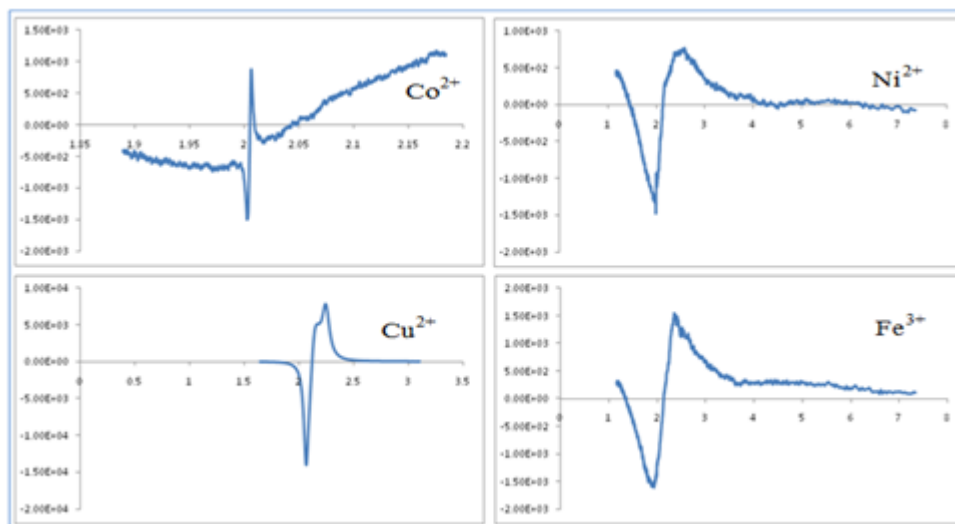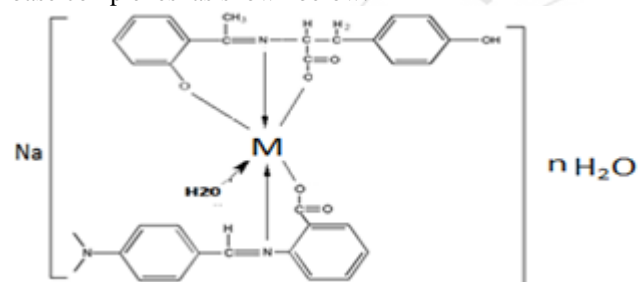
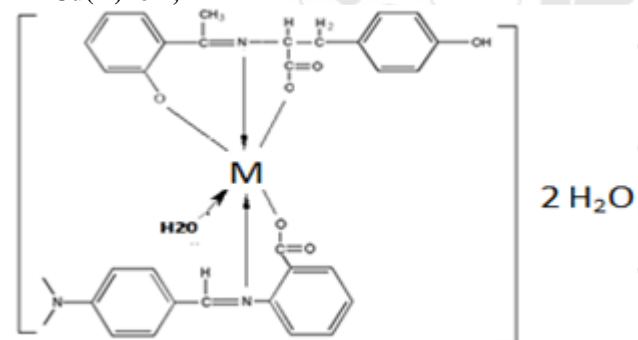**Figure 6:** E.P.R spectra of Co(II), Ni(II), Cu(II) and Fe(III)-L1L**2** mixed Schiff base complexes

4. Conclusion

From the previous mentioned physiochemical data,an octahedral geometry was proposed for all mixed Schiff base complexes as shown below:

M= Co(II), Ni(II), and Zn(II) ions, n = 3
M=Cu(II) ion , n=4

M=Fe(III) ion.

References

[1] S. Kumar, D.N. Dhar and P.N. Saxena (2009), *J. Sci. Ind. Res.***???,** 181.

[2] Chowdhury, D.A., Uddin, M.N. and Hoque, F. (2010), *J. Sci*. **37** (3), 443.

[3] Liu, J., Wu, B.,Zhang, B. and Liu, Y. (2006), *Turk. J. Chem.*, **30**, 41.

[4] Zinatloo-Ajabshir, S.,Salavati-Niasari, M. and Hamadanian, M. (2015),*RSC Adv*. **5,** 33792.

[5] El-ajaily, M.M., Al-barki, N.S. and Maihub, A.A.(2016), *Asian J.Adv.Basic Sci.,***4**(2), 123.

[6] Thorat, B.R., Mandewale, M., Shelke, S.,Kamat, P., Atram, R.G., Bhalerao, M. and Yamgar, R. (2012), *J. Chem. Pharm. Res.***4**(1), 14.

[7] Hamrit, M., Djebbar-Sid, S., Benli-Baitichy, O.,Khan, M.A. andBouet, G.M. (2000), *J. synth. React. Met.Org. Chem***30**(10), 1884.

[8] Abuamer, K.M., Maihub, A.A., El-ajaily, M.M., Torki, A.M., El- Aboukrisha,M.M. andAlmagani, M.A. (2014), *Inter. J. Org.Chem.,* **4**,7.

[9] Silverstein, R.M. and Webster, F.X. (1998), "Spectrometric Identification of organic Compound",6th .ed.,Wiley &Sons, INC., New York.·

[10]Raman, N., Ravichandran, S. and ThangarajanC. (2004),*J. Chem. Sci***., 116**, 215 .

[11]Panchal, P.K., Parekh, H.M.,Pansuriya, P.B. andPatel, M.N.(2006), *J. Enzyme Inhibit Med. Chem*., **21**(2), 203.

[12]Gowri,G .andLakshmi ,S.S. (2015), *Int. J. Front. Sci. Tech,* **3**(1), 26**.**

[13]Reddy, P.M., Prasad, A.V., Shanker, K. and Ravinder, V.(2007), *Spectrochim. Acta. A*.**68**, 1000.

[14]Shankar, K.,Ashok, M.,Reddy, P.M., Rohini, R., and Ravindar, V. (2009), *Int. J. Chemtech.Res* **3**, 777.

[15]Mosoarca, E. M., Tudose, R., Linert, W. and Costisor, O. (2006),*Chem. Bull. Politehnica Univ.(Timisoara)***, 51**(65), 1.

[16]Saranya, K., Lakshmi, S.S. Mahadevi, P. andLogesh, G. (2015), *J. Chem. Pharm***7**(7), 851.

[17]Ramam, N., .Kulandaisami, A andShunmugasundaram, A. (2001), *Trans Met Chem* **26**(1),131**.**

[18]Sagthaforoush, L.A., Aminkhani, A. and Chalabian, F. (2009), Trans. Met. Chem.,**34**, 899- 904.

[19]Singh, D.P., Kumar, K. and Sharma, C. (2010), *Synth. Reac.Inorg. Met-org. Chem* **40**(6), 378.