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Synthesis and Characterization of New Some Binuclear Complexes for Some Transition Element Metals with Schiff Base ligand Derived from 1-Chloro-2-(2-Chloroethoxy) Ethane

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Abstract: This research includes the preparation and identification of new Schiff's base ligand (L) by the reaction of compound 3,3- ((oxybis (ethane-2,1-diyl) bis (oxyl) dianlinewith orthohydroxy benzaldehyed. Seven new metal ion complexes of this ligand (L) were prepared through its direct reaction with the chlorides of Mn(II), Co(II), Ni(II), Cu(II), and Cd(II) ions respectively, in general formula $[M_2(L)(H_2O)_2]Cl_2$ M^{+2}=[Mn,Co,Ni,Cu]. The prepared complexes and ligand were identified by (FT-IR) spectroscopy ,Ultra violet-visible(UV-visible) spectroscopy and ^{1}H-NMR spectroscopy of the prepared ligand, also elemental analysis (C.H.N) of some of the prepared compounds has been carried out and the melting points, the molar conductivity and magnetic susceptibility. Tetrahedral geometry is suggested for all the complexes, the calculation results confirmed the suggested structures of all complexes.

INTRODUCTION

Schiff bases ligands have a prominent importance in coordination chemistry, as they are using in preparing many complexes by uniting with the elements or ions metalsowing to their potentiality for coordination[1].The term Schiff bases was given to compounds that have group(C=N)[2]. The scientist (Schiff) was considered the first who prepared the immine in 1864 by the simple condensation reaction between aldehydes or ketones (aliphatic or aromatic), with various primary amines or amino acids, as a reaction happens by way of a middle, unstable state to be transferred to output called anime, which is the output of carbon atom combination, by a double bond, with nitrogen atom[3]. It was found that Schiff bases complexes have anti-cancer effectiveness[4].The researcher Ying et al[5] had prepared a number of complexes by Schiff bases that contain pyridineand amide. They seemed to have effectiveness and efficiency against E. coli bacteria. Researcher Mohammed et al[6]prepared and studied biphenyl complexes of manganese (II), nickel (II), and copper (II) of the type Mn(II), Cu(II) and Ni(II)=M,$[M_2(L)Cl_2(H_2O)_2]$. As the used tetra dentate ligands were homogenous, the complexes were identified by spectroscopy measurements (^{1}H-NMR, UV-Vis, IR), and also C.H.N measurement and calculation of metal rate (M%),as complexes were in form of a tetrahedron. Khalaf et al[7] had prepared complexes of different nuclei that had the general formula $[MCl_3$ (AmoxH) MCl] as M = Zn (ll), Cd (ll) and M = Ti (lll) Fe (ll), AmoxH= amoxicillin. These compounds with transition elementsmetals form colored, claw complexes used in quantitative and qualitative accurateidentification for many metal ions [8].

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EXPERIMENTAL

Chemicals were purchased from Fluka, Merck and Aldrichchemical companies and used without further purification. Melting points weredetermined using in open capillary tubes in Electrothermal 9100 BZ melting point apparatus.IR spectrawere recorded on FT-IR (Shimadzu, FT-IR 8400 spectrophotometer) using KBr disc method.UV-Visible spectrum were recorded on UV-Visible Spectrophotometer- CECIL-CE1021. Molecular conductivity of complexes solutions were measuredusing a digital conductivity meter-WT-720-inoLab (Germany). The magnetic sensitivity of prepared complexes were measured using a magnetic susceptibility balance, Bruker B.M6. The ^{1}H-CNMRrecorded on Bruker Avance-III 400MHz FTNMRspectrometer using DMSO-*d*6. Elemental analyses were recorded on Euro vector, EA 3000A, Elemental Analyzer.

Preparation of the compound3,3$^-$-((oxybis(ethane-2,1-diyl)bis(oxyl)dianline[9].

