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SPECTROSCOPIC CHARACTERIZATION AND STUDIES OF NEWLY 2,2'-{BENZENE-1,3-DIYLBIS[NITRILO(*E*)METHYLYLIDENE]} DIPHENOL SCHIFF BASE AND ITS METAL COMPLEXES

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ABSTRACT

A new ligand 2,2'-{benzene-1,3-diylbis[nitrilo(*E*)methylylidene]} diphenol (L_D) was synthesized from the condensation reaction of o-phenylendiamine with salicylaldehyde in [1:1] ratio in the presence of glacial acetic acid as catalyst. Coordination complexes of this Schiff base with copper (II), cobalt (II) as nitrate salts and with Rhodium (III) as chloride salt to produce three metal complexes, with a Schiff base: Metal ion ratio of 2:1. The new complexes have been characterized using a variety of physico-chemical and spectroscopic techniques. The new Schiff base and its organometallic complexes were expected to show an interesting bioactivity against microbes and cancer cell lines.

KEYWORDS: Phenylendiamine, salicyladehyde, Schiff base.

INTRODUCTION

Azomethines Schiff bases are ligands that have R-C=N-R$^-$ group and due to their important roles as bioactive complexes, it has been widely prepared.[1-7] Because of their various applications, these ligands facing an increasing interest like biological properties and due to their donation and chelating properties Schiff bases were widely used as ligands in coordination chemistry and synthesis of bioactive complexes.[8-11] Ligands and their metal complexes have a wide applications in industry, especially in analytical reagents[12], dying[13-14] and catalysis.[15-18]

In this research, we synthesized one Schiff base 2,2'-{benzene-1,3-diylbis[nitrilo(*E*) methylylidene]}diphenol (L_D) derived of o-phenylendiamine with salicylaldehyde in [1:1] ratio and complexation reaction of this ligand with copper (II), cobalt (II) as nitrate salts and with Rhodium (III) as chloride salt to produce three chelating metal complexes, characterization to the synthesized compounds have been done to them by using different spectroscopic and analytical techniques.

MATERIALS AND METHODS

Materials

Chemicals that have been used in this research are: salicylaldehyde (BDH), o-phenylendiamine (BDH), Cupper(II) nitrate trihydrate (BDH), Cobalt (II)nitrate hexahydrate (fluka), Rhodium(III) trichloride hydrate (BDH). All chemicals were of analytical grade and were used as supplied without any further purification. Dimethyl sulphoxide (DMSO) (99% BDH), absolute ethanol (99.99%, BDH), dimethyl Diethyl ether (fluka), diethylether (fluka), glacial acetic acid (BDH).

Physical Measurements

Melting points were carried out using Gallen kamp M.F.B 600.01. The infrared spectra of the prepared compounds were recoded using FT-IR-8300-Shimadzu**,** in the wave length range of (4000-400) cm^{-1}. The metals content of the complexes were measured using atomic absorption technique by Perkin-Elmer-5000. The electronic spectra of the prepared compounds were obtained using (UV-Vis-160A) Shimadzu Spectrophotometer, of wave-length (200-1100 nm) all prepared compounds were dissolved in (DMSO) at (10^{-3} M). The molar conductivity measurements were carried out using Wissenschaftlich-Technisch Werk-statten 8120 Weilheim I.O.B, Drucker-Printer. The magnetic susceptibility values were obtained at room temperature using (Magnetic Susceptibility Balance), of Johnson mattey catalytic system division. The metals content of the complexes were measured using atomic absorption technique by Perkin-Elmer-5000.

Synthesis of, 2,2'-{benzene-1,3-diylbis[nitrilo(E)methylylidene]}diphenol Schiff Base (L_D)

The condensation reaction of o-phenylenediamine with salicylaldehyde in [1:2] ratio was dissolved in (25 ml) of absolute ethanol. Then, to this mixture, few drops of glacial acetic acid were added as catalyst, the resulting mixture was refluxed for two hours. The resulting precipitate was filtered, washed with diethyl ether and recrystallized. Then the product [L_D]

