

## Synthesis and Identification of Pd(II) and Ni(II) Dithiooxamide Complexes-Part I: Experimental

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**Abstract:** The compounds of PdCl<sub>2</sub>(PhCN)<sub>2</sub>, PdCl<sub>2</sub>(DMSO)<sub>2</sub>, PdCl<sub>2</sub>(DTO), NiCl<sub>2</sub>(DTO) were chosen for the present experimental work. The reaction of PdCl<sub>2</sub> with PhCN and DMSO gave two starting complexes PdCl<sub>2</sub>(PhCN)<sub>2</sub> and PdCl<sub>2</sub>(DMSO)<sub>2</sub> and then each of them reacted with DTO to give PdCl<sub>2</sub>(DTO). The reaction of NiCl<sub>2</sub>.6H<sub>2</sub>O with DTO gave NiCl<sub>2</sub>(DTO). All the prepared compounds were isolated and characterized by their melting points, vibrational and electronic spectra, and magnetic measurements with help from quantum calculations.

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### 1. INTRODUCTION

Dithiooxamide has a long record of use as a reagent for the detection and determination of many metals, including Pd(II) and Pt(II)<sup>[1]</sup>. The interest in this class of compounds is due to the presence of two thioamide moieties in one molecule; this moiety plays an important role in chemotherapy. A large number of biological active compounds are containing the thioamide (-N-C = S) moiety. It is included in many basic structures of drugs either to be a part of an open chain, e.g. dithiooxamide, thiosemicarbazides, isothiocyanates or involved in a heterocyclic ring, e.g.<sup>[2]</sup> mercaptotriazole, mercaptoxadizole.

A large body of novel platinum and palladium complexes, in both the cis- and trans-forms, with various donor ligands, e.g. beta-carboline alkaloids, pyrazoles, DMSO, ferrocenylphosphines have been tested for their antitumour activity against the number of fluid suspension, solid tumor, and cell lines. Remarkable cytotoxic effects against these cell lines were observed by some of these complexes. The preliminary results indicated that most of the trans-palladium complexes showed a better activity than the cis-platinum isomers and superior activity than that of the cis-palladium isomers. More importantly they showed activities equal to (or superior than) those of cisplatin, carboplatin and oxaliplatin (the anti-cancer drugs) in vitro.

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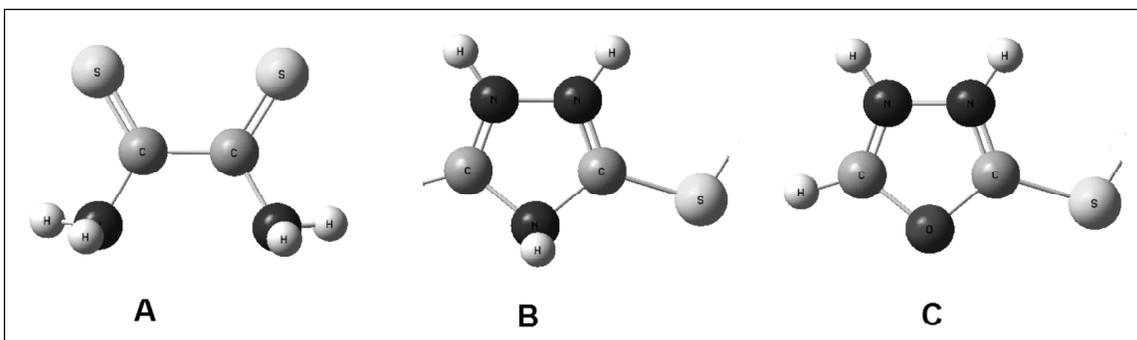


