

RESEARCH PAPER

Synthesis and characterization of bis (5-phenyl-1,3,4-oxadiazole-2-ylthio) mercury complexes with Pd(II) and Pt(II) metal ions

Beriwan M. H. Ameen, Hikmat A. Mohamad

Department of chemistry, College of education, University of Salahaddin-Hawler, Erbil, Kurdistan Region, Iraq.

ABSTRACT:

A complexes of Pd(II) and Pt(II) have been synthesized from a reaction of one mole of (5-phenyl-1,3,4-oxadiazole-2-ylthio)mercury (HgL_2) with two mole of $PdCl_2$ and $PtCl_2$ to give the colored complexes with general formula $[M_2Cl_4(HgL_2)]$ [where $M=Pd(II)$ or $Pt(II)$]. The results of identification indicated that all complexes have square planer shapes, which the metal coordinates to the ligand through Nitrogen, and Sulfur atoms of ligand (HgL_2). Characterization have been done by using FT- IR Spectroscopy, H^1 -NMR spectroscopy, UV-visible spectra, melting point and CHNS analysis.

KEY WORDS: $PdCl_2(II)$, $PtCl_2(II)$, 1,3,4-oxadiazole-2-thiol, spectral data.

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1. INTRODUCTION

The compounds that contain two nitrogen and one oxygen atoms in five membered ring are called Oxadiazole. It has four different types isomers, 1,3,4-oxadiazole is the most common isomers of the oxadiazole (Abbasi et al., 2018), (Srivastav and Pandeya 2011).

1,3,4-Oxadiazoles have a broad spectrum of biological activities include anti-inflammatory, antifungal, antitumor, P-Glycoprotein Inhibitors, pesticides and insecticides, Inhibitors, anticonvulsant activity etc (Roy et al., 2017). In addition to the oxadiazoles derivatives displayed an electrochemical, electro-optical, Luminescence and photo physical properties(Abbas et al., 2017).

There are several methods have been reported to synthesis 1,3,4-oxadiazols, for example cyclization of acid hydrazides with a different reagents such as thionyl chloride, phosphorous oxychloride and sulfuric acid, under reaction conditions. Since current years several efficient methods have been engaged for the synthesis of 1,3,4-oxadiazoles, from presented carboxylic and hydrazides acid (Aryanasab et al., 2011). There are wide recent research records highlighting the potential of the complexes of 1,3,4-oxadiazole dyes, liquid crystals, and inorganic light-emitting diodes (Aydogan et al., 2002.(Crystallography reports) (Mohamad et al., 2020). In this current work a new complexes of bis(5-phenyl 1,3,4-oxadiazole-2-ylthio) mercury (HgL_2) with Pd(II), and Pt(II) have been synthesized. Our interest aim is synthesize of new complexes in which binding with the central metal through nitrogen and sulfur atoms coordination to the central metal ions that they play important role biological and medical fields.

* Corresponding Author:

Beriwan Mohamad Hamad Ameen

E-mail: Birewan.hamadamin@su.edu.krd

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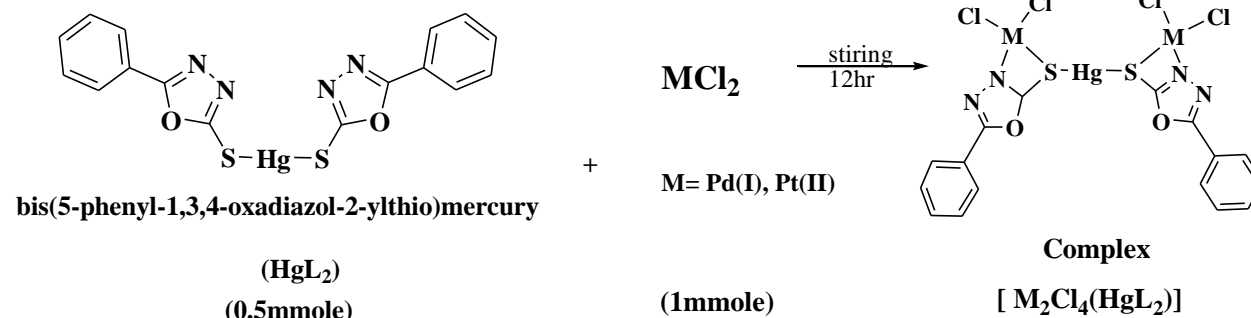
2. MATERIALS AND METHODS

