Synthesis, Characterization and Antimicrobial Study of nickel(II), palladium(II), platinum(II), rhodium(III), cadmium(II) and zirconium(IV) complexes with (E)-1-(benzo[d]thiazol-2-yl)-4-(hydroxy(2-hydroxyphenyl)methylene)-3-methyl-1H-pyrazol-5(4H)-one

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Abstract. New transition metal complexes of (E)-1-(benzo[d]thiazol-2-yl)-4-(hydroxy(2-hydroxyphenyl)methylene)-3-methyl-1H-pyrazol-5(4H)-one was prepared and their structures and formulas were confirmed by elemental analyses, EIMS, FT-IR and NMR spectra. The ligand (LH) was prepared through the ring closure of 2-hydrazino benzothiazole and 3-acetyl-4-hydroxy cumarine in dry methanol. The complexes of nickel(II), palladium (II), platinum(IV), cadmium(II), rhodium(III) and zirconium(IV) were isolated in solid state up on the direct reaction of their hydrated chlorides or nickel(II) nitrate with the free ligand solution. The solid structures of metal complexes were supported on the basis of elemental analyses, IR, UV-Visible spectra, as well as the molar conductivity and magnetic susceptibility. The thermal analyses of TG-DSC were done for the LH ligand and their rhodium (III) and palladium(II) complexes in argon atmosphere in order to conclude their structures and thermal stability and the thermo grams observed for the studied compounds have revealed the proposed structures. The data found from preliminary studies revealed that the nickel(II), palladium(II) and platinum(II) were square planner geometry in [MLCl(H2O)] formula, M= Ni, Pd, Pt(II), whereas the rhodium(III), zinc(II) and cadmium(II) were octahedral and tetrahedral geometry respectively in the formulas, [RhL2(H2O)2]Cl and [MLCl(H2O)], M=Zn and Cd(II) ions. However the zirconium(IV) complex was square pyramid with five-coordination number,[ZrOL2].The H NMR spectra of the cadmium(II) and platinum(II) complexes exhibited remarkable changes in the peaks of –NH- pyrazolinone ring and much less shifts in the other functional groups of phenolic and aromatic moiety indicating that the the active sites of coordination with the metal ions are the nitrogen atom of benzothiazole ring and the hydroxyl group linked at C3 at C3 of pyrazole ring. The biological activity of the solutions of the prepared compounds in DMSO as control was estimated against some positive and negative gram bacteria and the inhibition zone measured by diffusion method showed that the metal complexes have greater activity in their spectrum of antibiotics in compared with the employed standard drug in 20 ppm concentrations.

1. Introduction.
The pyrazoline based ligands are considered as main type of biologically important nitrogen containing heterocycles, which have received considerable attention in coordination chemistry [1-3]. The interesting subjects of transition elements involved the 2-pyrazole and benzothiazole derivatives have been exhibited many antimicrobial properties especially their chelates with copper (II), palladium (II) and platinum (II) [4]. The isomerization of ruthenium (II) complexes with 5-phrenyl-3-(2-pyridyl)-1H-pyrazole have also interested in supra molecules due to their sensitization with light energy employed in synthesis [5]. The rare earth metal complexes of 2-pyrazoline ligands endowed with anti-
HIV activity [6,7]. As well as the luminescence properties of aluminum (III) and copper (II) chelates involving pyrazoline-thiazole based ligand have studied and showed considerable applications in synthesis of fluorescent compounds [8,9]. The presence of pyrazoline moiety besides other heterocyclic rings like benzothiazole and which have wide applications in the field of colorimetric determination of heavy metals and light-diodes emitting industry.