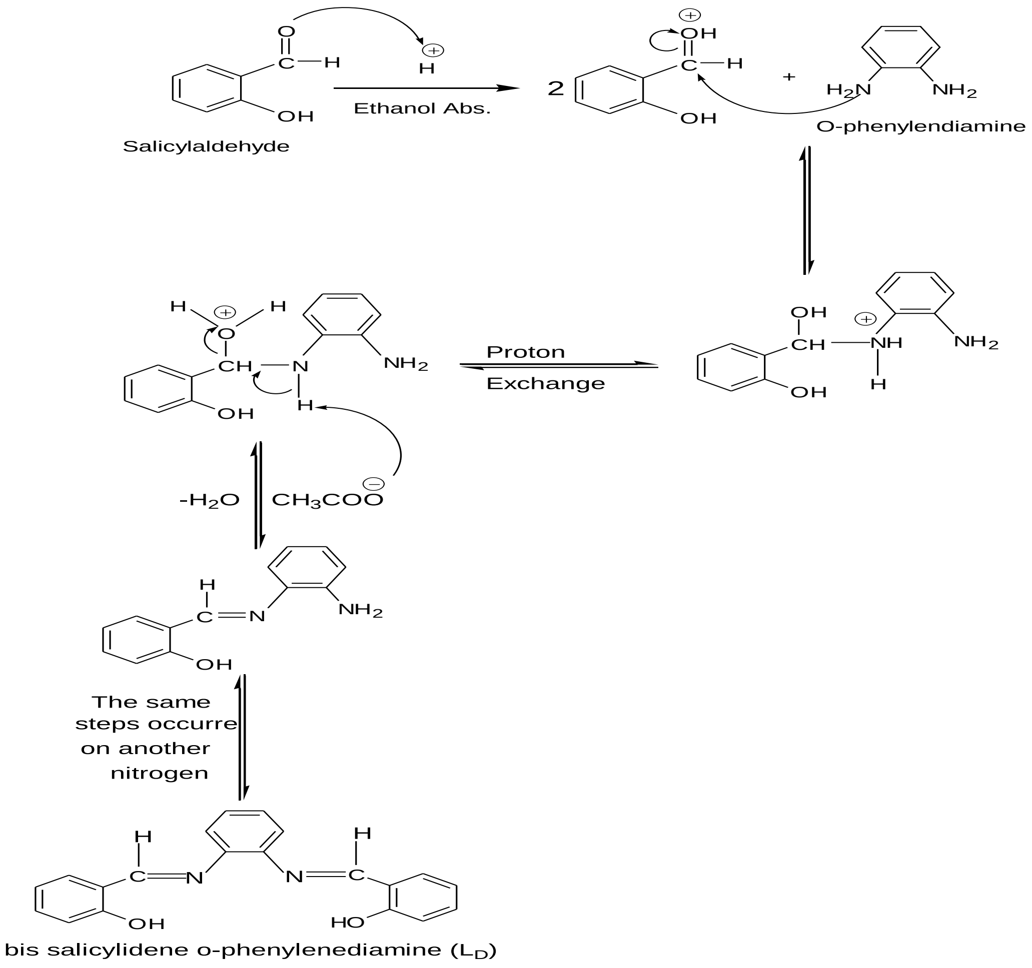
was dried under vacuum oven at 40C^{o} for two days. Pale green Schiff base collected with melting point 166 ºC and yield (90%).

Preparation of the metal complexes of [L_D]

A Solution of (0.94 mmole) Copper nitrate trihydrate, Cobalt nitrate hexahydrate, Rhodium chloride monohydrate dissolved in (10 ml) of absolute ethanol was added to (1.88 mmole) of [L_D] dissolved in (15 ml) of absolute ethanol. The mixture was refluxed with stirring for three hours, the resulting precipitate was filtered and washed with diethyl ether and recrystallized from hot ethanol then dried under vacuum at 40 ^{o}C for two days. Yields: 74-80%.

RESULTS AND DISCUSSION

The new Schiff base, 2'-{benzene-1,3-diylbis[nitrilo(E)methylylidene]}diphenol Schiff Base (L_D**)** has been prepared and characterized successfully. Three metal complexes were also synthesized by reacting metal ions salts Cu(II), Co(II) and Rh(III) with the new ligand. Scheme 1 shows the general mechanism of the synthesis route for the novel Schiff base.



Scheme 1: Synthesis Mechanism of the ligand (L_D).

All the physical measurements of the synthesized ligand (L_B), the metal complexes and the expected formula of the synthesized complexes are shown in Table (1). The data are very near to the expected formula to all the prepared compounds.

Table 1: Physical properties for [L_D] and their metal complexes:

Symbol	Colour	m.p.(C^o)	Yield (%)	Metal analysis (%)	
				Calc.	Found
L_D	Yellow range	164-166	90	-	-
L_D Cu(II)	Brown	290	85	15.29	14.96
L_D Co(II)	Bright green	283	79	11.36	12.42
L_D Rh(III)	Red	>300	87	11.97	11.58

The FT-IR spectra of L_D and their metal Complexes

The F.T.IR spectrum of [L_D] is shown in Figure 1, which show the following characteristic bands: A broad band appearing at (3360 cm^{-1}) has been assigned to stretching *v*(OH) group.[19-20] The strong band at (1276 cm^{-1}) assigned to the phenolic ν(C-O).[21]

The band at (1612 cm^{-1}) is due to azomethine group stretching while the bands (1585, 1560 and 1481) cm^{-1} due to the presence of ν (C=C) of aromatic ring system.[19, 22] The ν (C-H) of the aromatic moiety appeared around (3053-3056) cm^{-1} in the free ligand and its metal complexes.[19]

For the metal complex, [L_DCu(II)], [L_D Co(II)] and [L_D Rh(III)], shows *v*(C=N) band at 1608, 1607 and 1604 cm^{-1} respectively, while the *v*(C-O) were shifted to 1338, 1330 and 1319 cm^{-1} respectively.[22]

The presence of tow new weak band observed at 536 cm^{-1} and 441 cm^{-1} which assigned to υ(Cu-N) and υ(Cu-O) respectively while the bands 541 and 464 cm^{-1} refer to υ(Co-N) and υ(Co-O) bands, the new bands appeared at 536 and 468 cm^{-1} can is attributed to *v*(Rh-N), (Rh-O) [19-22]

Table (2) shows the most characteristic bands of [L_D] and the metal complexes.

