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Synthesis, characterization and biological studies on some metal (II) complexes with Schiff base [(4-chlorophenyl) imino]-3,3-dimethylcyclohexan-1-one

Amna Alameldeen H[1], Elmugdad Ahmed A[2], Mohammed Suliman Ali[3]
[1-3] Department of Chemistry, College of Science, Sudan University of Science and Technology, Khartoum, Sudan

Abstract
A new Schiff base ligand [(4-chlorophenyl)imino]-3,3-dimethylcyclohexan-1-one has been synthesized by condensation between dimedone and 4-chloroaniline in the molar ratio 1:1. This synthesized ligand was used for complexation with different metal ions like Fe (II), and Pb (II), by using a molar ratio of ligand: metal as 2:1 in ethanol. The ligand and metal complexes have been characterized by melting point, NMR (^{1}H and ^{13}C), UV–vis spectroscopy, FTIR, MS, and molar conductivity studies. In conductivity experiments, all metal chelates showed to be non-electrolytic in nature. The IR results demonstrate that the co-ordination sites are the nitrogen atoms of the azomethine and the oxygen atoms of the carbonyl groups. The anti-microbial activities of both the ligand and their complexes were screened against two Gram-positive bacterium (Staphylococcus aureus and Bacillus subtilis) and two Gram-negative bacterium (Escherichia coli and Pseudomonas aeruginosa). The anti-fungal activity was screened against Candida albicans, the results show that the metal complexes are more biologically active than the ligand.

Keywords: metal complexes, Schiff base, dimedone, anti-microbial

1. Introduction

Schiff base compounds are condensation products of primary amines and carbonyl compounds (aldehydes and ketones). These compounds have been known by different names such as imines, azomethines and, anils. They were discovered by a German chemist and Nobel Prize winner, Hugo Schiff in 1864 [1, 2], and have the general structure R1R2C=NR3 [3] where R1, R2 and, R3 are aryl, alkyl, cyclo alkyl or heterocyclic groups that are of different substitutes [4].

Schiff bases are an important class of ligands in coordination chemistry [5, 6], are able to coordinate to many different metals [7], and stabilized in various oxidation states. Bearing the excellent electron-donor group (C=N imino group), they can form various complexes with a wide range of metals including main group metals, transition metals, and lanthanide ions [8]. The stability of the Schiff base complex depends upon the strength ofthe C=Nbond, the basicity of the amino group and steric factors.

The synthesis, structure, and properties of Schiff base complexes have stimulated much interest for their noteworthy contributions in the development of single molecule magnets, material science [9, 10], catalysis of many reactions like carbonylation, hydroformylation, reduction, oxidation, epoxidation, hydrolysis etc. [11, 12]. Their broad range of biological activities, show antibacterial, antifungal, antitumor, antiviral activities and work also as therapeutic agents against biological disorders like cancer, inflammation, and allergy [13, 14].

Schiff base complexes can generally be prepared by the interaction of metal ions and concerned Schiff bases in suitable experimental conditions. In some cases, the complexes were prepared by reacting the metal ions, aldehydes or ketones and amines [15].

The present study deals with the synthesis, characterization and biological activity of the Schiff base [(4-chlorophenyl)imino]-3,3-dimethylcyclohexan-1-one derived from Dimedon and 4-Chloroaniline and its Fe(II) and Pb(II) metal complexes.

2. Materials and Methods

2.1 Chemicals

Dimedone purchased from LobaChemie, p. Chloro aniline purchased from Sigma, Ferrous Sulfate Heptahydrate purchased from CDH, Lead (II) acetate trihydrate purchased from CDH, Glacical acetic acid purchased from Sigma, Absolute ethanol purchased from DuKSAN, Absolute methanol purchased from LobaChemie, Chloroform ($CDCl_3$) purchased from Sigma.

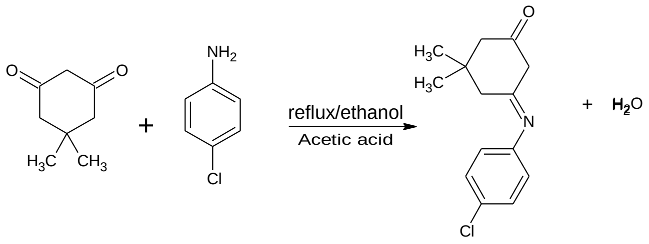
2.2 Instruments

JENWAY 7205 UV/Visible spectrophotometer in methanol at 25◦C, For (c = 1.0×10-3mol /cm-3) of the compounds using a 1 cm quartz cell in the range 200-800 nm, FTIR-8400S SHIMADZU Spectrophotometer in the range (400-4000) cm-^{1} using KBr disc, Bruker Avance III HD 700 MHz spectrometer (UK) equipped with 5 mm TCI H/C/N cryoprobe with $CDCl_3$, the proton decoupled ^{13}C NMR experiment was run using composite pulse decoupling scheme operating at 176.08 MHz.^{1}H NMR data were processed with TopSpin 3.5 pl 6 software, Chemical shifts (δ) are reported in ppm, Mass spectra Shimatzu,model Q.p-2010 plus, Melting pointelectrical, type (Gallenkamp, England), serial No. MFB, 600.100F. APP.NO2CO117.