2. Experimental section.

2.1. Instrumentation.
The identification of the synthesized ligand with it's metal complexes were carried out with the help of micro-elemental analyses using Carlo-Erba 1106 Elemental analyzer. The electronic spectra were recorded using Shimadzu spectrometer in the range (200-1000) nm in DMF solvent. The 1H and 13C NMR spectra were carried at Albait University, Jordan on Bruker 300 MHz spectrometer in DMSO-d6 solvent. The Fourier transform infrared spectra of the prepared complexes were recorded in KBr and CsI discs using Shimadzu model FT-IR 8400 spectrometer at the Laboratories of Chemistry Department, College of Science, university of Mustansiriyah, Iraq. The molar conductance measurements were made on an Hanna conductivity with a cell having a cell constant of 1.1 cm-1 in DMSO solutions. The proposal structures and formulas of the metal complexes were also confirmed by measuring the metal content (M%) with flame atomic absorption spectroscopy on Shimadzu A.A-670 spectrometer at instrumental analyses laboratory, Chemistry Department, university of Mustansiriyah, Baghdad, Iraq.

2.2. Materials.
The hydrated metal chlorides RhCl3·6H2O,PdCl2·6H2O,K2PtCl4,CdCl2, ZrOCl2·8H2O and Ni(NO3)2·6H2O were purchased from Sigma-Aldrich company and used without purification. The 3-acetyl-4-hydroxy cumarine and 2-mercapto-benzothiazole were supported by Sigma-Aldrich Company (99% purity). The 2-hydrazino benzothiazole was prepared according to the method reported in literature [13]. The molar ratio of metal to ligand was carried out according to the modified method in literature [14] as mentioned.

A series of solutions containing constant volume (5 ml) of the metal ion solution, prepared in the optimum concentration (10-3 M), and variable volumes of the ligand solution prepared in the same concentration (10⁻³ M) were mixed together. The absorption spectra were measured and M:L ratios were obtained by plotting the absorbance versus the mole ratio of the reactants, two straight lines of different slope are obtained the intersection occurs at a mole ratio that corresponds to the combining ratio in the complex.

2.3. Methods.

2.3.1. Synthesis of (E)-3-(4-(hydroxyl (phenyl) methylene)-3-methyl-5-oxo-4,5-dihydro-1H-pyrazole-1yl)quinoxalin-2(1H)-one. The free ligand (LH) was prepared according to the procedure established in literature [15] as shown below.

2-Hydrabenzothiazole (1.65 g, 10 mmole) in dry methanol (20 mL) was added to a solution of 3-acetyl-4-hydroxycumarine (2.053 g, 10 mmole) in methanol (15 mL) and the mixture was refluxed for 3 h. The solid crude product formed was filtered off, dried in air and recrystallized from hot methanol as a pale yellow solid.
Scheme 1.

Yield: 0.377 g, 65 %.
M.p.: 198-200 °C.
RF: 0.75 (ethanol:hexane, v:v, 2:1).
FT-IR (KBr, v, cm⁻¹): 3300-3670(Ar-OH,-C=C-OH), 1640(C=O, Pyrazoline),1630(-C=N-Pyrazole),1390(C,N-N),650-670(C-S)
Proton NMR (300 MHz, DMSO-d6, δ, ppm): 2.66 (s, 3H, CH₃), 6.2(t, 1H, HC=C-), 6.50-7.09 (m, 3H, J = 3 Hz, Ar-H), 7.70-8.09 (m, 4H, Ar-H), 12.00 (s, 1H, HN-C=OH pyrazole).
MS (m/z (%)): 352 (100) [M1+], 351 (90) [M+]

2.4. Synthesis of the metal complexes.
A methanolic solution (50 mL) Ni(NO₃)₂·6H₂O (0.01 mole, 0.455 g), CdCl₂ (0.01 mole,0.183 g) and K₂PtCl₄ (0.01 mole,0.415 g) was added with stirring to an ethanol solution of the ligand (0.01 mole,0.253 g) followed the adjusting the pH of the mixture to 8.0 by addition (1 ml) of 5% KOH solution then refluxed the mixture on water bath for 2 hours except the platinum(II) and palladium(II) which required stirring on water bath (70°C) for 30 minutes and removing the side product of potassium chloride led to afford orange to brown crystals. The obtained coloured solids were separated by filtration under suction, washed with methanol and dried in air overnight then recrystallization from mixture of acetonitrile: absolute ethanol to get purified coloured solids. The complexes of rhodium(III) and zirconium(IV) were prepared in molar ratio 2:1 (LH:M) according to the above mentioned method except ZrOL complex which was prepared by precursor the starting ZrOCl₂ solution of 10%(w/v) in deionized water with (1.22 gm,0.023 mole) of ZrO(OAC)₂. The filter containing ZrO(OAc)₂ then was dealt with the hot methanolic solution of LH (0.02 mole, 0.316 gm). The mixture was stirring on water bath for 6 hours then kept overnight at room temperature and the separated crude filtered, washed several times with methanol, distilled water and dried in oven to afford white off powder of [ZrOL₂] complex, Table(1).