Table (2): The most significant bands of F.T.IR spectra of [L_D] and their metal complexes in (cm^{-1})

Symbol	ν (O-H)	ν (C-H) Arom.	ν(C=N)	Phenolic ν (C-O)	ν(C=C) Arom.	ν (M-N)	ν(M-O)
L_D	3360	3053	1612	1276	(1585) (1560) (1481)	_	_
L_DCu(II)	-	3053	1608	1338	(1577) (1523) (1488)	536	441
L_DCo(II)	-	3056	1607	1330	(1579) (1525) (1473)	541	464
L_DRh(III)	-	3053	1604	1319	(1521) (1473) (1458)	536	468

Study of the Magnetic susceptibility and conductivity measurements

These magnetic measurements give an idea about the electronic state of the metal ion in the complex. Also provide information about the type of bonding and strength of ligand field of complexes by giving information about the number of unpaired electrons. [23]

The conductivity to all the complexes was measured; all the complexes are not ionic as shown in Table 3. The value of ($\mu_{eff.}$) that have been measured for all the metal complex it was found (1.95 B.M, 4.85 BM) for Cu(II) and Co(II) complexes respectively. The Rhodium (III) complex is diamagnetic which refer to strong field. These values are in the range of mononuclear octahedral geometry for all the metal complexes. [24]

Table (3): Magnetic moments, Conductivity and UV- Suggested Structures for Complexes of L_D in (10^{-3} M) DMSO solvent

Complex	Magnetic moment μeff. (B.M.)	Conductivity $\mu S.cm^{-1}$	λ_{max} (cm^{-1})	Suggested structure
L_D	-	-	25,510 29,498 33,112	-
L_DCu(II)	1.95	20.5	15,873	Octahedral
L_DCo(II)	4.98	17.8	8995 14,284 25,096	Octahedral
L_DRh(III)	Diamagnetic	21.6	22,522 29,997	Octahedral

UV-Vis Spectrophotometry

The electron adsorption spectra of the metal complexes were recorded at room temperature using DMSO as solvent. The compounds displayed UV/Vis bands in the region 200 nm to 400 nm. The data are shown in (Table 3). The Electronic spectra of Schiff base in (UV-Vis) region have been generally exhibit in three main bands, The first absorption band appeared at 302 nm (33,112 cm^{-1}) which can be attributed to ($\pi \rightarrow \pi^*$) transition for the aromatic system. The second absorption band are attributed to ($\pi \rightarrow \pi^*$) transition of imines group, which appeared at 339 nm (29,498 cm^{-1}), this band were not significantly affected by chelating. [25] The third absorption band appeared at 392 nm (25,510 cm^{-1}) assigned to ($n\rightarrow\pi^{*)}$ transition [26].Which are shifted to a longer wavelength (red shift) upon formation of the complexes. This shift may be attributed to the donation of the lone pairs of the nitrogen atoms of the Schiff base to the metal ion (N:→M).[27]

The brown color [L_DCu(II)] which suggest a strong field complex and show a broad band(1, 36) at (15,873 cm^{-1}) this band refer to distort octahedral geometry (Jahn-Teller distortion) (1, 28) which can be assigned to $^2Eg \rightarrow ^2T_2g$ transitions, the suggested structure for cupper complex shown in Figure 1

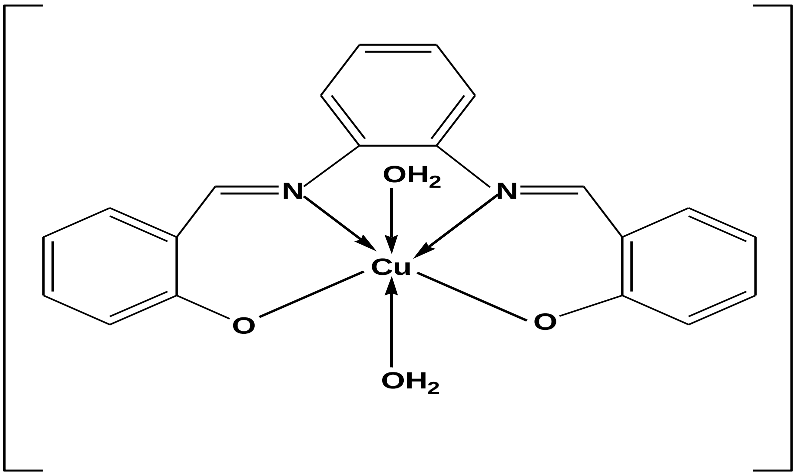


Figure 1: Suggested structure for CuL$_D$ complex.

The spectral behavior of [L_CCo(II)] shows two bands one at (14,284 cm^{-1}), and the other at (25,096 cm^{-1}) which was assigned to the transition [ν_2 ^4T_1g (F) → ^4A_2g (F)] and [$\nu_3$$^4T_1g$ (F) → ^4T_1g (P)] respectively. The value of ν_1 was calculated using Tanabe-Sugano diagram for d^7 system, and found to be (8580 cm^{-1}) which refers to ^4T_1g (F) → ^4T_1g (P) transition, 10Dq Value was also calculated from the diagram and found to be (8,995cm^{-1}) referring to a weak field state.[2] Figure 2 shows the suggested structure of CoL$_D$ complex.