2.3 Method

2.3.1Synthesis of Schiff bases

(1.4g, 0.01 mol) of dimedone dissolved in 25 ml of absolute ethanol. To this solution (1.3g, 0.01 mol) of 4.chloro aniline dissolved in 25 ml, hot absolute ethanol was added, followed by addition of few drops of glacial acetic acid. The mixture was refluxed for 6 h at 70 ◦C with constant stirring and then was cooled in ice. A yellow solid gradually precipited, filtered, washed thoroughly with cold distilled water and then dried in air and finally in a vacuum. The solid was recrystallized from ethanol.



Synthesis of Schiff base ligand [L1]

2.3.2 Synthesis of the complexes

The metal complexes were prepared by adding 25 ml of an ethanolic metal solution of $(CH_3COO)2Pb$. $3H_2O$ and $FeSO_4.7H_2O$ (0.001mol) with ethanolic solution of the prepared Schiff base (0.002mol). The resulting mixture was refluxed for 3 h, and the metal complex compounds were formed, filtered off, washed and dried.

2.3.3 In vitro antimicrobial activity

Antibacterial and antifungal activities of the ligand and its complexes were tested in vitro against the bacterial species Escherichia coli, Bacillus subtilis, Pseudomonas aeruginosa and Staphylococcus aureus; fungal species, Candida albicans by the paper disk diffusion method.

The test organisms were grown on nutrient agar medium in petri plates. The compounds were prepared in DMF and soaked in filter paper disk of 6 mm diameter and 1 mm thickness. The disks were placed on the previously seeded plates and incubated at 37 _C and the diameter of inhibition zone around each disk was measured after 24 h for bacterial and 72 h for fungal species.

3. Results and Discussion

3.1 Characterization of Schiff base ligand

3.1.1 Physiochemical data

The Schiff base [(4-chlorophenyl)imino]-3,3-dimethylcyclohexan-1-one [L1] was prepared by reacting 4.Chloro aniline with an equimolar amount of dimedone in ethanol. They are quite stable in air and melt or decompose above 180°C.The physical properties of [L1] are listed in table (1).

3.1.2 Mass Spectra

The electronic impact mass spectra of the ligand show molecular ion (M^+) peaks at m/z = 249a.m.u, corresponding to the $[C_{14}H_{16}CLNO]^+$, confirming the empirical formulae of the ligand. The spectra also show a series of peaks corresponding to various fragments of the compound (Figure-1).

3.1.3 Infrared spectra

The IR spectrum of the prepared ligand (table 2) show a strong band at 1583cm_1 which can be assigned to nC=N stretching mode of the azomethine function of the Schiff base ligand. Further, the Schiff base ligand exhibits a band at 1583 cm_1 corresponding to the nC=O group in dimedone moiety, the Schiff base are expected to behave as a bidentate with oxygen and nitrogen as donor atoms. (Figure-2)

3.1.4 Electronic spectra

The electronic spectrum of the ligand (Figure-3).show a band at 295 nm, is attributed to $n \rightarrow \pi^*$ transition of conjugation between the lone pair of electrons of p orbital of N atom in azomethine group and conjugated π bond of the benzene ring. The bands appearing at 225 nm and 255 nm are attributed to $\pi \rightarrow \pi^*$ of the benzene ring and $\pi \rightarrow \pi^*$ transition of the azomethine group.

3.1.5 NMR spectra

The ^1H NMR spectrum of the ligand (Figure-4).exhibited proton signals at 1.1 ppm was assigned for the two methyl groups, while the singlet at 2.17 ppm corresponds to methylene proton neighboring of imine, and signals at 2.37 ppm corresponds to methylene proton neighboring carbonyl group of dimedone moiety. Triplet signals observed in the 7.33 ppm due to the aromatic protons of the Schiff base.