Figure 1: A-Dithiooxamide, B-mercaptotriazole, C-mercaptooxadizole

The presence of the “soft” sulfur atom beside the “hard” nitrogen atom in this thioamide moiety (keeping a side the effects of the remainder of the molecule containing it), render these molecules to be potent ligands with a wide diversity and biological importance besides other applications<sup>[3]</sup>. Dithiooxamide forms cationic complexes  $[M(DTO)_2]X_2$  with Ni(II), Pd(II), Pt(II), and other metals, and also in these compounds the halogenide acts as a counter ion and is hydrogen bonded to the  $NH_2$  group,<sup>[4]</sup> consequently the  $NH_2$  fundamentals, especially clear in the  $3500-2500\text{cm}^{-1}$  region, exhibit strong ammonium character. Much of attention that dithiooxamide have received in the chemical literature, however, it has been focused on their metal complexes, the dithiooxamide and N,N-disubstituted dithiooxamides have a planar structure and exist in an S-trans conformation. In solution, when the crystal structure is destroyed, the molecules assume partially a cis configuration. The N,N-disubstituted dithiooxamide have interesting properties as complexing agents, since it is possible to obtain ionic, neutral or polymeric metal complexes depending on the pH of the solution, solvent or metal salt. Internal rotation around the C-C bond in the molecules of dithiooxamide allows the preparation of complexes, which contains the ligands with Trans or cis configuration<sup>[1]</sup>.

In 1973 Peryronel and co-workers<sup>[5]</sup> described Ni(II) and Pd(II) complexes of  $[H_2A$  (dithiomalonamides)], prepared in acid and neutral media, and proposed S,N coordination for the cationic species and S,S coordination for the neutral complexes. Martin<sup>[6]</sup> reported on  $M(HA)_2$  with  $M=Ni(II)$ , Pd(II), and Pt(II). Also, other metals such as Zn(II)<sup>[7]</sup>, Cu(I)<sup>[8]</sup> and Sb(III)<sup>[9]</sup> have been discussed. The magnetic susceptibility temperature dependence was measured over (77-300) °K range.

In 2002 we reacted DTO with both n-propyl chloride and p-nitrobenzaldehyde gave the two new derivatives, PDTO and SDTO, respectively, the reaction of copper chloride with both DTO and SDTO gave the dinuclear octahedral,  $[Cu_2(DTO)(Cl)(H_2O)_4]$  complex, and mono-nuclear octahedral  $[Cu_2(SDTO)_2(H_2O)_2]Cl_2$  complex, respectively, these prepared compounds were isolated and characterized by their melting points, vibrational and electronic spectra, metal analysis, thermal analysis, and magnetic measurements, Ab-initio method of high level was used for calculating the relative energies and IR spectra of the

three compounds (DTO, PDT0, and SDTO). The *Abinitio* calculations indicated the tautomeric structure of DTO and helped to predict the most stable structures<sup>[10]</sup>.

Several studies have been reported on palladium (II) square planar complexes and bonding properties<sup>[11-16]</sup> and Ni(II) complexes<sup>[17-20]</sup>. Ternary palladium (II) complexes are frequently used models to mimic the binding properties of various platinum drugs<sup>[21]</sup>. Desseyn and coworkers<sup>[22]</sup> have described three different kinds of Pd(II) polymers with dithiooxamide derivatives (N-methyl dithiooxamide and N,N-dimethyl-dithiooxamide) exhibit two hydrogen atoms which can be removed in alkaline media, forming mixed polymeric complexes with Ni(II), Cu(II), Zn(II) and Cd(II) with PdS<sub>4</sub> and MN<sub>4</sub> surrounding in polymeric structure<sup>[23]</sup>. Ray and Sathyarayana<sup>[24]</sup> proposed S,S-coordination for the cationic species Ni(H<sub>2</sub>A)<sub>2</sub>Cl<sub>2</sub> in analogy with dithiobureto complexes. Two novel nickel (II) dinuclear complexes [Ni(cyclam)<sub>2</sub>(DTO)](CLO<sub>4</sub>)<sub>2</sub> and Ni<sub>2</sub>(TAA)<sub>2</sub>(DTO)](CLO<sub>4</sub>)<sub>2</sub>, (TAA=N(CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>3</sub>, cyclam=1,4,8,11-tetrazacyclotetradecanes have been proposed and studied by elemental analysis, IR, electronic spectra and magnetic measurements.

In this article we present synthesis of Palladium (II) and Nickel (II) complexes of dithiooxamide. We also demonstrate the utility of quantum method how to help in identification in addition to UV, FTIR and other measurements.