2.5. Biological Activity.
Four types of bacteria strains were used, Gram Negative bacteria, Escherichia Coli(E-Coli), proteus Mirabilis(pro.) , and Gram Positive bacteria, Staphylococcus aureas (Staph), Bacillus(Ba.). These bacteria were diagnosed and cultured on Eosin Methylene Blue (EMB) and Muller Hinton Agar medium for use in this experiment, and in measuring the deactivating capacity of the prepared compounds. The deactivating capacity agent of the isolated bacteria of these compounds was tested by using the holes method. In this method the holes were saturated with 100µm of (20 ppm) of the given compound and left for about 15 min in order to spread on the medium then incubated at 25°C for 24 hour. The deactivation diameters were measured by special ruler designed for this purpose.

3. Results and discussion.
The prepared metal complexes in the recent work were non-hygroscopic (stable at the room temperature) and in the form of amorphous solids. The solubility of the metal complexes were tested in common organic solvents and it is obtained that all complexes were sparingly soluble in methanol,
ethanol and acetonitrile whereas their solubility was high in DMSO and DMF. The results obtained from (CHNS) analyses are in well-agreement with their calculated values then confirm the expected structures and molecular formulas. As well as the molar conductance data of complexes solutions in DMF showed no electrolytic properties except the rhodium(III) complexes which was conductive in the (70 S.cm⁻¹.mole⁻¹), Table 1. The two different tautomeric forms (LA and LB) [10] can be envisaged for ligand of these, A and B are stabilized by intramolecular hydrogen bonding, Scheme(2).

![Scheme 2. Tautomeric forms of LH ligand](image-url)

However, the Job method was applied to reach the optimum conditions for preparation of metal complexes in solution. Here, the figure(1) displays the formation of Rh(III) complex in 2:1 molar ratio LH/Rh III in ethanol solution with adjusting the PH of medium to 8.50 which assists in deprotonation the ligand LH and gives anionic L¹⁻ form that is more capable of binding through enol form HC=C=O moiety and –C=N- of pyrazole ring.

### 3.1. IR spectral study.

The important IR spectral bands of ligand and corresponding complexes along with assignments are presented in Table 2. The absence of a band in the region 1735 cm⁻¹ related to lactone starting material[15] indicates the attack of HN- moiety on the carbonyl of cumarine in 2-C position [13,15].

The strong absorptions at 1640, 1630, 1480 and 3500-3670 cm⁻¹ could be assigned to lactone -C=O, -N=C-, C-N and -phenolic -OH [5,13]. However, the appearance of strong absorption in the free ligand at 970-1020 cm⁻¹ and 1390-1370 cm⁻¹ reveals the –C-N and N-N modes of pyrazoline ring. As well as the medium intensity band at 650 cm⁻¹ reveals the C-S bond of thiazole ring [11,15]. In the complexes, it is obviously that remarkable shifts to lower frequency region (1648-1677 cm⁻¹) and (1600-1550) cm⁻¹ due to the formation of M-O and M-N bonds since the drift of lone pairs on oxygen and nitrogen atoms moved to vacant orbitals of the metal ions .Figures(1, 2 and 3). In the spectra of all metal complexes, a weak bands were appeared in the far-infrared regions 312-388 cm⁻¹, this may be attributed to (M-Cl)bond and support the participation of chloride ions in inner sphere of metal complexes structures [18]. Furthermore, the nickel(II) complex displayed medium band around 1490 and 970 cm⁻¹ which are characterized to the asymmetric and symmetric stretching of –N=O bond of nitrate –NO₃- present in the inner sphere of Ni(II) complex suggesting the linkages of Ni-N=O via nitrogen atom of the nitrate anion. The bands due to v(NH) are broadened in all the complexes due to the overlapping of v(OH) bands of enol form of the ligand to H-N-of pyrazoline ring [11,17]. The new bands in the far-IR spectra for all metal complexes in the 500-560 cm⁻¹ and 422-460 cm⁻¹ regions are assigned to v(M–N) and v(M–O), respectively [18]. The complexes exhibited a broad band in the region (3400-3600) cm⁻¹ that are assigned to coordinated water molecules [13,15]. The zirconium(IV) complex showed strong absorption around 890 cm⁻¹ assigning to Zr=O bond [16].