The compound 3,3$^-$-((oxybis(ethane-2,1-diyl)bis(oxyl)dianline was prepared from reaction of (0.02mmol 2.18g) 3-Amino phenol dissolved in 10ml of absolute methanol inaround flask of (100ml), and (2mol KOH) was added as well. The mixture was stirred until completely dissolved, then (0.01mmol 0.12g) of (dichlorodiethylether) dissolved in (10ml) of absolute methanol was added to it, the mixture was stirred with increasing heat up to 70 °C. After (10min) brown precipitate was formed. Reflux continue for (3h) to complete the reaction, then the mixture was vaporized to (1/4) of the original size and left for 24 hours to complete the precipitation. Filtered and washed by ether for several times and recrystallized from ethanol where brown, needle-like crystals were formed of high purity. Figure (1) shows the reaction process.

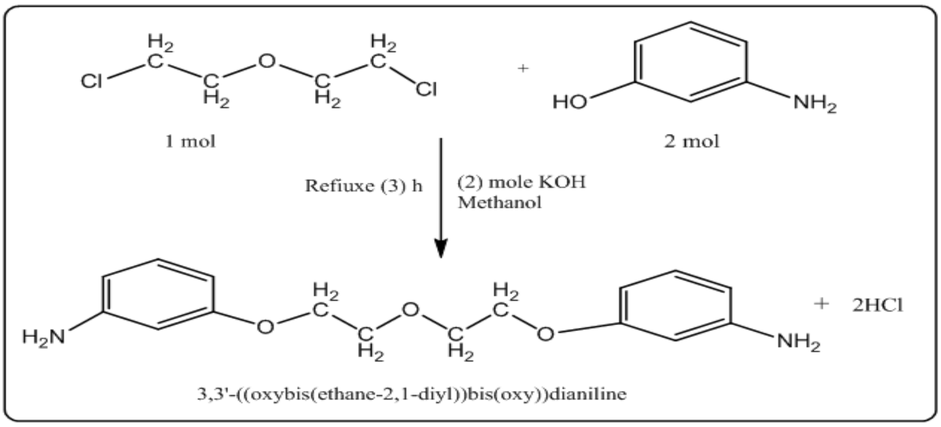

Figure 1: Preparation of compound 3.3- ((oxybis (ethane-2,1-diyl) bis (oxyl) dianline

Preparation of Ligand 2,2'-(1E،1'E)-(3,3'-(2,2'-oxybis(ethane-2,1-diyl)bis(oxy))bis(3,1phenylene))bis(azan-1-yl-1-ylidene)bis(methan-1-ylidene)diphenol(L)[10]

In a round flask capacity (100ml), (0.994g, 0.002mmol) of the compound 3,3- ((oxybis (ethane-2,1-diyl) bis (oxyl) dianline was dissolved in (30ml) of ethanol. A few drops of glacial acetic acid were added to the solution with continuous stirring, then, slowly added, (0.488g, 0.004mmol) from orthohydroxy benzaldehyed. The mixture was left under reflux for one hour, the precipitate was filtered and washed with cold ethanol (5ml), then by (5ml) of diethyl ether and left to get dry. It gave a brown precipitate, yield 76% and melting point (125-127 °C). Figure (2) shows the preparation process.

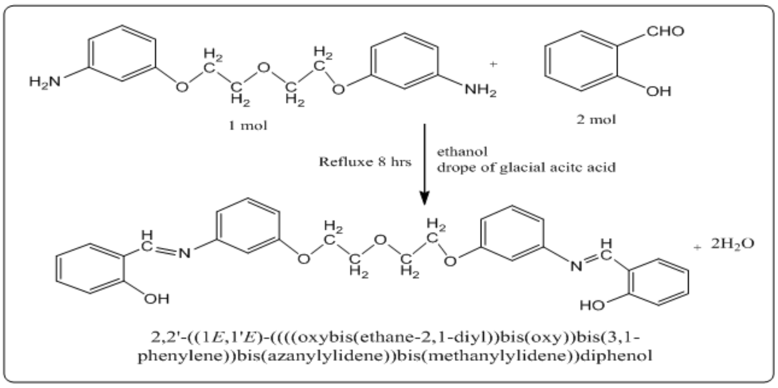

Figure 2: Preparation of ligand (L).

Preparation of Complexes [9,10]

Preparation of Complex $[Mn_2L_1(H_2O)_2]Cl_2$.