2.1 Experimental Notes:

All chemical are of reagent grade, and used as supplied (Fluka), (Merk) ,(Alpha), or (B.D.H). Shimadzu FT-IR. 8400 spectrometer was used to recorded infrared spectra in the (400-4000) cm^{-1} range. Melting Point-MPD-100Pixel Technology CO., Limited was used to measured melting point. UV-Visible spectra were obtained using a Perkin-Elmer 330.The elemental analyses for Carbon, Hydrogen, Nitrogen and Sulfur atoms were performed by Innovation at the Nelson Mandela Metropolitan University for CHNS analysis.¹H-NMR, ¹³C-NMR spectra of complexes were recorded by Bruker ultra shield 300 MHz with TMS as internal reference, in (Al-ALBait) University Central Labs (Jordon).

2.2 Preparation of the Complexes

A clear solution of bis(5-phenyl 1,3,4-oxadiazole-2-ylthio) mercury (HgL_2) (0.5mmole)



in ethanol (10ml) was added to a suspended solution of MCl_2 ($\text{M} = \text{Pd(II), Pt(II)}$) (1mmole) in (10ml) ethanol, the brown precipitate was formed after stirring for 12hrs. The precipitate was filtered and wished by diethyl ether. Analytical calculated % for $[\text{C}_{12}\text{H}_{12}\text{S}_2\text{N}_2\text{Pd}_2\text{Cl}_4]$: C (21.12), H (1.10), N (6.16), S (7.04),M (23.39) Found: C 20.76, H 0.98, N 5.15, S 6.85, M (23.04) and for Analytical calculated.% for $\text{C}_{12}\text{H}_{12}\text{S}_2\text{N}_2\text{Pt}_2\text{Cl}_4$ C (17.67), H (0.92), N (5.15), S (5.89), M (35.89) Found: C 17.28, H 0.68, N 4.59, S 5.29, M 35.28.

3. RESULTS AND DISCUSSION

3.1 Reactions of the preparation $[\text{M}_2\text{Cl}_4(\text{HgL}_2)]$

Complexes:

(HgL_2) were taken in DMSO-d^6 solvent. ¹H NMR (295K, ppm, d^6 -DMSO) for $[\text{Pd}_2(\text{HgL}_2)\text{Cl}_4]$: 6.73-7.85 (d, 1H, H2); and 7.43-7.85 (d, 1H, H (4)).

¹H NMR (295K, ppm, d^6 -DMSO) for $[\text{Pt}_2(\text{HgL}_2)\text{Cl}_4]$: 6.64-6.98 (d, 1H, H2); and 7.65-7.95 (d, 1H, H (4)) (Aziz et al., 2017).

3.4 UV-Visible spectra of complexes: The UV-visible spectrum of $[\text{Pd}_2(\text{HgL}_2)\text{Cl}_4]$,

The band at 22321cm^{-1} , which attributed to transition $^1\text{A}_1\text{g} \rightarrow ^1\text{E}_\text{g}$ other high energy bands observed at 31251cm^{-1} , 35087cm^{-1} which assigned to $\text{Pd}^{+2} \rightarrow \text{C}=\text{N}$ charge transfer transitions, it's reasonable to assigned square planer geometry (Hassan, 2014)

The UV-Visible spectrum of $[\text{Pt}_2(\text{HgL}_2)\text{Cl}_4]$ shows three bands at 25000cm^{-1} , 30769 , 36363cm^{-1} , the bands at 30769cm^{-1} 36363cm^{-1} may assign to M-L charge transfer transition, while the band

3.2 FT-IR spectra for complexes: The band of ν (C=N) shifted to 1608cm^{-1} , this shifting to a higher frequency from the (HgL_2) indicated the coordination of nitrogen to metal ions of Pd(II) and Pt(II) (Jawdat et al., 2017). Upon complexation the stretching vibration of ν (C-O-C) in the free ligand shifted to a higher frequency appears at 1078cm^{-1} in the complexes. The ν (C-S) band of the free ligand was displayed at 704cm^{-1} , this band was observed within $(698)\text{cm}^{-1}$ for complexes of Pd(II), Pt(II), the shifting to lower frequency from free ligand indicated to the coordination of (C-S) to the metal ions (Ameen et al, 2018).