### 3.2. Mass spectra study.

The absorptions of ionization impact mass spectra of the LH recorded a main peak at M⁺ = 352due to the molecular ion related to free ligand LH that is remarkably gives strong evidence for ring closure of hydrazine-intermediate formed via condensation of acetyl moiety of cumarine with amino one of
hydrazine benzothiazole, Scheme 2. The other peaks at 285 and 167 were assigned to cleavage of benzothiazole moiety and phenoxy groups. The other peaks in the MS spectrum may have ascribed to the breaking of weak points of methyl, hydroxyl and phenyl groups in the chemical structure of the ligand.

3.3. Electronic spectra and magnetic moments.
The UV-Vis spectra of the ligand (LH) in methanol within the range (200-1000) nm displayed mainly three peaks. These transitions at 220,370,470 could be ascribed to the moderate energy $\pi \rightarrow \pi^*$transition of the aromatic rings. Furthermore, the sharp ($\lambda_{max}$) peaks at (370,470 nm) were related to the $\pi \rightarrow \pi^*$ transition of intermolecular charge-transfer taken place through the azo group (-C=N-, -C=C and |-C=O), [10,15]. The pale coloured solution of zirconium (IV) and cadmium complexes showed high intensity absorptions around (240-390) and (322-470) nm, these absorptions could be assigned to LMCT of L→ Cd and Zr=O respectively[18]. The brown solution of nickel (II) complex in DMF showed two d-d transitions around 498 and 509nm that are assigned to the $^1$A$_1g\rightarrow ^1$B$_1g$ and $^1$A$_1g\rightarrow ^1$B$_2g$ respectively, which are typical transitions for square planner Ni(II) complexes[18]. The pale red solutions of palladium(II) and platinum(II) complexes in DMF solvent recorded low intensity peaks in regions (470-400) and (480-520) nm assigning to $^1$A$_1g\rightarrow ^1$B$_2g$ and $^1$A$_1g\rightarrow ^1$B$_2g$ respectively [18,19] thus ascribing the low spin square planer environments around Pd(II) and Pt(II) ions[20]. However, the absorptions of Rh(III) complex in DMF at 326, 562 and 889 and 630 confirms the octahedral rhodium(III) complexes [21].

3.4. $^1$H NMR study.
The ligand LH displays two sharp singlets at 12.00 ppm attributed to the resonance of de shielded protons of pyrazole ring N-C-OH in S-position of pyrazole ring. As well as the proton of -OH group attached to phenyl group that mainly belonged to cumarine derivative was appeared at 7.41 ppm as singlet peak which support the ring closure occurred by attaching of lone pair of $\text{NH}$- on the carbon atom C-O of lacton moiety [11,13]. However the absorption of aliphatic -CH$_3$ was observed in the region 2.10-2.50 ppm as singlet peak which is strong proof for the keto-enol forms of the free ligand in solution.