The^{13}C NMR spectra (Figure-5).exhibit absorption signal due to carbonyl (C=O) at 207.07 ppm, while the Signal observed at 161.05ppm were attributed to imine group carbon. The chemical shifts of aromatic carbons appear in the 128.46ppm. Beside these signals, a signal nearly 30.97 ppm appeared which corresponding to carbon atom of two methyl groups.

3.2 Characterization of metal Schiff base complexes:

3.2.1 Physiochemical data:

The physical properties of the metal Schiff base complexes and molar conductance data are listed in Table 1.It was found that all the metal complexes have comparatively higher melting point than the schiff base. This indicated the higher stability of the compound after binding with metal. The low conductivity values of the metal complexes suggest their non-electrolytic nature.

Table 1: Physical properties for synthesized Compound

Compound	Yield (%)	Color	M.P. (°C)	molar conductance Ohm^{-1}cm^{2}mol^{-1}
L1	80.3	Dark Yellow	198	-
Fe L1	57.7	Cream	>300	29
Pb L1	46.2	Pale yellow	210	26

3.2.2 Infrared spectra

The IR spectra of the complexes on comparison with that of the free ligands reveal remarkable changes. On complexation the band at 1583cm^{-1} for the azomethine group in the free ligand was shifted to a higher and lower frequency in the1622 cm$^{–1}$,and 1573 cm^{-1} to FeL1 and pbL1 respectively indicating the coordination of the azomethine nitrogen atom to the metal ion. The band at 1610 cm$^{–1}$ for C=O group of the free ligand has been shifted to 1652 and 1606 cm$^{–1}$ in the complex indicating the linkage between the metal ion and carbonyl oxygen atom. Further, the spectrum of all the complexes shows new bands in the (613, 557 cm$^{–1}$) and (447 and 480 cm$^{–1}$) regions, which may probably be due to the formation of M–O and M–N bonds, respectively. (Figure 6, 7)

The IR results demonstrate that the co-ordination sites are the nitrogen atoms of the azomethine and the oxygen atoms of the carbonyl groups.

Table 2: IR spectral data of the Schiff base ligand and its complexes (cm^{-1})

Compound	ν C=O	ν C=N	ν C=C,Ar	ν C-N	ν M-N	ν M-O
L1	***1610***	***1583***	***1446***	1155	-	-
L1Fe	1652	1622	1490	1101	447	613
L1Pb	1606	1573	1492	1147	480	557

3.2.3 Electronic spectra

The electronic spectra of all the Schiff base complexes show similarities, which indicates similarity in their structures and generally show the characteristic bands of the free ligands with some changes in frequencies. Upon complexation, the absorption bands of the complexes are slightly shifted to longer wavelength (Red shift) compared to those of the free ligand. These modifications of the shifts of the absorption bands indicate the coordination of the ligand to the metal ion.

In the spectrum analysis of schiff base [(4-chlorophenyl)imino]-3,3-dimethylcyclohexan-1-one optimum absorption was measured at 295 nm. While in case of metal complexes red shift in the spectra was observed. Fe has given optimum absorption at 300 nm, and Pb at 315 nm. (Figure 8, 9)

3.2.4 Antimicrobial activity

The Schiff base ligand and its metal complexes have been monitored for their antibacterial activity against various pathogenic bacteria such as Bacillus subtillus (B.S) Staphylococcus aureus (S.a),Escherichia coli (E.c), Pseudomonas aeroginosa (P.s),and antifungal activity against Candida albicans (C.a) (Table 3). A comparative study of the growth inhibition zone values of Schiff base and its complexes show that metal complexes display higher antibacterial and antifungal activity than the free ligands.

Table 3: Antimicrobial activity of synthesized compounds

Compound	Inhibitation growth zone diameter at 100mg/100ml				
	B. S	**S.a**	**E.c**	**P.s**	**C.a**
L1	-	13	10	12	10
L1Fe	15	-	20	16	17
L1Pb	12	-	14	12	12

Conclusion

Fe (II) and Pb (II) complexes with the Schiff base ligand derived from Dimedone and 4-chloroaniline were synthesized and characterized by various physico-chemical methods. The bonding of ligand to metal ion is confirmed by spectral studies like UV–Visible, FT-IR, and conductance measurements. The lower molar conductance values suggested the non-electrolytic nature of the complexes. The coordination of the Schiff base to the metal atom was found to be through the azomethine nitrogen, and the carbonyl oxygen atoms. Antibacterial and antifungal studies of the ligand and complexes have also been studied which indicate that activity increases on chelation.