3.3¹H-NMR, spectra for complexes : The ¹H-NMR, spectra for a new complexes of

at 25000cm^{-1} , is donated to ${}^1\text{A}_{1g} \rightarrow {}^3\text{B}_{2g}$, these transitions value were indicated to square planner geometry (Amin, 2011).

5. CONCLUSION

The main work in this research includes the synthesis of new Palladium(II) and platinum(II) complexes with (HgL_2) ligand. According to the IR, ${}^1\text{H-NMR}$, UV-visible spectroscopy, melting point and CHNS analysis, both complexes of

$[\text{Pd}_2(\text{HgL}_2)\text{Cl}_4]$, $[\text{Pt}_2(\text{HgL}_2)\text{Cl}_4]$ have a square planer geometry and the metal ions coordinates to the ligand through Nitrogen, and Sulfur atoms of the ligand (HgL_2) .

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Table 1: Yield%, Colors, molecular weight, , melting points and elemental analysis for the synthesized complexes(CHNS)

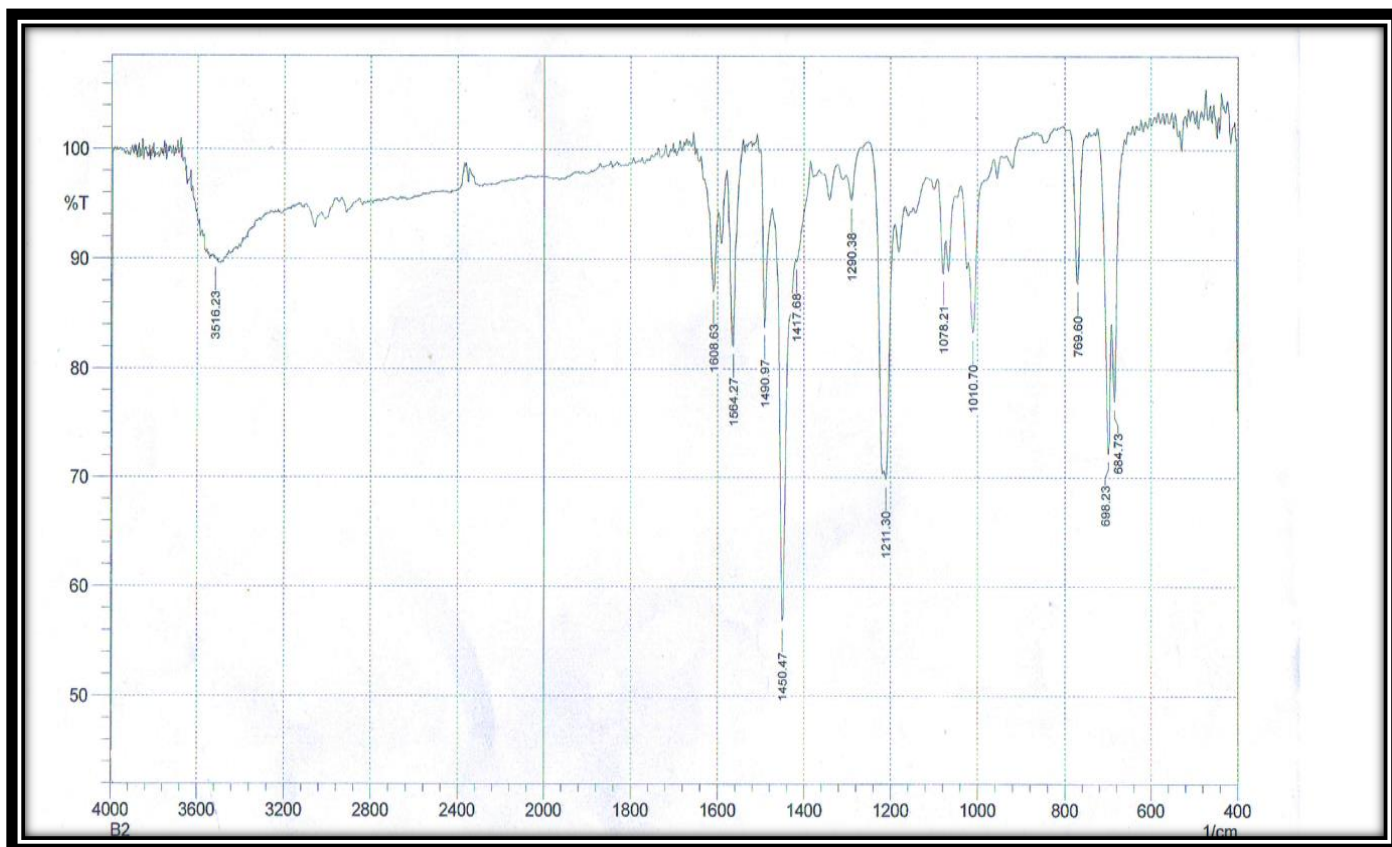
No.	Complexes	Yield%	Color	M.Wt	M.P($^{\circ}\text{C}$)	(Calculated) Found %				
						C	H	N	S	M
1	$[\text{Pd}_2(\text{HgL}_2)\text{Cl}_4]$	58	Brown	909.56	>300	(21.12) 20.76	(1.10) 0.98	(6.16) 5.79	(7.04) 6.85	(23.39) 23.04
2	$[\text{Pt}_2(\text{HgL}_2)\text{Cl}_4]$	65	Greenish-brown	1086.90	258	(17.67) 17.28	(0.92) 0.68	(5.15) 4.59	(5.89) 5.29	(35.89) 35.28