It was put in to a 50ml round flask a mixture of (0.4g, 0.0008mmol) ligand (L) dissolved in 5ml of ethanol. Then gradual addition, with slow stirring, of (0.32g, 0.0016mmol) manganese chloride ($MnCl_2.4H_2O$) dissolved in 5ml of distilled water and by mole ratio (1:2) (metal:ligand), so that a light green precipitate was formed. The mixture was left under reflux for 3hours and to get cold. The precipitate was filtered then washed by 3ml of absolute ethanol, after that it got dried and gave yield 70%.

The other complexes were prepared by the same method applied in the preparation of manganese complex. Figure (3) explains the process of preparation.

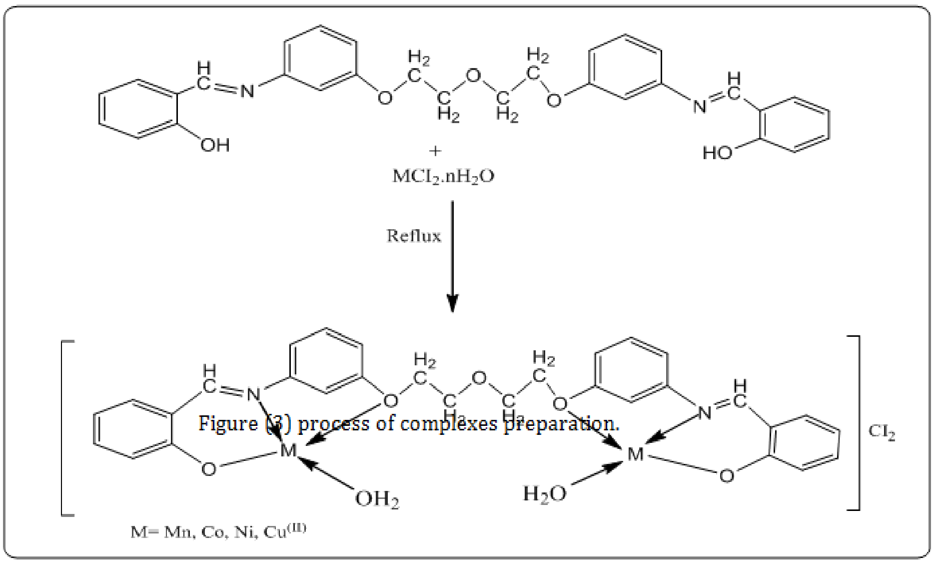

Figure 3: Process of complexes preparation.

RESULTS AND DISCUSSION

The prepared ligand was determined by ^1H-NMR spectroscopy, IR and UV-Visspectroscopy. The complexes were prepared throughout reacting ligand (L) with divalent metal ions of (manganese, cobalt, nickel and copper). Chlorine rate in the prepared complexes was calculated and the accurate analysis for elements (C.H.N). The actual results were in harmony with the theoretical values, and that indicates the validity of the proposed formula, in addition to the measurement of electric conductivity, which confirmed the ionic character of the prepared complexes by rate of (1:2). Results are included in table (1).

^1H-NMR spectrum for Ligand (L)

The spectrum of ^1H-NMR for ligand showed signs at(δ=4.228, 2.246ppm,4H) belong to the protons of methylene groups (CH_2). Also several signs at (δ =7.059-8.580 ppm)belong to protons aromatic rings; the appearance of a single sing at (δ= 11.620ppm) belong to the proton of immine group (N=CH), and a single sing at(δ= 5.679 ppm) belong to hydroxyl proton (OH).

IR spectrum of compound 3.3 - ((oxybis (ethane-2,1-diyl) bis (oxyl) dianline

The most important thing to distinguish FT-IR spectrum for this compound, figure (3-1), is the appearance of two absorption bands at wave number (3360 cm^{-1}) and (3296cm^{-1}), related to the stretching of (NH) symmetric and asymmetric bond, which affirms that amine group. The band at (3028) cm^{-1} is due to stretching the aromatic bond (C-H)in addition to two bands at (2951 and 2837) cm^{-1}that are belong to stretching the aliphatic bond(CH),also appearance of bands at (1072) cm^{-1} and (1151) cm^{-1}, that are due to belong to stretching the bond (C-O-C) [11].

