Preparation and Spectral Characterization of Some Novel Heterocyclic ligands Derivative from 2,4,6-tri oxo tetra hydro pyrimidine and their complexes with Pd(II)

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Abstract:-
The Novel Heterocyclic ligands N-phenyl-4-[(2,4,6-trioxotetrahydro pyrimidin-5(2H) ylidene)methyl] amino]benzene sulfonamide (L 1) and 5-[(3-hydroxy phenyl)methylene]pyrimidine-2,4,6 (1H,3H,5H)-trione (L 2) were prepared to give the final poly dentate Heterocyclic with different donor at om system. All the synthesized ligands were characterized using 1H,13CNMR, Mass Spectra, C.H.N. microanalysis and studied by FTIR, UV.-Vis. techniques. with TLC technique for each steps of prepare reactions and melting points. New complexes of the general formulae [Pd (L1)2] and [Pd (L2)2] , have been isolated. The complexes were characterized by elemental analyses, conductivity measurements, magnetic susceptibilities and spectroscopic (IR, 1H NMR and UV-Vis ) studies and melting points. All the data are discussed in terms of the nature of the bonding and the possible structural types. All preparation of complexes of Pd (II) ion were deduced according to the molar ratio (2:1) (L:M) depending on the Micro elemental Analysis (C.H.N.S). The Ligands behaves as a Didentate ligand in the monomeric complexes. According to the results obtained, Square Plainer structure suggested for the prepared complexes.

Keywords: Heterocyclic ligands, Micro elemental Analysis, Pd(II) complexes.

1. Introduction
Heterocyclic compounds are one of the important classes of organic compounds [1]. The significance of these compounds, apart from their diverse chemical and structural characteristics, The chief importance of Heterocyclic compounds are present in proved application in biologically active molecules in a wide spectrum of activity in nature like most of the members of proteins, chlorophyll, amino acids other plant pigments, vitamin B, enzymes and drugs. Some compounds derivative from hetero cycles are produce from different chemical reactions in order to form five, six and seven-membered rings like pyrazoles, oxazine as well as, 1,3- oxazipene respectively [2,3].
The synthesis, spectral determination, physical properties and elemental analysis of different types of Heterocyclic ligands and their complexes with transition and non – transition elements have great attention in many years of research, the synthesis of transition metal complexes containing Heterocyclic ligands have important area of study in inorganic chemistry [4]. a great interest of Heterocyclic ligands derived from pyrimidine as chelating ligands and their metal complexes in coordination chemistry because of the widely studied of these ligands and their metal complexes in clinical such as antibacterial, anticancer and antibiotics [5].and many other industrial applications, such as the manufacturing of medicines and spectral analytical applications by determination trace amount of elements in different samples of food, water and air [6,7]. Barbituric acid (BA) is also an important derivative of pyrimidine class and is used for the detection and determination of number of compounds [8]. However, literature on the use of pyrimidine is found that the metal complexes derived from 2,4,6-tri oxo tetra hydro pyrimidine have wide variety applications in different areas[9,10].the aim of the present study was to Preparation and Spectral Characterization of Pd (II) Complexes with the Newly synthesized hetero cyclic Ligands derived from barbituric acid, Tri methyl orthoformate and aromatic amines.
2. Experimental

2.1. Materials and physical measurements

All chemicals used were of highest purity (BDH, Fluka or Merck) and used without further purification.

The purity of Heterocyclic ligands and path of reaction were monitored using thin layer chromatography on silica gel-G (Merck grade) with ethanol and benzene mixture as mobile phase. The melting points were measured in open capillaries, with the help of (Stuart) melting point (SMP30, England) melting point apparatus were uttered in °C.Elemental analysis was carried out by means of micro analytical unit of (EURO EA3000 Singl ) C.H.N element analyzer. Absorption spectra were recorded using Shimadzu UV-Vis 1700 spectrophotometer, for solution of the complexes in aqueous ethanol at room temperature. Using 1cm quartz cell. IR spectra were recorded with FT-IR-8000 Shimadzu, in the range of (4000-400) cm\(^{-1}\) using KBr disc.Auto Electrical conductivity measured by Digital conductivity meter WTW,720 with solute concentration of 10\(^{-3}\)M in DMSO at room temperature, the metal percentages were determined using atomic absorption technique by Atomic Absorption spectrophotometer -5000, perkin – Elmer. Magnetic susceptibility magnitudes had been found at room temperature by the Gouy technique and Johnson Mathey Catalytic system.