3.5. Effect of pH and Concentration on Pd(II)-L Solutions.
The UV-Vis spectra of Pd(II)-ligand mixed solution with a concentration range of (10$^{-3}$-10$^{-7}$) M were studied. The concentration of 10$^{-4}$ M was obeyed the Lambert-Beer's law and showed a clear intense color. A straight line, with correlation factor (r = 0.98), was obtained when the absorbance plotted against the molar concentration. The data obtained were tabulated in Table (4). The optimum concentration was chosen for complex solutions giving rise to a constant ($\lambda_{max}$) at different pH values. Table (4) includes the absorbance and ($\lambda_{max}$) of the complex solution at different pH and concentrations. It is obvious that the concentration of (0.75 x10$^{-5}$M) for Pd(II) solution are subjected to be the optimum concentration. The influence of the pH was studied at pH range (3.5-8.5). The absorbance-pH curve was carried out at certain ($\lambda_{max}$) and several concentrations. The curve exhibit two broad plateaus at pH range (4-5) and (7.5-8.5) represent the presence of two species in the solution at these two pH ranges. The descending part of the curves may represent the dissociation of the two complexes formed at more basic medium. However, the results suggest pH 4.5 and 8 as an optimum pH for the two formed species in solution. At the same time the descending part of the curve may represent the dissociation of the formed complex at more basic medium.

3.6. Thermal analyses (TG-DSC).
The thermo gram curve of LH at temperature range (100-595.5) $^0$C showed one decomposition step. The TGA peak observed at 595.5$^0$C indicated the loss (C$_{11}$H$_{10}$N$_2$O$_2$S) fragment (det.=13.38mg, 71.17%, calc.=11.24mg ) Figure(4). The endothermic a peaks may be indicate combustion of the organic ligand in an argon atmosphere. The TG curves of [RhL$_2$(H$_2$O)$_2$Cl] complex
displayed thermal decomposition with loss weight percent (9.85mg, 46.9%, calc.= 10 mg) in the temperature range (100-324.37)°C indicating the cleavage of chloride ions present in the outside the coordination sphere and two coordinated molecules of water in rhodium(III) complex. As well as the degradation of the organic molecule started before the temperature 324°C.

The second step of TG curve exhibited (4.55mg, 21.68.9%, calc 4.45mg), Figure(5). The thermogram of [PdLCl(H₂O)] is shown in Figure(6). The TGA peak at 225.49 °C assigned to the loss of (C₇H₉N₃OSCl) (det.= 9.8mg, 46.53%, calc.= 9.9mg). The second step recorded at 326.58 °C (10.43mg, 49.7%, calc=10.27mg), The differences between the observed and calculated may be related to sublimation process. The DSC curve indicated endothermic decomposition processes [15, 18] at temperatures 248.7°C.

3.7. Biological Activity.
The screening of cytotoxicity of the prepared compounds against some negative and positive bacteria were carried out via diffusion method [23] and the results are presented in Table (6). The results of the present study show that the complexes have a relatively strong deactivating capacity against the G+staph. and G-pro.Specimen of bacteria, while different deactivating capacity was recorded for G+Bacillus and G-E.Coli specimen of bacteria. However, introduction of metal in complexes increase the deactivating capacity of the ligand [23,24]. For a comparison between the biological activity of Ciproflaxine and the ligand and its complexes which were prepared by us, it was noted that the effectiveness ligand and its complexes was the biggest ones of the standard drug in (20 µg/ml) and it is observed that cadmium(II) and platinum(II) complexes showed the maximum inhibition for growth the micro-organisms understudy[24].

Table 1. The physical properties and elemental analysis of the prepared metal complexes.

| Compound         | Color    | M.p. (°C) a | C% Calculated | H% Calculated | N% Calculated | S% Calculated | M% b  |
|------------------|----------|-------------|---------------|---------------|---------------|---------------|-------|
| LH               | Pale yellow | 200-202    | 64.22         | 5.11          | 14.77         | 10.10         | -     |
| [NiL(NO₃)(H₂O)]  | Brown    | 298         | 44.02         | 3.28          | 11.41         | 6.53          | 11.95 |
| [PdLCl(H₂O)]     | Brown    | 277         | 42.20         | 3.15          | 8.20          | 6.26          | 20.77 |
| [PtLCl(H₂O)]     | Orange   | 301         | 35.98         | 2.68          | 6.99          | 5.34          | 32.46 |
| [RhL₂(H₂O)₂]Cl  | Green    | 299         | 49.18         | 3.67          | 9.56          | 7.29          | 11.70 |
| [ZrOL₂]         | White    | 290-292     | 53.25         | 3.48          | 10.35         | 7.90          | 11.23 |
| [CdLCl(H₂O)]    | yellow   | 292dec      | 41.71         | 3.11          | 8.11          | 6.19          | 21.69 |

a Dec: Decomposed.
b Content of metal was done by flame atomic absorption spectroscopy.
### Table 2. FT-IR absorptions of the LH and its metal complexes.