Table.2 Infrared spectral and Electronic spectral bands of the prepared complexes

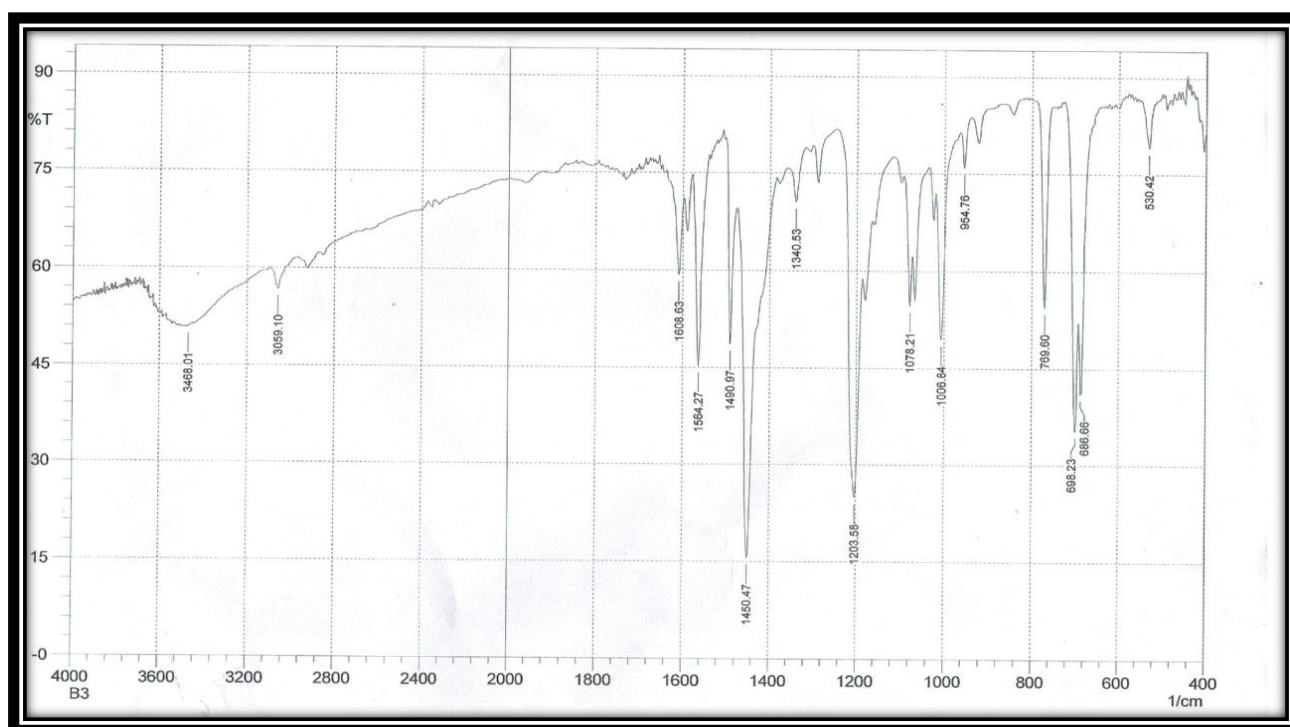
No.	Complexe	IR spectra cm^{-1}				Band Absorption		Assignment
		C=N	C-O-C	C-S	M-N	cm^{-1}	nm	
1	$[\text{Pd}_2(\text{HgL}_2)\text{Cl}_4]$	1608	1078	698	530	35087 31250 22321	285 320 440	C.T C.T ${}^1\text{A}_{1g} \rightarrow {}^1\text{E}_g$
2	$[\text{Pt}_2(\text{HgL}_2)\text{Cl}_4]$	1608	1078	698	570	36363 30769 25000	275 325 400	C.T C.T ${}^1\text{A}_{1g} \rightarrow {}^3\text{B}_{2g}$