## 2. Experimental Part

### *Instruments*

All chemicals used were of the highest available purity, and used as supplied, except DTO which was recrystallized from hot ethanol. IR spectra were measured as CsI discs on a Shimadzu 8300 FTIR spectrometer and electronic spectra were recorded in dimethylsulphoxide solution using Shimadzu UV-Vis 160 Å' Ultraviolet spectrophotometer. Thermograms (TG, DTG) were obtained using a Thermo Hake model 6200 Thermal Analyzer of Seiko Instruments Inc. Magnetic susceptibility measurements were measured at room temperature using a Bruker BM6 instrument. The metal content was measured using a Shimadzu-AA 670 G Atomic Absorption spectrophotometer. Gallen Kamp M.F.B 600.01 of melting point apparatus was used to measure the melting point of all the prepared compounds.

### *Synthesis*

#### *A. Preparation of the Starting Materials*

1- Dichlorobis(benzonitrile) palladium(II): A (0.0023 mol, 0.4g) of palladium chloride was dissolved in (12 ml) of benzonitrile. The mixture was refluxed in a water bath to dissolve a maximum amount of palladium chloride. The product was filtered to remove unreacted palladium chloride. (100 ml) of petroleum ether (60-80°C) was added to the resulting solution to get yellow precipitate which was dried in a vacuum oven. The yellow ppt. product was identified by FTIR spectra<sup>[25]</sup>.

2-Dichloro bis(dimethyl sulfoxide) palladium(II): A (0.0023 mol, 0.4g) of palladium chloride was dissolved in (12ml) of dimethyl sulfoxide. The mixture was heated until all palladium chloride was dissolved then after the mixture was cooled and added (100ml) of diethyl ether, a yellow precipitate was formed. The yellow ppt. was dried under vacuum and identified by FTIR spectra<sup>[26]</sup>.

#### B. Preparation of Metal Complexes of DTO

1- Palladium (II) complex of dithiooxamide: A (0.00025 mol, 0.031g) of dithiooxamide was dissolved in (10ml) of ethanol and then added to dichlorobis (benzonitrile) palladium (II) or dichlorobis (dimethyl sulfoxide) palladium(II) (0.00026 mol) which was dissolved in 5ml of ethanol. The mixture was heated and a dark brown precipitate was formed, which was dried in a vacuum oven. The product was identified by their FTIR and UV-Visible spectra.

2-Nickel(II) complex of dithiooxamide: A (0.0004 mol, 0.1g) of DTO was dissolved in (20 ml) of hot ethanol. The resulting solution was added to (0.0004 mol, 0.2g) of hydrate nickel chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ) which was dissolved in (5ml) of distilled water-ethanol mixture (3:1 ratio). The mixture was heated and the resulting (deep-blue) precipitate was filtered, washed with distilled water and then with ethanol and dried under vacuum. The product was identified by its FTIR and UV-Visible spectra.

### 3. Experimental Measurements

#### 3.1. Dithiooxamide (DTO) Complexes of Ni (II) and Pd (II) ions

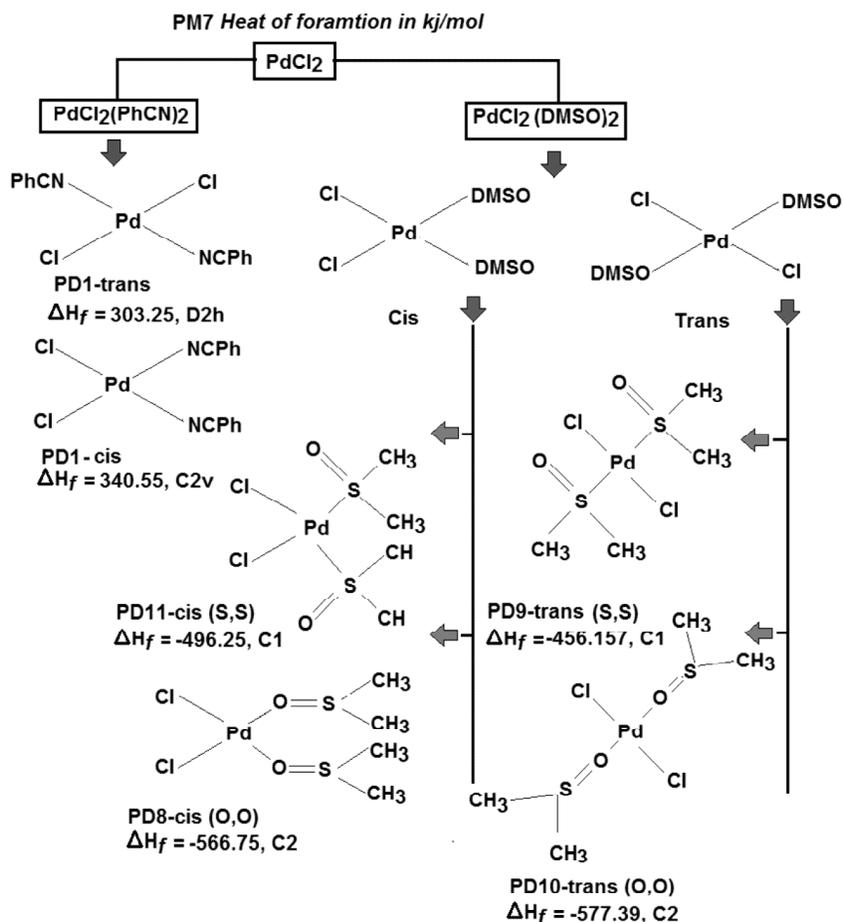
Both Ni(II) and Pd(II) have  $d^8$  configuration therefore they form diamagnetic square planar complexes with strong field ligands and  $dsp^2$  hybridization, although Pd(II) ion can form such structure even with weak field ligands, due to its size effect, while Ni(II) form paramagnetic tetrahedral structure with weak field ligands ( $sp^3$  hybridization)<sup>(27)</sup>.