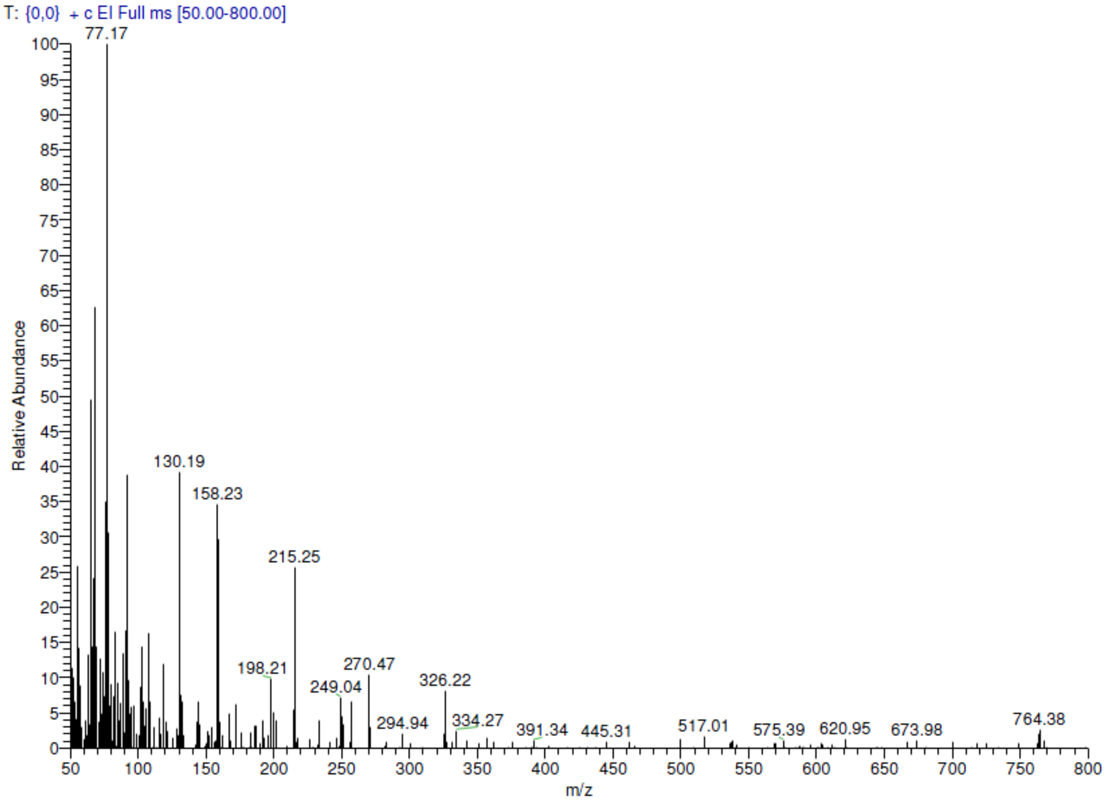


Fig 1: EI-mass spectrum of the ligand L1

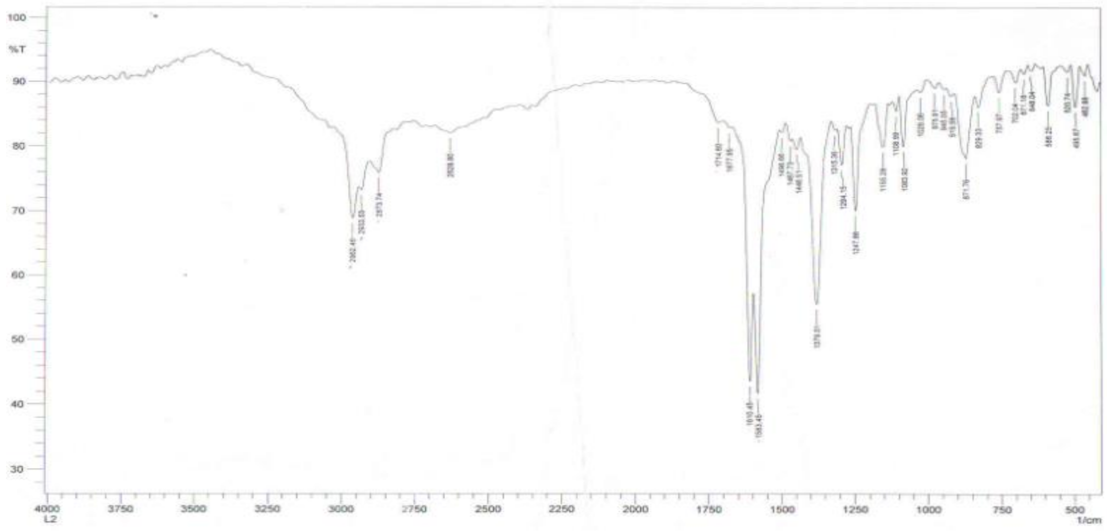


Fig 2: Infrared spectrum bands (KBr) cm^{-1} of the ligand L1

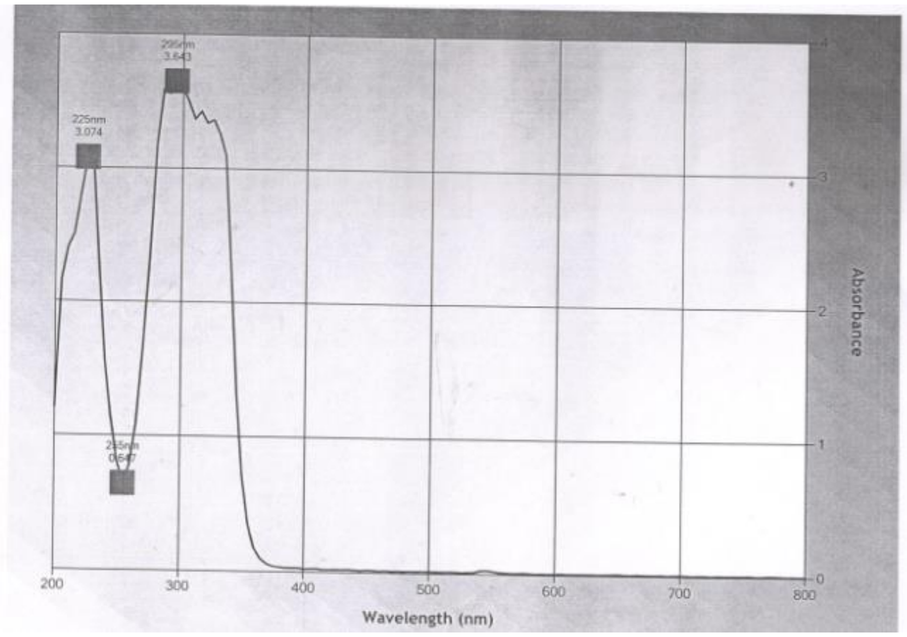