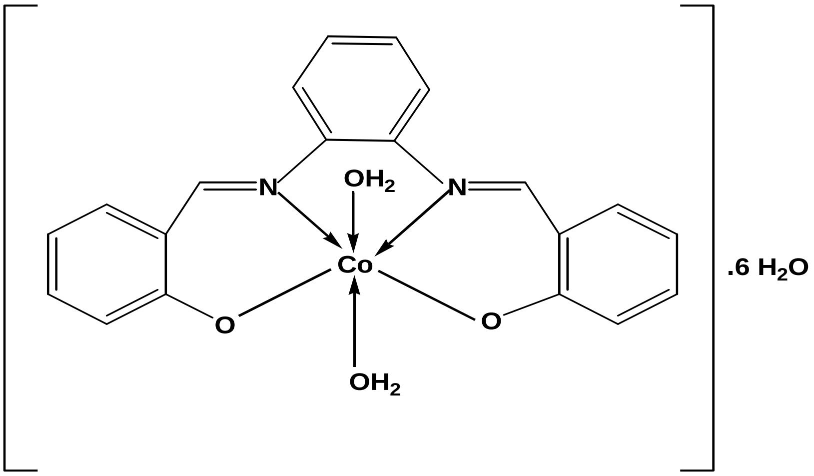


Figure 2: Suggested structure for CoL_D complex.

The electronic spectra of red color of [L_DRh (III)] complex, shows tow absorption band at (22,522 cm^{-1}), a second band (29,997 cm^{-1}) which can be assigned to [ν_1 $^1A_{1g} \rightarrow {}^1T_{1g}$, and ν_2 $^1A_{1g} \rightarrow {}^1T_{2g}$] transitions, which refer to low spin crystal-field and octahedral geometry for this complex (1, 2, 28) Figure 3 shows the suggested structure of RhL_D complex.

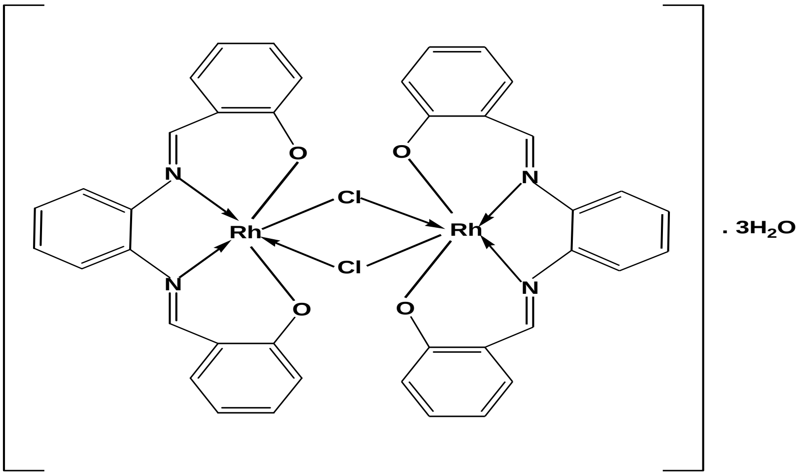
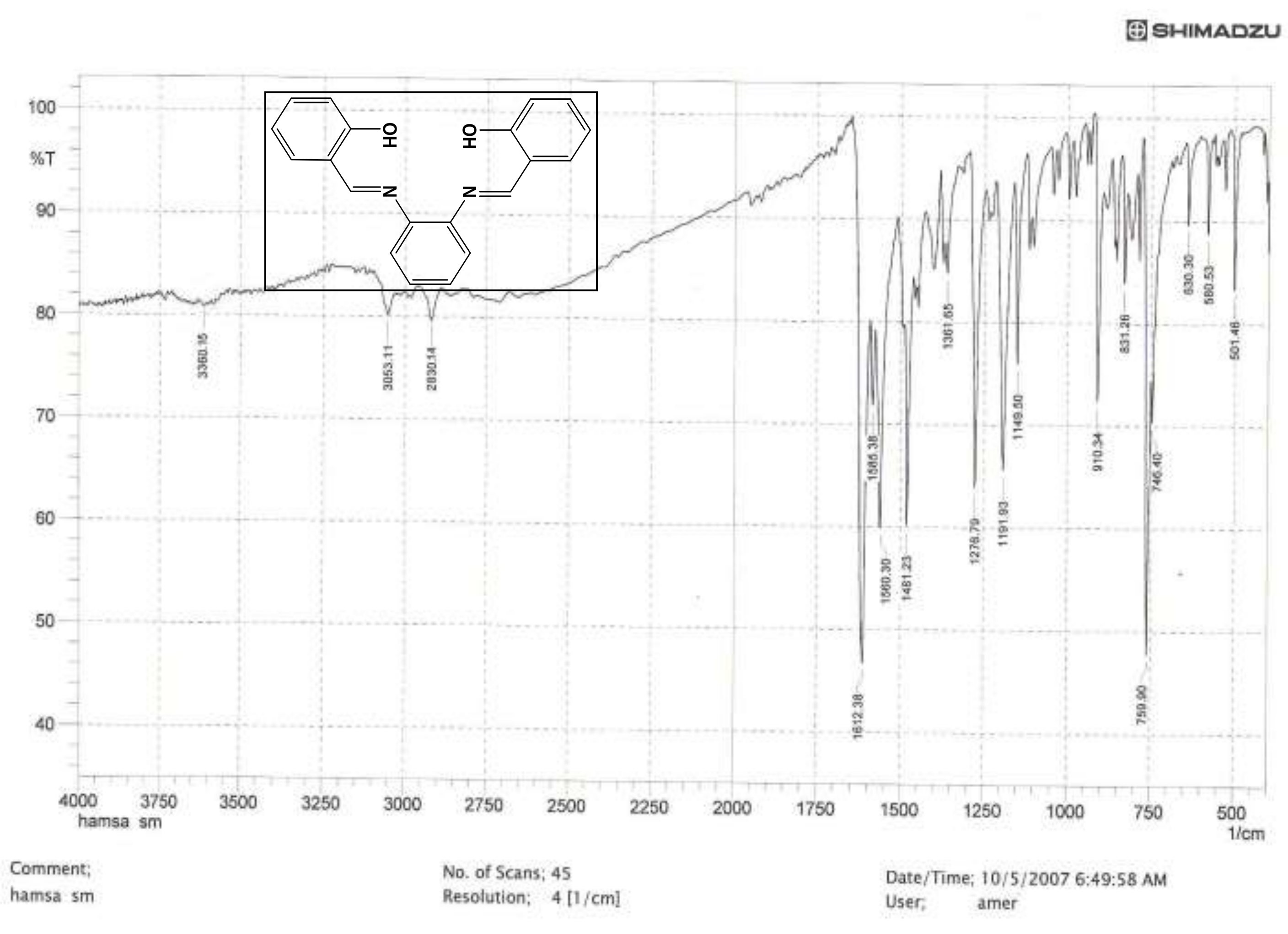