The coordination of DTO with Ni(II) or Pd(II) ions, as a bidentate ligand can in principle take place through either (a) the two nitrogen atoms (b) the two sulfur atoms, or (c) one nitrogen and one sulfur atoms, these possibilities will be reflected in the IR spectra of the complexes, and will be discussed through the theoretical calculations at DFT level in the next paper. However until now the vibrational analysis of Ni(II) and Pd(II) complexes of DTO, mono-substituted, and disubstituted DTO were always vague, as only some fundamentals were tabulated without any further discussion<sup>(28)</sup>.

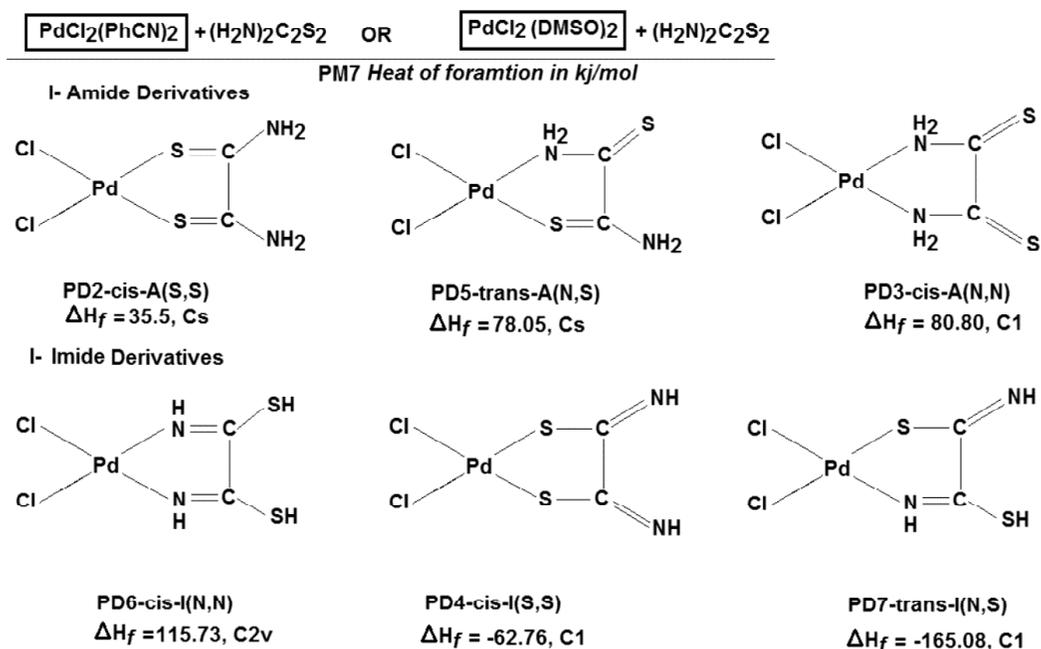
In our present work we took in consideration all probabilities of coordination behavior of DTO (rubeanic acid) with Ni(II) and Pd(II) ions, in addition to the (DMSO) and (PhCN) complexes of Pd(II) in account to calculate the theoretical vibrational frequencies and energy parameters for each probable geometry.