| Compound          | νNH,OH | vC=O | νC=N | νC=H   | νC-N  | νM–N | νM–O | νM–Cl |
|-------------------|--------|------|------|--------|-------|------|------|-------|
| LH                | 3383   | 1666 | 1624 | 2947,2862 | 1377(s) | -    | -    | -     |
| [NiL(NO₃)(H₂O)]   | 3400   | 1655 | 1590 | 3050,2964 | 1370(s) | 510  | 460  | 1300,950, N=O |
| [PdLCl(H₂O)]     | 3300   | 1640 | 1577 | 3010,2987 | 1377(m) | 530  | 440  | 322(w) |
| [PtLCl(H₂O)]     | 3500   | 1648 | 1580 | 3010,2967 | 1389(m) | 522  | 450  | 374(w) |
| [RhL₂(H₂O)₂]Cl    | 3460   | 1654 | 1616 | 3010,2977 | 13929(w) | 550  | 459  | 322(w) |
| [ZrOL₂]          | 3519   | 1659 | 1600 | 3010,3000 | 1375(m) | 500  | 438  | 890   |
|                   | 3400   | 1650 | 1578(s) | 3000.2963 | 1372(w)0 | 502  | 432  | (Zr=O) |

s = strong, m = medium, br = broad, w = weak.

### Table 3. The electronic spectra and molar conductance of the prepared complexes.

| Compound          | UV-visible, λ (nm) | μ (BM) | Λm (S.mol⁻¹.cm²) | Geometry     |
|-------------------|--------------------|--------|------------------|--------------|
| LH                | 220,370,470(CT)    | -      | -                | -            |
| [NiL(NO₃)(H₂O)]   | 300, 498,509       | 0.00   | 11               | Square planner |
| [PdLCl(H₂O)]     | 280,470,400        | 0.00   | 17               | Square planner |
| [PtLCl(H₂O)]     | 350,480,520        | 0.00   | 10               | Square planner |
| [RhL₂(H₂O)₂]Cl    | 326,562,889        | 0.00   | 70               | Octahedral   |
| [ZrOL₂]          | 240,390(CT)        | 0.00   | 10               | Square pyramid |
| [CdLCl(H₂O)]     | 322, 470(CT)       | 0.00   | 12               | Tetrahedral  |

* Λm = molar conductance was measured in DMF solutions.
Table 4. Absorbance at $\lambda_{\text{max}}$ for molar concentration of Pt (II)-Ligand complex solutions at pH = 8.5.

| Molar Conc. $\times 10^{-4}$ | Absorbance |
|-----------------------------|-------------|
| 0.25                        | 0.232       |
| 0.50                        | 0.443       |
| 0.75                        | 0.695       |
| 1.00                        | 0.940       |
| 1.25                        | 1.150       |

Table 5. TGA / DSC data of LH ligand and some metal complexes.

| Compound                  | Decomposition step | TG Temperature | Removes species | Wt. loss (Calc.)mg | Wt. loss Found mg |
|---------------------------|--------------------|----------------|-----------------|-------------------|-------------------|
| [LH] $\text{C}_{18}\text{H}_{15}\text{N}_{3}\text{O}_{3}\text{S}$ | 1st (Residue)     | 71-595.5       | (C$_{11}$H$_{10}$N$_{3}$O$_{2}$S) | 11.24             | 11.38             |
|                           |                    | Over 595       | (C$_{7}$H$_{5}$O)          | 11.24             | 11.38             |
| [RhL$_2$(H$_2$O)$_2$Cl]    | 1st               | 100-324.37     | (C$_{18}$H$_{18}$N$_{2}$O$_{2}$Cl) | 10                | 9.85              |
| $\text{C}_{38}\text{H}_{32}\text{N}_{6}\text{O}_{8}\text{S}_{2}\text{RhCl}$ | 2nd               | 324.3-595.2    | (C$_{12}$H$_{18}$N$_{2}$O$_{2}$)    | 4.55             | 4.55              |
|                           | Residue           | 600            | (C$_{6}$H$_{6}$N$_{2}$O$_{4}$Rh)  | 6.55             | 6.60              |
| [PdLCI(H$_2$O)]           | 1st               | 115-225        | (C$_{9}$H$_{9}$N$_{3}$OSCl)      | 9.9               | 9.8               |
| $\text{C}_{18}\text{H}_{19}\text{N}_{3}\text{O}_{4}\text{SPdCl}$ | 2nd               | 225-326        | C$_{9}$H$_{7}$O$_{3}$Pd          | 10.27            | 10.43             |
|                           | Residue           | 595            | Decomposition of complexes      |                   |                   |