Figure 3: Suggested structure for RhL_D complex.

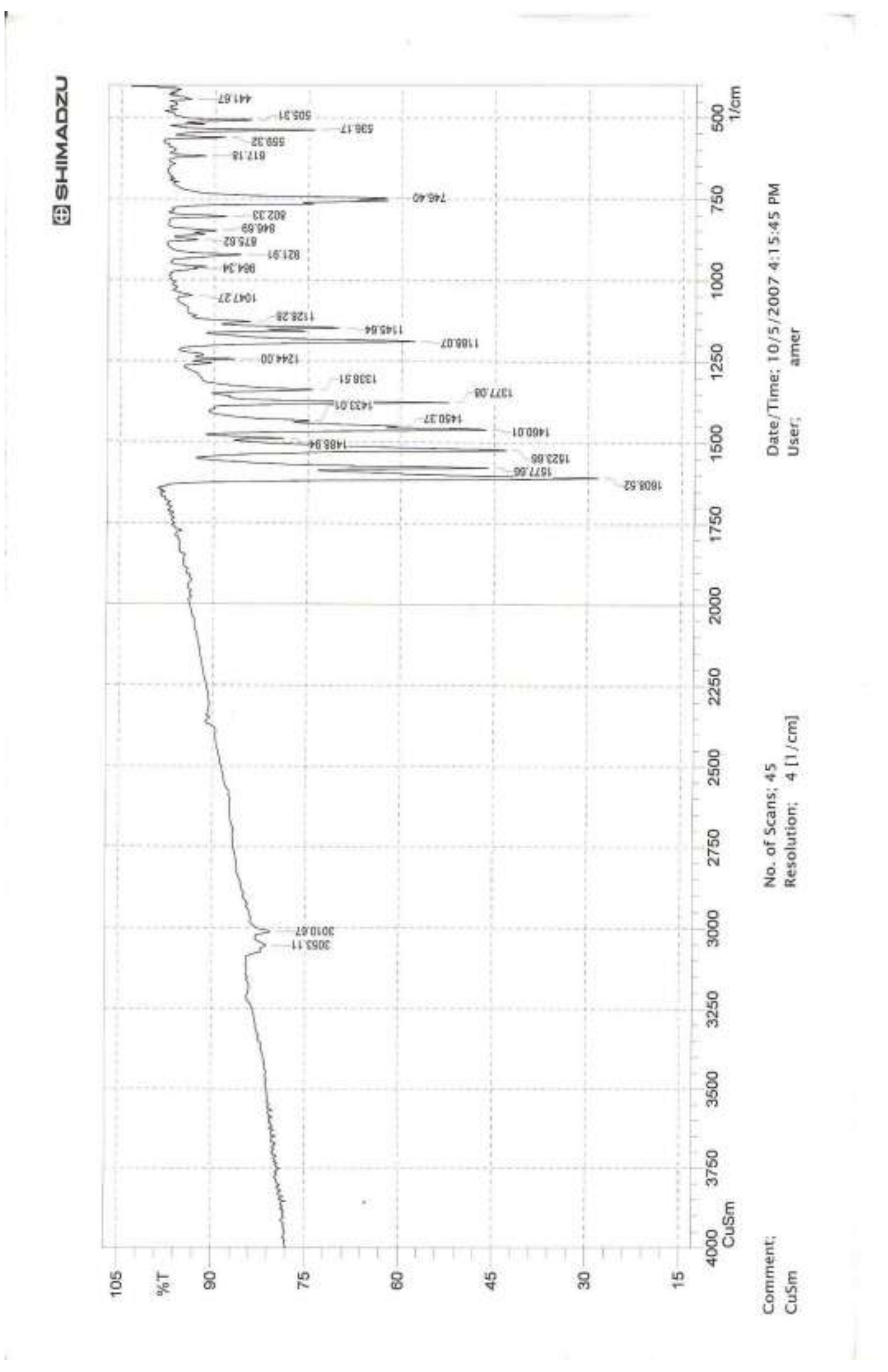
Table (4): Chemical formula and the name of L_D and its complexes