Fig 3: Ultra violet spectrum of the ligand L1

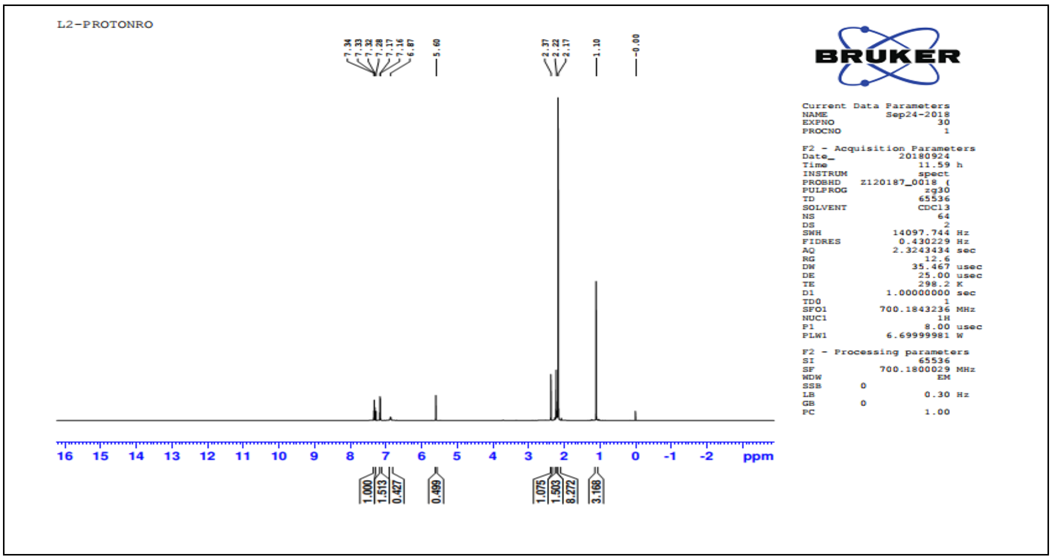


Fig 4: ^{1}HNMR of the ligand L1

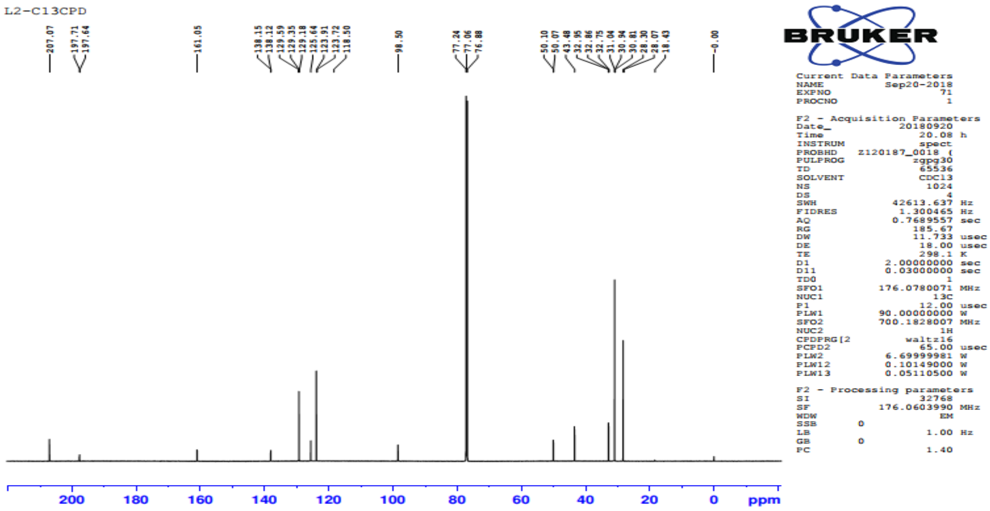


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Fig 5: ^{13}CNMR of the ligand L1