IR spectrum of ligand [L]

spectrum of IR for ligand, figure (1), showed the following distinct bands: broad absorption at (3385) cm^{-1}due to stretching the phenolic bond (OH) linked to phenyl ring and a distinct band at (1614 cm^{-1}) due to (C=N) indicating the disappearance of the distinct band of aldehyde carbonyl[9]. The appearance of this band and disappearance of (C = O), and also the disappearance of the two bands, that belong to υas, s (NH_2) in the ligand, is an evidence for the information of Schiff bases and also bands appearance at (1041)cm^{-1} and (1114) cm^{-1}, which are belong to stretching (C-O-C) [12].

IR spectra of prepared complexes

IRspectra for the complexes$[Cu_2(L_1)(H_2O)_2]Cl_2$,$[Co_2(L_1)$ $(H_2O)_2]Cl_2$,$[Ni_2(L_1)$ $(H_2O)_2]Cl_2$, $[Mn_2(L_1)$ $(H_2O)_2]Cl_2$,showed absorption band at (1602) cm^{-1}, (1600) cm^{-1}, (1608) cm^{-1}, (1604) cm^{-1} and (1608) cm^{-1}, that were displaced towards a lower frequency for the absorption band that belong to immine group, is an indicator of consistency throughout this group[13,14], see figure (2). In addition to the change of bond (C-O-C) stretching owing to the consistency of the oxygen atom with the metallic ion, which appeared at (1140-1022) cm^{-1}.Also displayed new band at (524-565)cm^{-1}and (437-468) cm^{-1}, which are due tostretching the bond (M-N), (M-O) respectively. It is an evidence of the metallic ion and the prepared ligand consistency, as shown in table (2).

UV - Vis Spectra for Ligand [L] and its prepared Complexes

UV-Vis spectrum for free ligand (L), figure (3) showed six absorption peaks at wavelength (220, 215, 245, 340, 365)nm attributed to the electronic transitions of ($\pi\rightarrow\pi^*$)[15] of the group (C=N) that conjugated with phenyl ring tied to a carbon atom. UV-Visiblespectrum for the complex $[Mn_2(L)$ $(H_2O)_2]Cl_2$showed absorption peaks at (210, 215, 233, 260, 275, 365)nm belong to the ligand transfer, as for the peak at (390)nm (ε_{max}=529 molar^{-1}.cm^{-1})it belongs to the interference of mid-tense peak of charge transfer and the peak of electronic transfer type $^6A_1\rightarrow 4A_1$,^4E (^4G). These results comply to the spectrum studies mentioned for manganese complexes (II) tetrahedron [16].

UV-Visiblespectrum for the complex $[Co_2(L)$ $(H_2O)_2]Cl_2$showed absorption peaks at (233, 306, 355, 345, 360)nm belong to the ligand transfer, but the two peaks at (716, 764)nm (13089 and 13966)cm^{-1} (ε_{max}=17-19 molar^{-1}.cm^{-1})successively are attributed to the electronic transfer (d-d) type $^4A_2\rightarrow{}^4T_{1(P)}$ and $^4A_2\rightarrow{}^4T_{1(F)}$ comply to electronic spectra for cobalt complexes (II) tetrahedron [17].

UV-Visiblespectrum for the complex $[Ni_2(L)(H_2O)_2]Cl_2$, figure (4),showed absorption peaks at (210, 235, 245, 285, 290, 365)nm belong to the ligand transfers. As for the peak at (395)nm (ε_{max}=742 molar^{-1}.cm^{-1})it belongs to the spectroscopy of charge transfer integrated withelectronic transition (d-d) type $^3T_{1\,(F)}\rightarrow{}^3T_{1\,(P)}$ [18]. UV-Visiblespectrum for the complex $[Cu_2(L)(H_2O)_2]Cl_2$, figure (4), showed absorption peaks at (225, 230, 240, 275, 290, 345)nm belong to the ligand transfers. As for the peak at (450)nm (ε_{max}=123 molar^{-1}.cm^{-1})is attributed to the electronic transition (d-d) type($^2T_2\rightarrow{}^2E$), and this result agrees with studies of spectroscopy for copper complexes (II) tetrahedron[19].

UV-Visiblespectrum for the complex $[Cd_2(L)(H_2O)_2]Cl_2$ showed absorption peaks at (205-370)nm belong to the ligand spectra. Results are stated in table (3).