\(^1\)H NMR spectra of the ligands and their Pd(II)complexes were recorded on Bruker (Avance III, Bruker 300MHz NMR spectrophotometer using TMS as an interior standard and the values are expressed in ppm.

2.2. Preparation of Novel Heterocyclic ligands

The preparation of the novel heterocyclic ligands N-phenyl-4-[(2,4,6-trioxotetrahydro pyrimidin-5(2H)-ylidene)methyl]amino]benzene sulfonamide (L\(_1\)) and 5-[(3-hydroxy phenyl)amino]methylene]pyrimidine-2,4,6(1H,3H,5H)-trione (L\(_2\)) include two steps: In a round bottom flask Mixture of Barbituric acid (0.006 mole) in (15 mL) EtOH and Trimethylorthoformate (0.0125 mole) was heated under reflux for 5h. The reaction mixture was then evaporated to dryness. The residue was dissolved in EtOH (10 mL), aromatic amines (0.005 mole) was added, the reaction mixture was stirred at ambient temperature overnight. The product percentage were (84%) and (62.7%) respectively. The preparation of heterocyclic ligands are showed in Scheme 1.

![Scheme 1: Preparation of the ligands](image)
3. Preparation of Palladium complexes

The (1:2) chelate complexes of the metal and the ligands are prepared by dissolving (0.002 mol) Heterocyclic ligand (L₁) or (L₂) in (25 ml) of hot ethanol. The corresponding metal salt [Pd (pph₃)₄] [Palladium acetate] (0.001 mol) was dissolved in hot ethanol(25 mL) was mixed with hot ethanol solution of the ligands (L₁) or (L₂) and refluxed for (1 hr) on a water bath, on cooling the contents. The complexes separated out in each case. The product was filtered, washed with ethanol and dried under vacuum. The product percentage were (80%) and (78%) respectively. Table 1 collects the physical properties and analytical data for those complexes.

![Table](image)

4. Results and discussion

The metal complexes are insoluble in water and soluble in DMF, DMSO, acetone, CHCL₃, methanol and ethanol.

4.1 Infrared spectra of ligands L₁ and L₂ and their complexes with Pd(II)

The IR spectral data of Heterocyclic ligands (Fig 1 and Fig 2) and their complexes (Fig 3 and Fig 4) are presented in Table 2. The IR spectra of the complexes were compared with those of the free ligands in order to determine the coordination sites that may be involved in chelation. The spectrum of free ligands L₁ and L₂ shows two weak bands (3062 & 3095) cm⁻¹ which due to υ (C-H) aromatic and (2821 & 2891) cm⁻¹ due to aliphatic respectively, these bands are in stable positions in both ligands and their complexes.

The Band in IR spectrum of free ligand at (1730 & 1708) cm⁻¹, assignable to stretching vibration υ (C=O) group of pyrimidine ring respectively these bands are in stable positions in both ligands and their complexes [12]. The appearance of a new non-ligand band around (450 & 420) cm⁻¹ in IR spectra of Pd(II) complexes with L₁ and L₂ due to υ (M-O) substantiates respectively [13]. The two bands at (1683 and 1695) cm⁻¹ in IR spectrum of free ligands L₁ and L₂ can be attributed to the stretching vibration of two Carbonyl groups υ (C=O)in pyrimidine rings, which were shifted to higher frequency in the IR spectra of the newly complexes of Palladium(II). These shifting indicated the coordination of the ligand with metal ion via nitrogen atom [10, 11].