Table(3): ${}^1\text{H-NMR}$ data for synthesized complexes

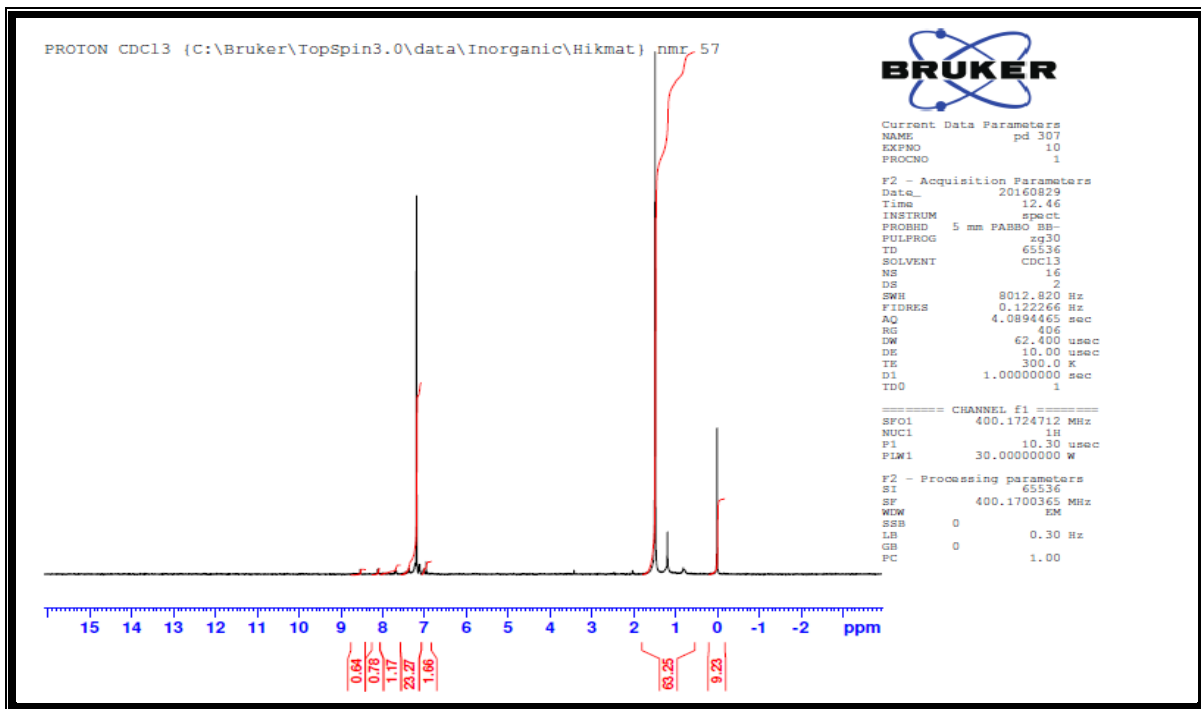
No.	Complexe	${}^1\text{H-NMR}(\text{ppm})$	
		(d, 1H, H2)	(d, 1H, H4)
1	$[\text{Pd}_2(\text{HgL}_2)\text{Cl}_4]$	6.73-7.85	7.43-7.85
2	$[\text{Pt}_2(\text{HgL}_2)\text{Cl}_4]$	6.64-6.68	7.65-7.95