Magnetic Measurements

Out of magnetic moment, which shows the number of the single electrons in the outer cover of the metallic ion, it can be known that the compound is of high or low spin. Depending on these rules, cobalt complex (II) with ligand (L) showed magnetic moment of (5.65) BM[17]; and nickel complex (II) with ligand (L)showed magnetic moment of (3.57) BM, and by this it falls within the range of nickel complexes (II) tetrahedron, high spin [17]. As for copper complex (II), it showsmagnetic moment (2.52) BM, so it is paramagnetic due to the existence of one electron as expected for the copper ion (II) [20]. Certain researches have mentioned that these is a difference in the value of magnetic moment for copper(II) tetravalent; as complexes of tetrahedral structure give magnetic moments equal to (2.0-2.20B.M), while copper complexes (II) of plane square structure[21,22] give magnetic moments around (1.80-1.90 B.M). Results are stated in table (4).

Table 1: Physical properties and analysis data of the ligand L and its synthesized metal complexes.

Compounds	**M.P ˚C**	**M.wt**	**Color**	**Yield %**	**(Found %) , Calculation %**			
					C	**H**	**N**	**metal**
[L]	125-127	496.55	Brown	76	(73.18) 72.56	(5.61 5.68	(5,75) 5.64	----
$Mn_2L(H_2O)_2]Cl_2$	320d	640.44	Light green	70				17.16 (16.65)
$[Co_2L(H_2O)_2]Cl_2$	350d	648.43	Light brown	76	59.67 (58.88)	5.33 (6.04)	4.49 (4.12)	18.18 (19.34)
$[Ni_2L(H_2O)_2]Cl_2$	222-225	647.96	Green	66	50.12 (49.67)	4.21 (4.02)	3.90 (2.56)	18.12 (19.34)
$[Cu_2L(H_2O)_2]Cl_2$	350d	657.66	Green olive	64				19.32 (19.56)
$[Cd_2L(H_2O)_2]Cl_2$	350d	755.39	White yellowish	77				29,76 (30.4)

Table 2: Data of IR spectrums (cm^{-1}) of ligand and its complexes

Molecular formula	**υ(C–H) aromatic**	**υ(C–H) aliphatic**	**υ(C= N) υ(C-N)**	**υ(O-C-O)**	**υ(M-N) υ(M-O)**
[L]	(3020)w	(2949) (2897) w	(1614)s (1151)w	(1088,1118)m	-
$[Mn_2(L)(H_2O)_2]Cl_2$	(3028)w	(2941)w	(1602)s (1169)w	(1043, 1113)m	(536,569)w (447,462)m
$[Co_2(L)(H_2O)_2]Cl_2$	(3084)w	(2945) (2868)w	(1602)s (1149)m	(1043, 1112)m	(549,563)w (480,496)w
$[Ni_2(L)(H_2O)_2]Cl_2$	(3005)w	(2962)w	(1608)m (1147)w	(1035, 1120)m	(532,560) w (472,450)w

Table 3: Data of the electronic spectra and the suggested forms of the complexes

Complexes	**λ (nm)**	**υ (cm^{-1})**	**Assignment**	**Suggested structure**
$[Mn_2(L)(H_2O)_2]Cl_2$	210 215 233 260 275 365 390	47619 46511 42918 38461 36363 27397 25641	L,F L,F L,F L,F L.F L.F C.T and $^6A_1 \rightarrow 4A_1, ^4E\ (^4G)$	Td
$[Co_2(L)(H_2O)_2]Cl_2$	233 306 355 345 355 360 716 764	42918 32679 28169 28985 28169 27777	L.F L,F L.F L.F L.F L.F $^4A_2 \rightarrow {}^4T_{1(P)}$ $^4A_2 \rightarrow {}^4T_{1(F)}$	Td
$[Ni_2(L)(H_2O)_2]Cl_2$	210 235 245 285 365 395	47619 42553 40816 35087 27397 25316	L.F L.F L.F L.F C.T and $^3T_1(_F) \rightarrow {}^3T_1\ (_P)$	Td
$[Cu_2(L^2)(H_2O)_2]Cl_2$	225 230 240 275 290 345 450	44444 43478 41666 36363 34468 28985 22222	L.F L.F L.F L.F L.F L.F $^2T_2 \rightarrow {}^2E$	Td
$[Cd^2(L^2)(H_2O)_2]Cl_2$	205 215 225 270 290 310 350 370	46780 46511 44444 37037 34482 32258 28571 27027	L.F L.F L.F L..F L.F L,F C.T C.T	Td