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concluded that the two ligands behaves as a pidentate ligands coordinated to the metal ions via oxygen atom of carbonyl group of pyrimidine ring and nitrogen atoms of (NH-CH=C) group as showed in Figer1,2,3 and 4.

Table (2):- Characteristic IR absorption bands of the ligands L1 , L2 and their complexes in cm⁻¹ units.

| Compound | (O-H) | (C-H) aro. | (C-H) alpha. | (N-H) | (C=O) Amic | (S=O) | (M-N) | (M-O) |
|----------|-------|------------|--------------|-------|------------|-------|-------|-------|
| C₁₀H₁₃N₅O₅S | - | 2821 | 3062 | 3201 | 1683 1643 | 1708 | 1361 1138 | --- |
| C₁₁H₉N₃O₄ | 3700 | 2891 | 3095 | 3412 | 1695 1614 | --- | --- | --- |
| [Pd( C₁₀H₁₃N₅O₅S )₂] | --- | 2850 | 3066 | 3190 | 1695 1643 | 1730 | 1361 1138 | 586 450 |
| [Pd ( C₁₁H₉N₃O₄)₂] | 3700 | 2891 | 3151 | 3398 | 1701 1612 | 1716 | --- | 524 420 |

Fig.(1):- IR spectrum of the ligand (L₁)

Fig.(2):- IR spectrum of the ligand (L₂)
4.2. Electronic spectra

The Electronic spectra of the two ligands (L₁ and L₂) (Fig.5 and Fig.6) and their Pd(II) complexes were studied and the spectral data were listed in table (3). The UV-Vis spectra of the Heterocyclic ligands were characterized mainly by three absorption peaks at (216 and 241) nm assigned to (π → π*) and at (302)nm assigned to (n → π*) for (L₁) and (242 and 275) nm assigned to (π → π*) and at (307)nm assigned to (n → π*) for (L₂). These electronic transitions were shifted towards higher or lower frequency in the electronic spectra of the two prepared complexes, confirming the coordination of the ligand with metal ions.

The electronic spectrum of Pd (II) complex with the ligand (L₁) in (Fig.7) showed two new absorption peaks, the first peak at (360)nm and the other peak at (695)nm may be assigned to charge transfer spectrum. These two peaks were a good agreement of Sauer planer geometry for Pd(II) complex [16]. The electronic spectrum of Pd (II) complex with the ligand (L₂) in (Fig.8) showed two new absorption peaks, the first peak at (340)nm and the other peak at (629)nm may be assigned to charge transfer spectrum. These two peaks were a good agreement of Sauer planer geometry for Pd(II) complex.
Fig. (5):- Absorbance spectrum of ligand (L₁)

Fig. (6):- Absorbance spectrum of ligand (L₂)

Fig. (7):- Absorbance spectrum of ligand (L₁) with ion complex of Pd(II)
Table (3):-The electronic spectra of the ligands L₁ ,L₂ and their chelate complexes with Pd(II)

| Compounds                        | λ<sub>Max</sub> nm | Transition       |
|---------------------------------|-------------------|-----------------|
| C₁₆H₁₃N₅O₅S                    | 216               | π → π*           |
|                                 | 241               | π → π*           |
|                                 | 302               | n → π*           |
| C₁₁H₉N₃O₄                      | 242               | π → π*           |
|                                 | 275               | π → π*           |
|                                 | 307               | n → π*           |
| [Pd( C₁₆H₁₃N₅O₅S )₂]          | 218               | Intra - ligand  |
|                                 | 251               | Intra - ligand  |
|                                 | 277               | Intra – ligand  |
|                                 | 360               | C.T             |
|                                 | 695               | C.T             |
| [Pd ( C₁₁H₉N₃O₄)₂]            | 203               | Intra - ligand  |
|                                 | 261               | Intra - ligand  |
|                                 | 278               | Intra – ligand  |
|                                 | 340               | C.T             |
|                                 | 629               | C.T             |