Fig(1): The Infrared spectrum of $[Pt_2(HgL_2)Cl_4]$



Fig(2): The Infrared spectrum of $[Pd_2(HgL_2)Cl_4]$



Fig(3): The ^1H -NMR for $[\text{Pd}_2(\text{HgL}_2)\text{Cl}_4]$

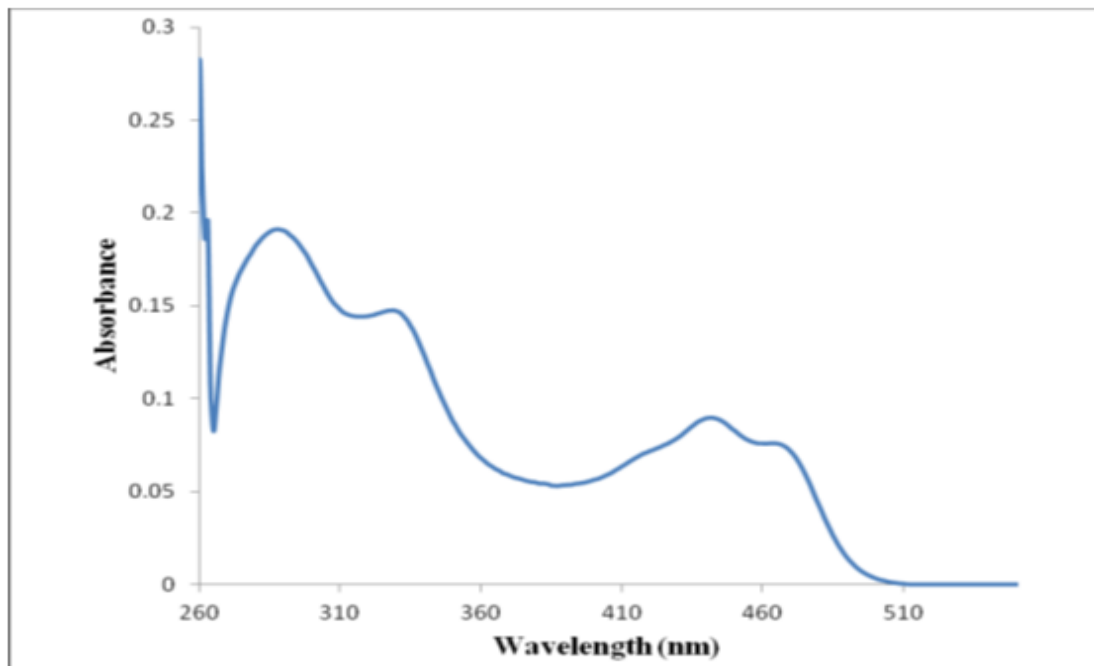
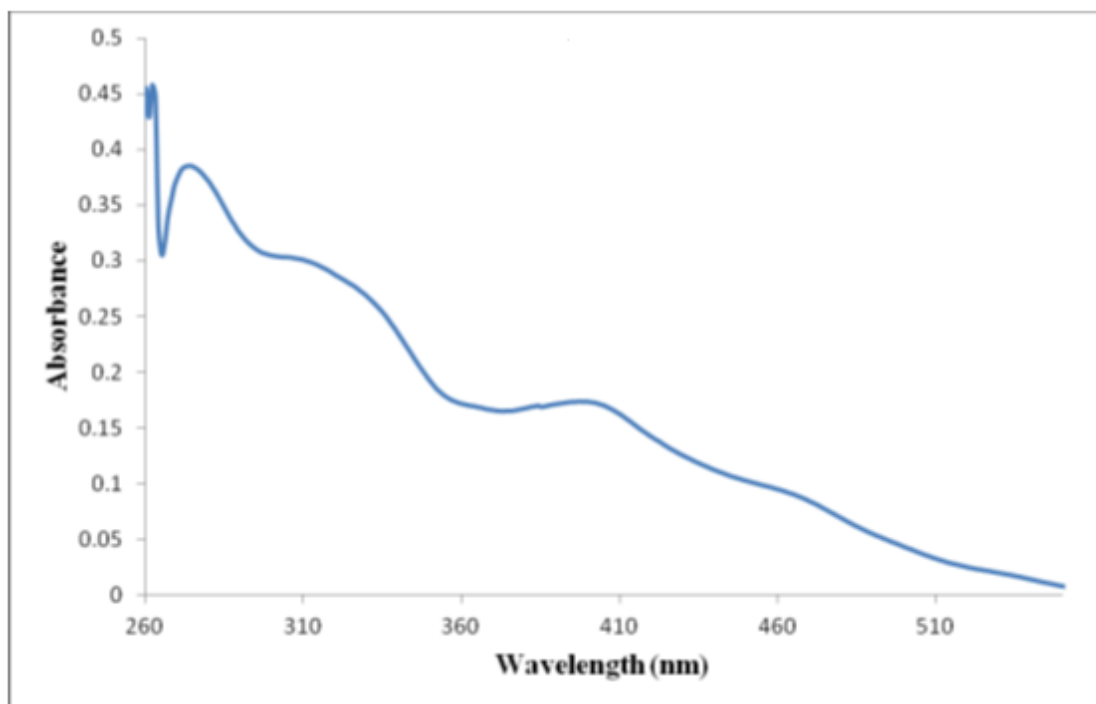