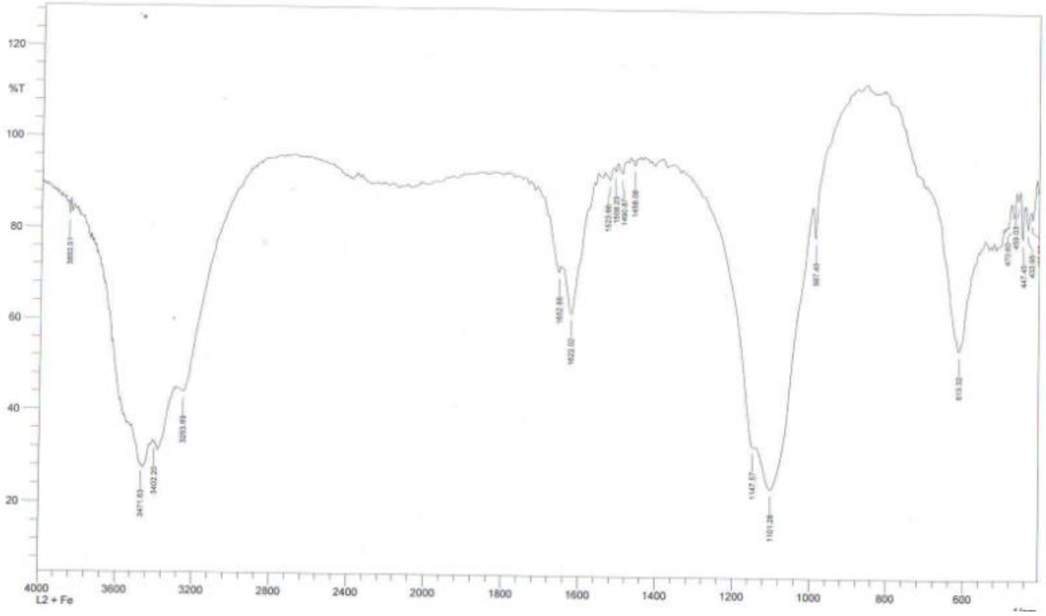

Fig 6: Infrared spectrum bands (KBr) cm^{-1} the FeL1

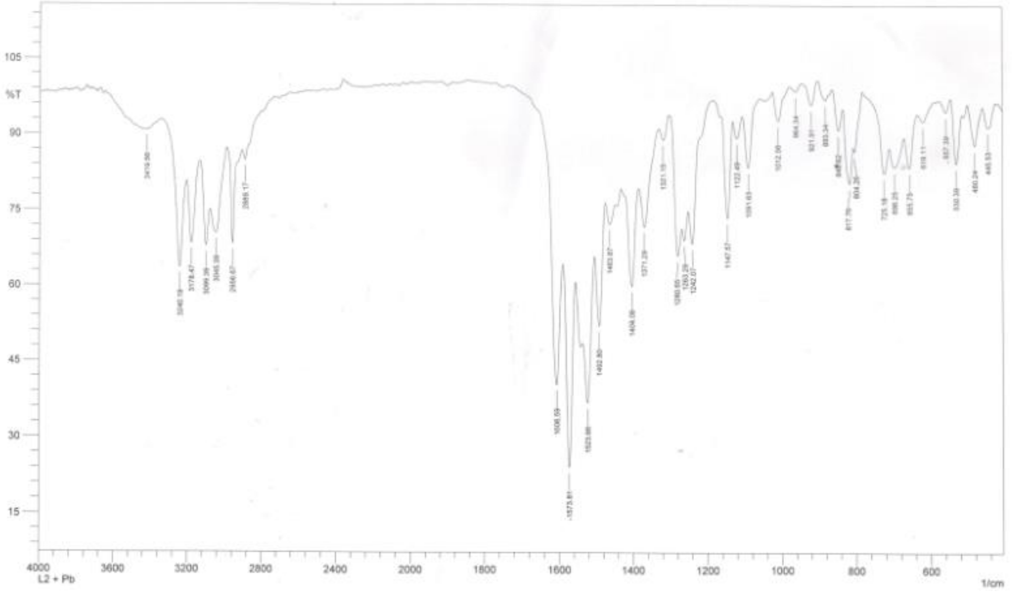

Fig 7: Infrared spectrum bands (KBr) cm^{-1} of the PbL1

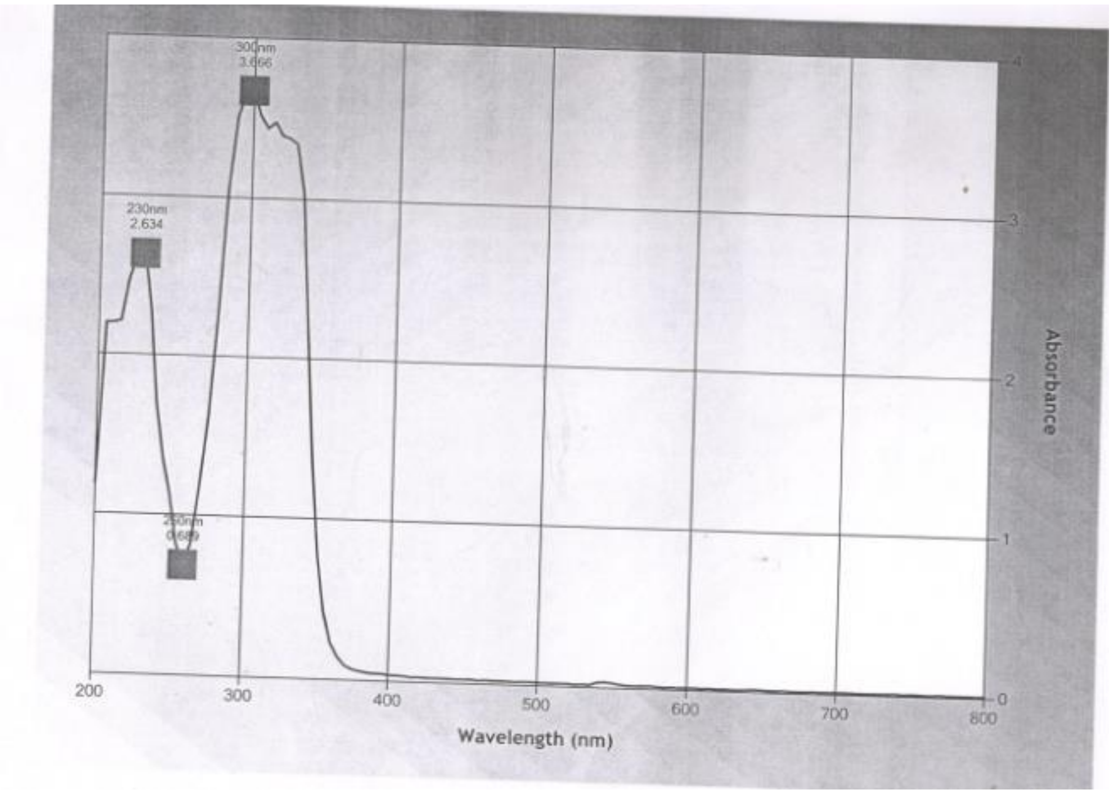

Fig 8: UV-visible spectrum of the FeL1

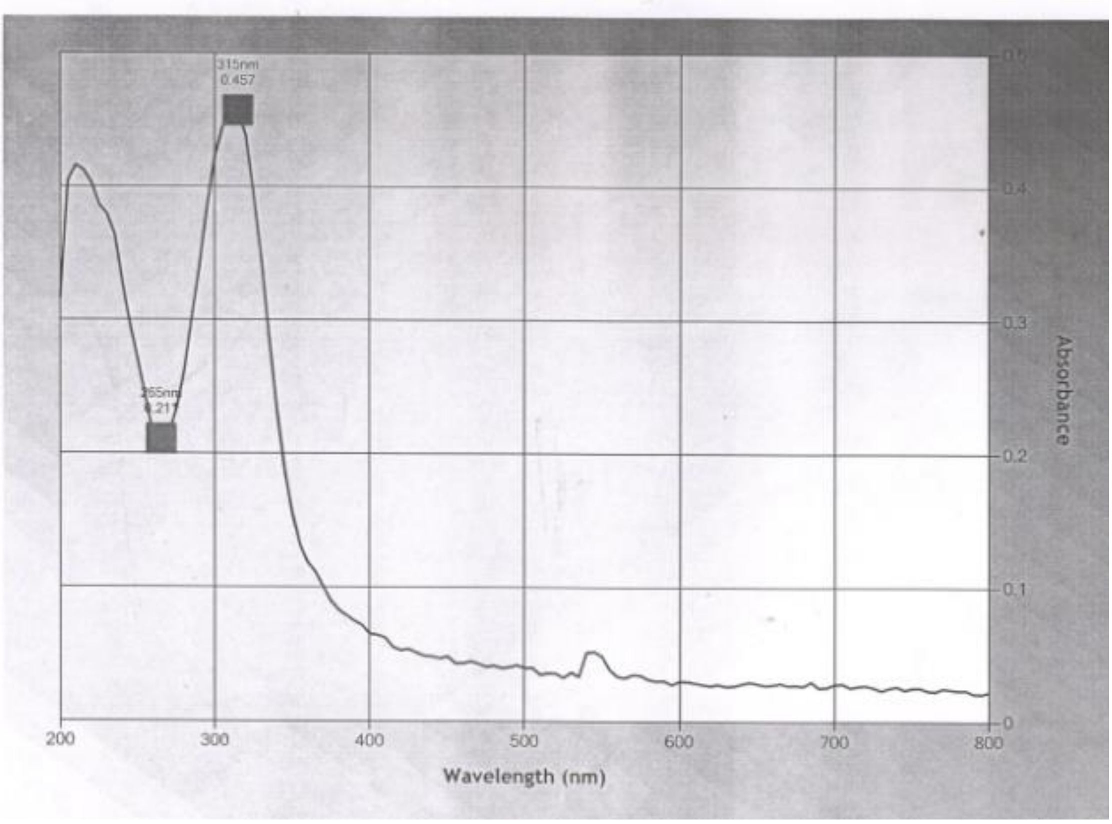

Fig 9: UV-visible spectrum of the PbL1

References

1. Ashraf MA, Mahmood K, Wajid. IPCBEE, 2011; 10:1-7.
2. Brodowska K. Lodyga-Chruscinska, CHEMIK, 2014; 68:129-134.
3. Zhang L, Zhang Y, Tao HB, Sun XJ, Guo ZJ, Zhu LG. J. Mol. Struct. Theochem. 2002; 617:87-97.