Symbol	Chemical formula	Name
L_D	$C_{20}H_{16}N_2O_2$	bis salicylidene -2-phenylenediamine
L_DCu(II)	$[CuL_D(H_2O)_2]$	diaquo [bis salicylidene -2-phenylenediamine] copper (II)
L_DCo(II)	$[CoL_D(H_2O)_2]. 6H_2O$	diaquo [bis salicylidene -2-phenylenediamine] cobalt (II). water(6)
L_DRh(III)	$[Rh_2(L_D)_2(Cl)_2]. 3H_2O$	di-µ-chloro bis[(bis salicylidene -2-phenylenediamine) rhodium(III)].water (3)

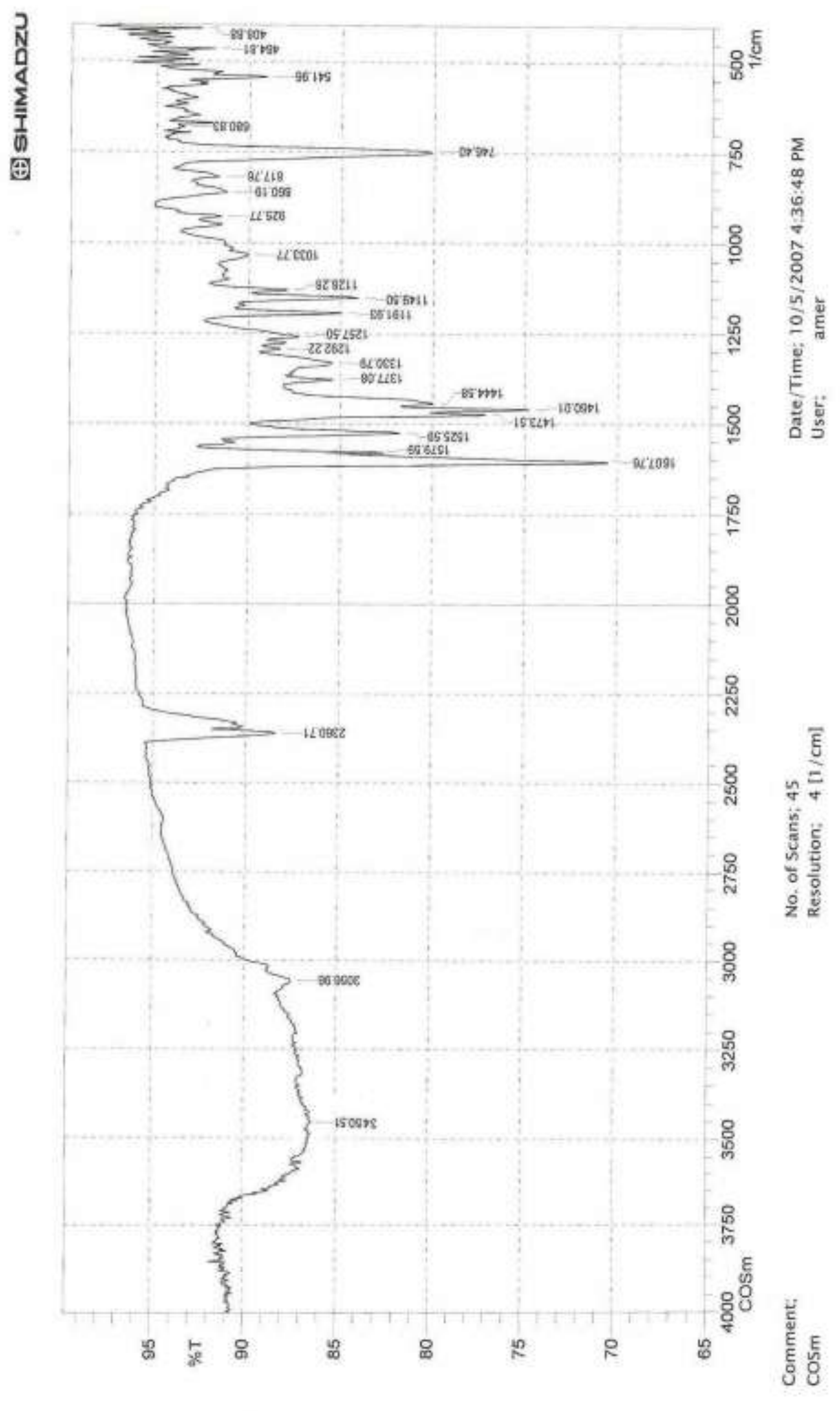
Appendix A



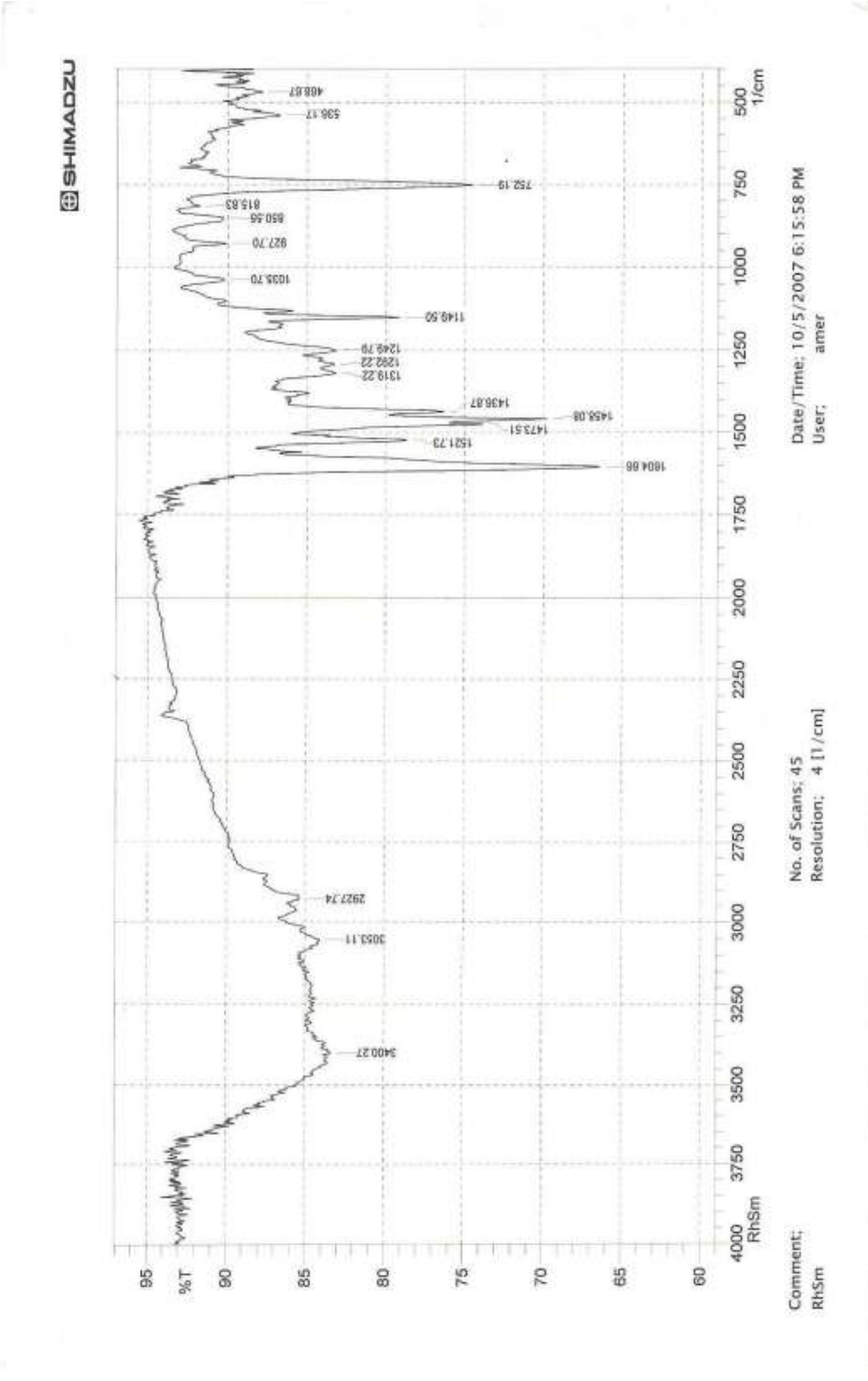
Appendix A1: F.T.IR spectrum of [L_D].



Appendix A2: F.T.IR spectrum of [$L_DCu(II)$].

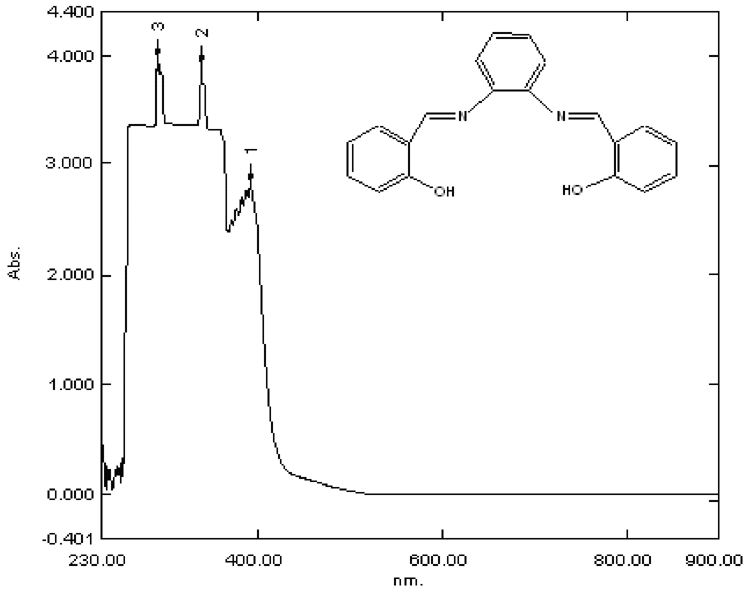


Appendix A3: F.T.IR spectrum of $L_DCo(II)$.