Scheme-1&2 show all the possible geometries and coordination sites of Pd (II) complexes with DMSO and PhCN as seen in Figure 2 which will be argued theoretically in details in the next paper, while scheme-3 illustrates the different binding sites of DTO with Ni(II). The reaction of the dark-brown PdCl<sub>2</sub> with warm PhCN gave a brownish- yellow fine precipitate, with 26% yield, of M.P. 120°C while the reaction of PdCl<sub>2</sub> with hot DMSO gave a bright yellow fine precipitate, with 44.5% yield of M.P. 189 °C.

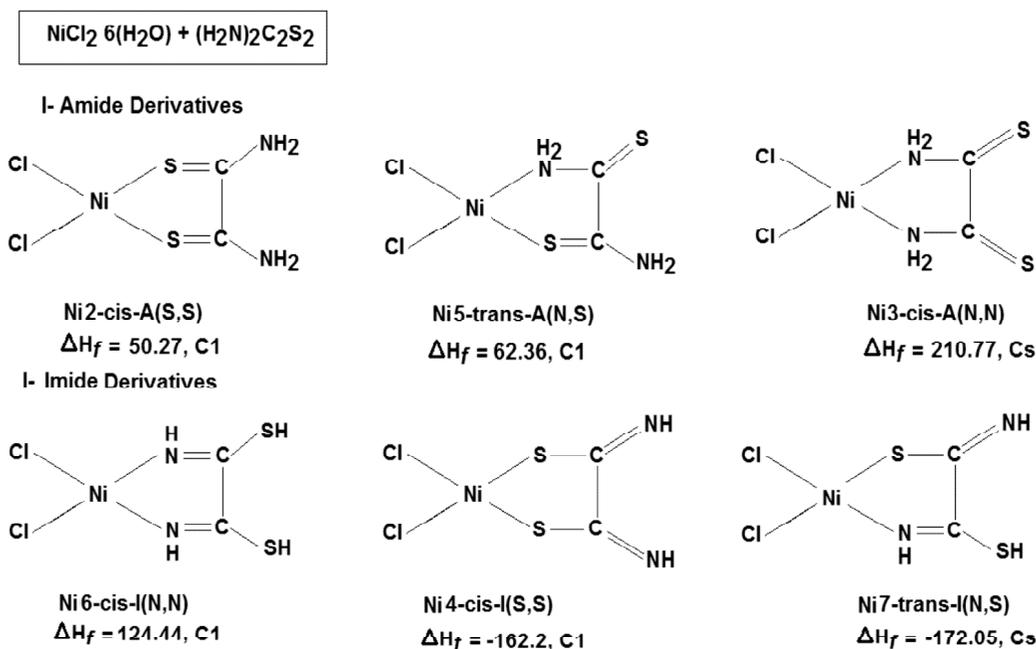
The heat of formation  $\Delta H_f$  were calculated for Pd(II) and Ni(II) complexes using PM7/MOPAC2012. Both ions prefer the coordination with sulfur atoms of cis amide which gave the most stable configuration among the neutral species (see  $\Delta H_f$  values in schemes 1-3). When Pd(II) coordinated to the nitrogen atoms it prefers amide form while Ni(II) prefers imide. The PM7 calculation showed that PD7 and Ni7 complexes, negatively charged (-1), are highly stable ( $\Delta H_f$  -165.08 and -172.05 kJ/mol respectively).