Table (4) Magnetic moment (µeff=B.M.) and molar conductance of solid L-metal complexes at 298K.

complexes	Gram suscep. Xgx 10^{-6}	Molar Sensitivity $X_M\times10^{-6}$C .g . s. u	Diamagnetic correction D x10^{-6}c.g.s	Paramagnetic atomic suscept XAx10^{-6}	µeff, (B.M)
$[Mn_2(L)(H_2O)_2]Cl_2$	19.094	13222.94	187.6	13410.56	5.65
$[Co_2(L)(H_2O)_2]Cl_2$	16.399	11389.4	191,46	11580.86	5.25
$[Ni_2(L)(H_2O)_2]Cl_2$	6.949	4831.64	187.69	5019.26	3.44
$[Cu_2(L)(H_2O)_2]Cl_2$	7.786	5088.10	216.51	5304.69	3.57

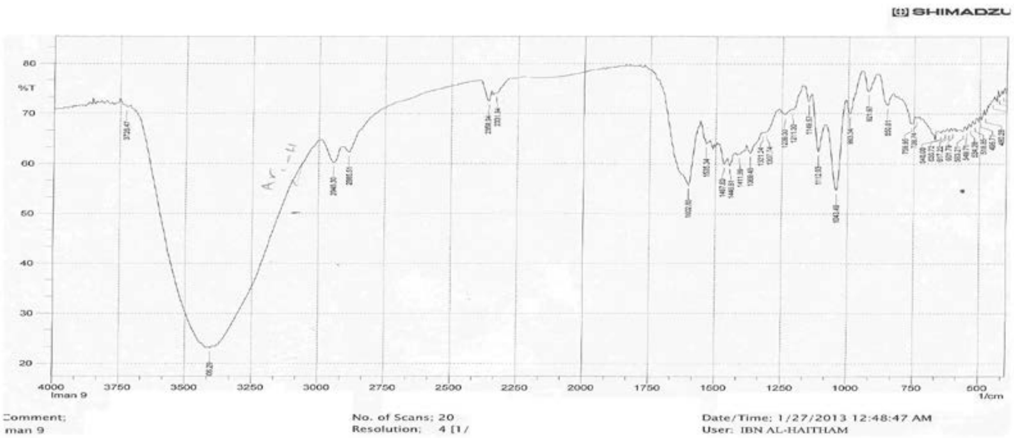

Figure (1): Infrared spectrum of ligand [L].