4. Cozzi PG. Chem. Soc. Rev. 2004; 33:410-421.
5. Wilkinson G, Gillard RD, McCleverty JA (Ed.). Comprehensive Coordination Chemistry, Pergamon, Oxford, 1987.
6. Shen X, Yang QLC, Xie Synth. React. Inorg. Met. Org. Chem. 1996; 26:1135.
7. Khalil SME. Chemistry Papers, 2000; 54:12.

8. Lehn JM. Supramolecular Chemistry, VCH, Weinheim, 1995; E.C. Constable, in Comprehensive Supramolecular Chemistry, eds. Sauvage, J.P; Hosseini, M.W. Pergamon, Oxford, 1996; 9:6.
9. Ramade I, Kahn O, Jeannin Y, Robert F. Inorg. Chem. 1977; 36:930.
10. Miyasaka H, Ieda H, Matsumoto N, Crescenzi R, Floriani C. Inorg. Chem. 1998; 37:255.
11. Khan MMT, Shukla S, Shark J. J. Mol. Catal. 1990; 57:30l.
12. De Clercq B, Lefebvre F, Verpoort F. App1. Catal. A. 2003; 247:345.
13. Pyta K, Przybylski P, Huczyn Ski A, Hoser A, Wozniak K, Schilf W, *et al*. Brzezinski, Journal of Molecular Structure. 2010; 970:147-154
14. Tisato J, Refosco F, Bandoli F. Coordination Chemistry Reviews, 1994; 135:325.
15. Dwyer FP, MelIor DP. Che1ating Agents and Metal Chelates", Academic Press, London, 1964.