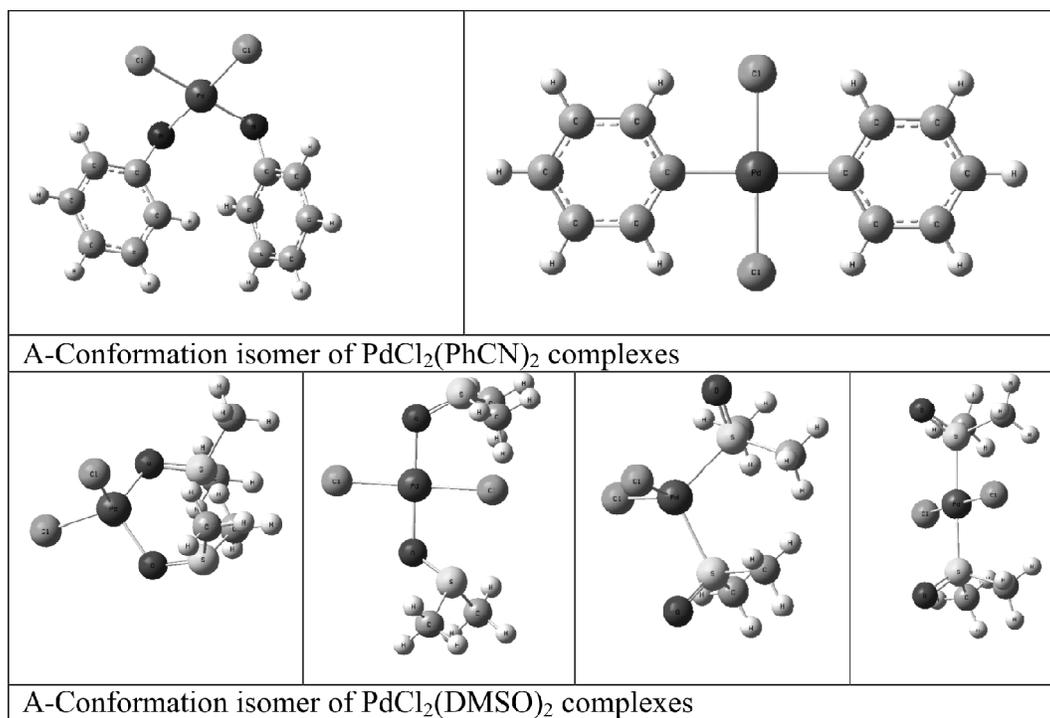
**Scheme 1:** The possible geometries and coordination behavior of Pd(II) complexes with DMSO and PhCN



**Scheme 2:** The possible geometries and coordination behavior of Pd(II) complexes with DTO

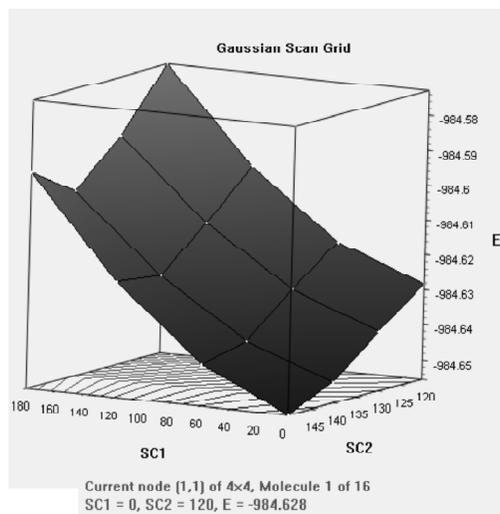


**Scheme 3:** The possible geometries and coordination behavior of Ni(II) complexes with DTO



**Figure 2:** Conformation isomers of  $\text{PdCl}_2$  Complexes

The potential energy surface PES was calculated with scanning the dihedral  $\text{SC1} = \varphi_{\text{S-C-C-S}}$  and the angle  $\text{SC2} = \theta_{\text{C-C-N}}$  at DFT level B3LYP/6-311++G(3df,2pd) using Gaussian 09W. The result shows that the DTO has only one stable structure which obtained at  $\varphi = 0$  and  $\theta = 120$  (i.e. cis conformer) as seen in Figure 3.