5. H-NMR Spectra
5.1. N-phenyl-4-[[2,4,6-trioxotetrahydroimidin-5(2H)ylidene)methyl]amino benzene sulfonamide (L₁)
H¹-NMR (DMSO<sub>δ</sub> , MH₂) δ 5.69-7.5 (m,4Hbenzene ring) , δ 7.62-8.09 (m ,4Hpyrimidine ring) , δ 10.94(s,1H,NH<sub>aldehyde</sub>), δ 11.45-11.56(d,2H,NH<sub>barbituric acid</sub> ) , δ 11.60 (s,1H,NH) , δ8.5(s,1H,CH=C). as showed in(Fig9)[9].
5.2. 5-[(3-hydroxy phenyl)amino]methylene]pyrimidine-2,4,6(1H,3H,5H)-trione (L2)

H1-NMR (DMSO d6, MH Z) δ 5.94-7.30 (m, 4H benzene ring), δ 9.8(s,1H,OH), δ 10.8-10.9(d,2H,NHbarbituric acid), δ 11.32 (s,1H,NH). δ8.9(s,1H,CH=C) as showed in (Fig10)[10].

5.3. Palladium complex with the heterocyclic ligand L1

H1-NMR (DMSO d6, MH2) δ 5.95-7.53 (m,4H benzene ring), δ 7.64-8.08 (m,4Hpyrimidine ring), δ 10.94(s,1H,NHsulfapyridine), δ 11.85-11.90(d,2H,NHbarbituric acid), δ 11.08 (s,1H,NH), δ8.59(s,1H,CH=C). as showed in(Fig11).
5.4. Palladium complex with the heterocyclic ligand \( \text{L}_2 \)

\( ^1\text{H}-\text{NMR} \) (DMSO\(_d6\), MHz) \( \delta 5.92-6.89 \) (m, \( 4\text{H benzene ring} \)), \( \delta 7.25-7.30 \) (m, \( 4\text{H pyrimidine ring} \)), \( \delta 9.88\) (s, \( 1\text{H,OH} \)), \( \delta 10.59\) (s, \( 2\text{H,NH dibutylating acid} \)), \( \delta 11.12\) (s, \( 1\text{H,NH} \)), \( \delta 8.84\) (s, \( 1\text{H,CH=C} \)) as showed in (Fig12).

(Fig.12):- 1H-NMR Spectrum for Pd(II) complex with \( \text{L}_2 \)

6. Conductivity measurements

The two soluble complexes showed molar conductivity values at (15.81 and 9.95) S.cm\(^{-2}\).mol\(^{-1}\) in DMSO solvent in \( 10^{-3}\)M at room temperature respectively. These values indicate low conductivity and Non-ionic structure (1:2) of these complexes [10]. The conductivity values were listed in table 4[13].

Table (4):- Molar Conductivity of the prepared complexes

| Complexes                             | Molar Conductivity S.cm\(^{-2}\).mol\(^{-1}\) | Proposed Geometrical |
|---------------------------------------|---------------------------------------------|----------------------|
| [Pd( \( \text{C}_{16}\text{H}_{13}\text{N}_{5}\text{O}_{5}\text{S} \))\(_2\)] | 15.81                                       | square Planar        |
| [Pd( \( \text{C}_{11}\text{H}_{9}\text{N}_{3}\text{O}_{4} \))\(_2\)] | 9.95                                        | square Planar        |

7. Suggested Structure

On the basis of elemental microanalysis, molar Conductivity and spectroscopic studies for the heterocyclic ligands \( \text{L}_1,\text{L}_2 \) and Pd(II) complexes, we suggest that the two ligands behaves as Didentate on Complexation with metal ions via the oxygen atom of carbonyl group of Pyrimidine ring and nitrogen atoms of (NH-CH=C-) group. All we found that the ratio M:L was 1:2. According to these results, The two complexes of Pd (II) have square planar geometry as showed in (Fig.13 and Fig14).
Fig.(13): The suggested structural Pd (II) with Heterocyclic ligand (L₁)

Fig.(14): The suggested structural Pd (II) with Heterocyclic ligand (L₂)

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