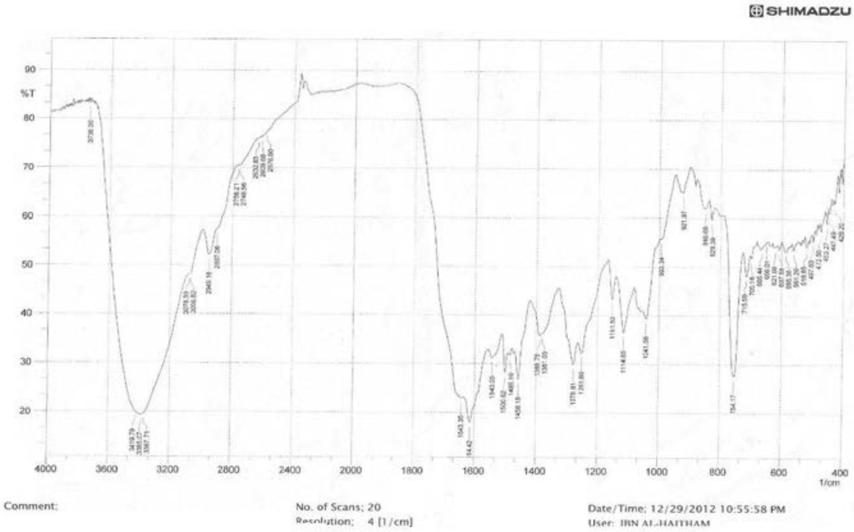

Figure (2): IR spectrum of complex $[Co_2(L)(H_2O)_2]Cl_2$

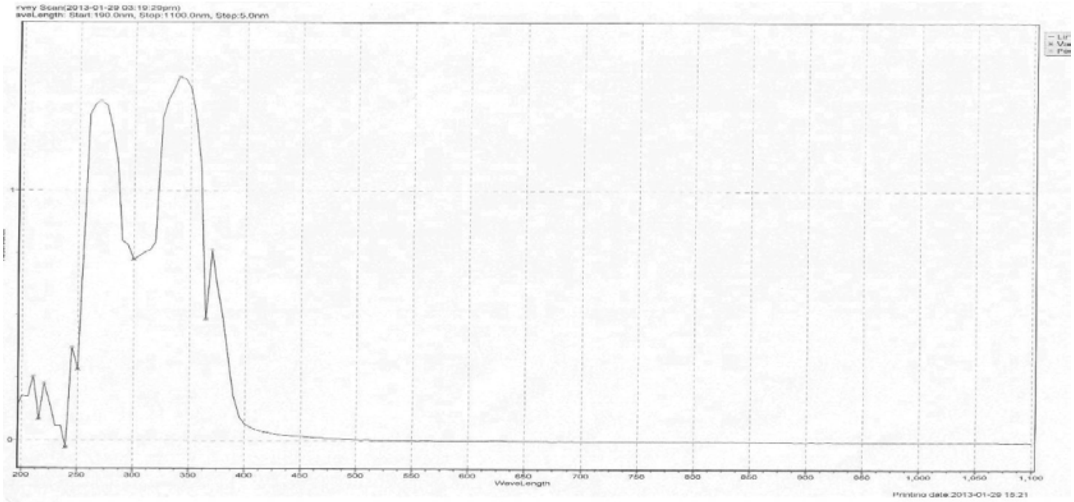

Figure (3): UV-Visible Spectrum of Ligand [L]

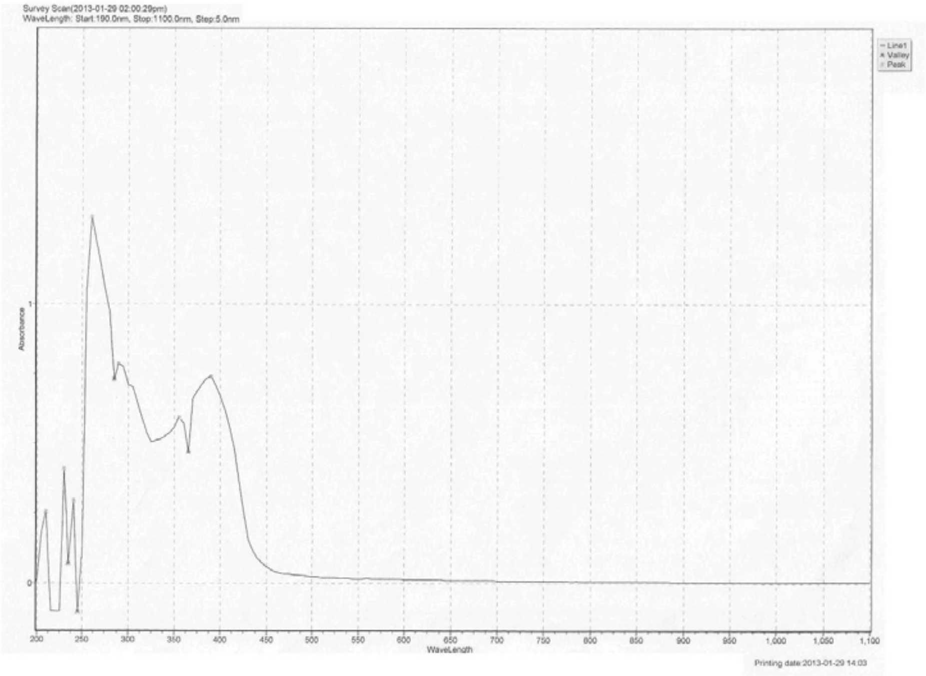

Figure (4): Ultraviolet-visible spectrum of complex $[Ni_2(L)(H_2O)_2]Cl_2$

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