**Figure 3:** The most stable configuration of DTO

**Table 1**  
**Physical Data for PdCl<sub>2</sub>(PhCN)<sub>2</sub>, PdCl<sub>2</sub>(DMSO)<sub>2</sub>, PdCl<sub>2</sub>(DTO), NiCl<sub>2</sub>(DTO) Complexes**

<i>Symbol</i>	<i>Reaction Solvent</i>	<i>Color</i>	<i>Yield %</i>	<i>Melting point C°</i>
DTO	Ethanol	Orange	-	142 (dec.)
PdCl <sub>2</sub> (PhCN) <sub>2</sub>	Ethanol	Brownish-yellow	26	117-120
PdCl <sub>2</sub> (DMSO) <sub>2</sub>	Ethanol	Bright -yellow	44.5	189
PdCl <sub>2</sub> (DTO)-1	Ethanol	Dark Brown	50	221-223
PdCl <sub>2</sub> (DTO)-2	Ethanol	Dark Brown	65	223-225
NiCl <sub>2</sub> (DTO)	Ethanol	Dark-blue	70	220

(1) PdCl<sub>2</sub>(DTO) starting with PdCl<sub>2</sub>(PhCN)<sub>2</sub>

(2) PdCl<sub>2</sub>(DTO) starting with PdCl<sub>2</sub>(DMSO)<sub>2</sub>

### 3. Results and Discussion

#### 3.1. Infrared Spectroscopy Study

The FTIR spectra of both (DMSO) and (PhCN) of Pd(II) complexes are shown in Figures 4&5. Table-2 shows the diagnostic absorption of these complexes. The spectrum of (DMSO) complex of Pd(II) shows clearly the formation of trans isomer, since a strong sharp band appeared at (1116) cm<sup>-1</sup> for a single S-O stretch, and single Pd-S and Pd-Cl stretching frequencies at (414) and (349) cm<sup>-1</sup> respectively. These data also indicate the coordination with S-atom rather than O-atom. These assignments were based on the argument of Nakamoto<sup>[29]</sup> and our DFT calculation which will be published. The spectrum of (PhCN) complex of Pd(II) shows that the geometry to be trans-isomer, this is due to the appearance of one Pd-Cl band stretching frequency in the range (300-330cm<sup>-1</sup>) i.e. at 320 cm<sup>-1</sup>. On the other hand, the cis-isomer should give two bands in the above range<sup>[29]</sup>. This result was more indicated by the appearance of the νCa ≡ N at (2284) cm<sup>-1</sup>, which came at a higher frequency compared to (2230) cm<sup>-1</sup> of the free benzonitrile.

The spectra of both Pd-DTO complexes, prepared from either PdCl<sub>2</sub>(PhCN)<sub>2</sub> or PdCl<sub>2</sub>(DMSO)<sub>2</sub>, were nearly identical, indicating the formation cis-dichloro complexes of the chelating DTO scheme-2 in both cases. Two bands were observed at (306) and (322) cm<sup>-1</sup> assigned as nPd-Cl<sub>sym</sub> and as<sub>sym</sub> frequencies respectively, were shown in Figure-6&7, Table 3.

The spectrum of free DTO as shown in Figure-6, shows νN-H bands at (3294) cm<sup>-1</sup> and (3215) cm<sup>-1</sup> which are representing, respectively, the "free" asymmetrical and symmetrical vibration modes of primary amine; νN-H of secondary amine appears at (3138) cm<sup>-1</sup><sup>[30]</sup>. The appearance of these three νN-H bands in the spectrum of DTO means that thione-thiol tautomerism can be suggested to take place. These three bands were reduced in intensity in the formation of the Pd(II) complexes. The dithiol-diimino → dithione-diaminotautomerization in DTO confirmed by FTIR and UV study<sup>[31]</sup>. The recent studies confirmed the fact that when the alkyl replaces the hydrogen of the nitrogen of DTO it will lose the tautomerism and it coordinate through the 2S which leads to the formation of the polymeric complexes<sup>[32,33]</sup>.

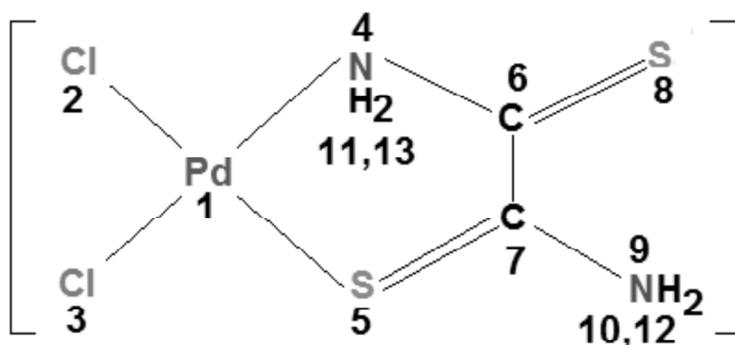
Thioamide band (I) appeared at  $(1589) \text{ cm}^{-1}$  in the spectrum of DTO, Figure 8 which was shifted to lower frequency and appeared at  $(1572) \text{ cm}^{-1}$  in the spectra of both Pd complexes as shown in Figure 6 & 7.