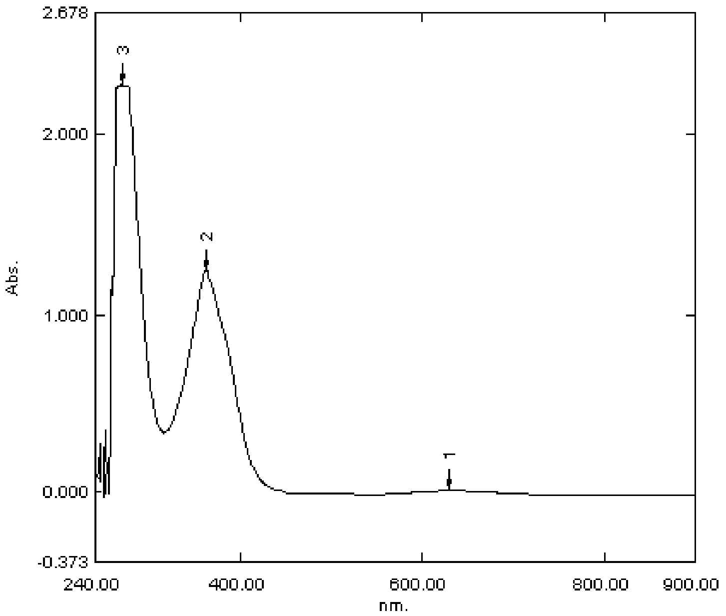


Appendix A4: F.T.IR spectrum of [LDRh(III)].

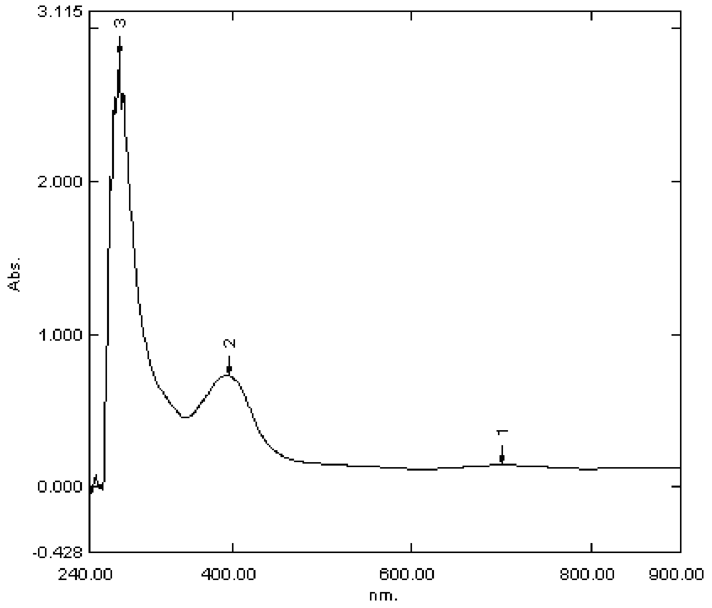
Appendix B



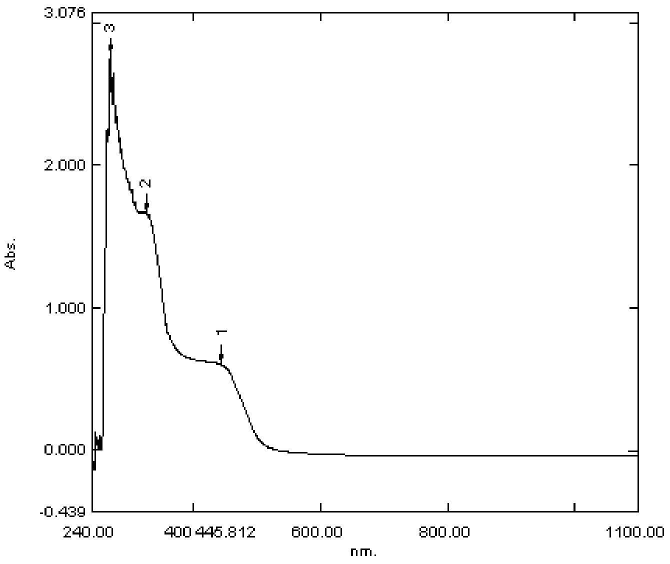
Appendix B1: Electronic Spectrum of L_D



Appendix B2: Electronic Spectrum of L_DCu(II)



Appendix B3: Electronic Spectrum of L_DCo(II)



Appendix B4: Electronic Spectrum of L_DRh(III)

CONCLUSIONS

1- New Schiff base have been prepared successfully.

2- The brown color of Cu (II) complex of L_D ligand refer to the ligand behaves as ligand with strong field with Cu (II) ion.

3- The crystal-field splitting (10Dq) value which was calculated for Co (II) and Rh (III) complexes show that increases when increases number of donor atoms in the ligand (according to chelating effect on 10Dq).

4- The prepared Schiff base ligand behaves as ligand with strong filed when complexions with Rh(III) metal ion because the large size of this metal and have high oxidation state (according to effect of size and charge of the metal ion on 10Dq).

5- Table 4 shows the suggested chemical formula of the new synthesized complexes and their names.

6- Appendix A represent four Infra red spectra of the new complexes.

7- Appendix B represent four UV-Vis spectra of the new complexes.

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