Fig.(4): UV-visible spectrum for $[\text{Pd}_2(\text{HgL}_2)\text{Cl}_4]$



Fig(5): UV-visible spectrum for the $[Pt_2(HgL_2)Cl_4]$

REFERENCES

- Abbas Z. M., Hussain D. F. and Shakir. M. R., 2017. Synthesis of Some New Heterocyclic Fused Rings Compounds Based on 5-Aryl-1,3,4-Oxadiazole In AL-Haitham J. for Pure and Appl. Sci., 30(2) , pp. 161-176.
- Abbasi M. A., Rehman A. U., Siddiqui S. Z., Ali Shad S. A., 2018. Synthesis and Bioactivity of Novel Tri-Heterocyclic Molecules: {4-[3-({[5-(Substituted)-1,3,4-Oxadiazol-2-Yl] Sulfanyl)Methyl] Benzoyl]-1-Piperazinyl}(2-Furyl)Methanones . Arc.Org. Inorg.Chem. Sci. 1(2), pp.57-64 .
- Ameen B. M. H. Mohamad A.H. ,2018. Synthesis and characterization of Pd(II) and Pt(II) complexes with bis [Hg (2-apt)].Kirkuk. U. J. S.S. , 13(3), pp.(12-22).
- Amin K.F.M., 2011. Synthesis and characterization of tetranuclear metal complexes of the type $[M_2(btzS)_4M_2Cl_4]$. M.Sc., Thesis, Sulamani University.
- Aryanasab F., Malike H. and Saidi R. M., 2011. A Novel One-Pot Synthesis of 2-Alkylthio-1,3,4-oxadiazoles in Water J. Iranian chem. Soc., 8(2), pp. 525-530.
- Aydogan F., Turgut Z., and Ocal N., 2002. Synthesis and Electronic Structure of New Aryl- and Alkyl-Substituted 1,3,4-Oxadiazole-2-thione Derivatives Turk. J. Chem., 29, pp.159-169.
- Aziz M.Y., Bayiz Y. K. and Hawaiz F. E., 2017. One-pot Three Component Synthesis of Some New Azo-Pyrazoline Compounds Derived From 5-((3-chloro-4-methylphenyl)diazenyl)-2-hydroxybenzaldehyde, Z. J. of Pure and Applied Sciences, 29(4), PP. 134-139.
- Hassan N. H., 2014. Synthesis and characterization of some complexes of bis (2-mercaptobenzimidazole)mercury (II) with Ni(II), Pd(II), Ag(I), Pt(II), Pb(II) and their adducts. M.Sc., Thesis, Salahaddin University.
- Jawdat H.A., Maha S. H. and Dardaa A. I. , 2017. Synthesis, Characterization and Study of Biological Activity of Some 1, 3, 4 – Oxadiazole Derivatives and Complexes with Some Metals and Transition Metals Diyala J. for pure Sc., 13(2), pp. 92-110.
- Mohamad H., Gerber T. I. and Hosten E., 2020. The Reaction of (1,3,4-Oxadiazole-Thiolato)Mercury(II) with Triphenyl Phosphine, Crystallography Reports, 65(7), pp.1117-1120.
- Roy P. P., Bajaj S. , Maity T.K. , and Singh J. 2017. Synthesis and Evaluation of Anticancer Activity of 1, 3, 4-Oxadiazole Derivatives against Ehrlich Ascites Carcinoma Bearing Mice and Their Correlation with Histopathology of Liver .Ind. J. Pharm. Edu. and Resc. 51, pp. 260-269.
- Srivastavs S. and Pandeya S.N. , 2011. Various Approaches for Synthesis of Oxadiazole derivatives. Tnter. J. Res. Ayru. Pharm. , 2(2), pp.459-468.