Table 6. Diameters (cm) of deactivation of bacteria of the LH and it’s complexes.

| No. | Compound     | G+(Staph.) | G+(Ba.) | G+(E-Coli) | G-(Pro.) |
|-----|--------------|------------|---------|------------|----------|
| 1   | DMSO         | 0.0        | 0.0     | 0.0        | 0.0      |
| 2   | LH           | 0.5        | 0.55    | 0.72       | 0.76     |
| 3   | NiLNO$_3$(H$_2$O) | 0.78   | 0.74    | 1.00       | 2.6      |
| 4   | PdLCl(H$_2$O) | 0.92       | 1.2     | 1.21       | 2.9      |
| 5   | PtLCl(H$_2$O) | 0.99       | 1.90    | 1.23       | 1.7      |
| 6   | [ZrOL$_2$]   | 0.92       | 1.01    | 0.73       | 0.5      |
| 7   | CdLCl(H$_2$O) | 0.99       | 1.80    | 1.09       | 1.0      |
| 8   | Ciproflaxine | 0.8        | 2.5     | 0.66       | 0.90     |
4. Conclusions.

According to the results obtained from elemental analyses, proton NMR, EIMS, IR and UV-Visible spectra, the complexes of nickel(II), palladium(II) and platinum(II) with the new LH pyrazoline based-ligand were square planner with diamagnetic properties. However, the rhodium(III) complex was formed as octahedral geometry in 2:1 molar ratio L/M in basic medium, whereas, the structure of cadmium(II) complex was tetrahedral in 1:1 mole ratio. Furthermore, the zirconyl complex was square pyramid with [ZrOL2] formula due to the molar ratio 2:1 of ligand LH to metal Zr(IV) in methanolic solution. The vibration frequencies of the metal complexes were compared with the IR spectra of free LH ligand and it is found that LH behaved as monobasic bi dentate Lewis base via nitrogen of thiazole ring besides acidic –OH in 3-C position of pyrazolinone moiety. As well as the ligand and rhodium(III) and palladium(II) complexes were confirmed their thermal stability with the help of TG-DSC analyses. The scheme 3 shows the proposed geometry of the prepared complexes. The solutions of LH and its complexes in DMSO were screened their biological activity against some bacteria and it is found that the complexes of cadmium(II) and platinum(II) have the greatest activity due to the lipophilicity of their structure which make them more penetrate to cell wall of these bacteria.

\[ M= \text{pt(II), pd(II), Cd(II), } x=\text{Cl}, \ni(\text{II}), x=\text{NO}_3 \]

Scheme 3. Square planner on Ni(II), Pd(II), Pt(II), square Zr(IV), octahedral Rh(III) and tetrahydra of Cd(II) complexes.
Figure 1. FTIR spectra of LH complex in CsI disc.

Figure 2. FTIR spectra of Rh(III)-L based ligand in CsI disc.
Figure 3. Near IR spectra of Pt(II)-L based ligand in CsI disc.

Figure 4. TG-DSC analysis of LH ligand in Ar atmosphere.
Figure 5. (TG/DTG and DSC) Thermo gram of \([\text{RhL}_2(\text{H}_2\text{O})_2\text{Cl}]\) in argon gas.

Figure 6. (TG/DTG and DSC) Thermo gram of \([\text{PdLCl}(\text{H}_2\text{O})]\) in argon gas.

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