Thioamide band (II) was found at  $(1431) \text{ cm}^{-1}$  this band was split into two bands of higher and lower frequencies in both complexes as reported in Table 3.

Thioamide band (III) found at  $(1197) \text{ cm}^{-1}$  in free DTO, have contribution from N-C-S stretching vibration, was also split into two bands in the spectra of Pd-complexes, at higher and lower frequency due to the contribution of  $\nu\text{C-N}+\text{C}=\text{S}$  vibrations respectively<sup>[34]</sup>, as seen in Figures 8 & 9 and reported in Table 3.

Thioamide band (IV) which is due to  $\nu\text{CS}$ , was found at  $(837)\text{cm}^{-1}$  in the case of free DTO, and observed at  $(750) \text{ cm}^{-1}$  for  $\text{PdCl}_2(\text{DTO})$  which was prepared from  $\text{PdCl}_2(\text{PhCN})_2$ , Figures-6 and at  $(752)\text{cm}^{-1}$  for  $\text{PdCl}_2(\text{DTO})$  which was prepared from  $\text{PdCl}_2(\text{DMSO})_2$ , Figures 7, the red shift can be attributed to reduced bond order of the  $\text{C}=\text{S}$  bond upon complexation<sup>[35]</sup>. No band was observed due to  $\nu\text{S-H}$  in the spectrum of the complexes, which indicate that the ligand became only in the thione form in the complex<sup>[36]</sup>. The theoretical IR calculated at DFT level B3LYP/6-311++G(3df,2pd) showed a very close spectrum as seen in Figure 9.

Three new bands were observed at  $(560)$  and  $(491)$  and  $(322)\text{cm}^{-1}$  in both Pd complexes spectra, which may assigned as  $\nu\text{Pd-N}$ ,  $\nu\text{Pd-S}$  and  $\nu\text{Pd-Cl}$  frequencies<sup>[29]</sup>. According to the above experimental data, structure-I for the Pd-complex can be suggested. PM7 theoretical IR showed three bands  $(561)$ ,  $(445)$  and  $(315) \text{ cm}^{-1}$  which are belong to  $\nu\text{Pd-N}$ ,  $\nu\text{Pd-S}$  and  $\nu\text{Pd-Cl}$  respectively.

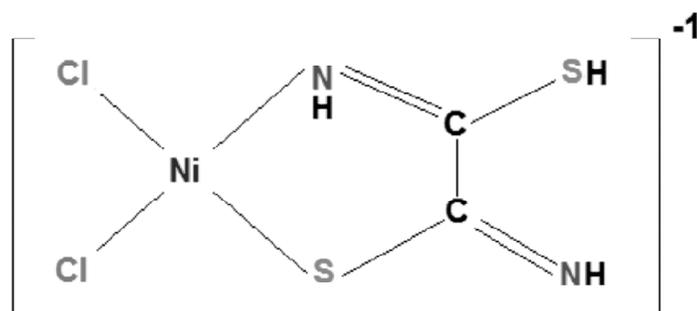


Structure I

The FTIR spectrum of the Ni(II) complex of DTO, Figure 10, Table 3, shows the  $\nu\text{N-H}$  at  $(3261)$  and  $(3139) \text{ cm}^{-1}$  to be assigned as asym and sym vibrations, respectively. The thioamide band (I) ( $\sigma\text{NH} + \nu\text{C}=\text{N}$ ) is situated in the range  $(1561-1477) \text{ cm}^{-1}$  in the present Ni complex it was split into two bands;  $(1602)$  and  $(1520) \text{ cm}^{-1}$ . Band (II) was found split into two bands;  $(1473)$  and  $(1370) \text{ cm}^{-1}$ .

From the increased double bond character of C-N group and decreased C=S bond character, in addition to the appearance of the  $\delta$ N-H mode at higher wavenumber, in analogy with C-H vibration, as the increased S-character in the hybridized N-orbitals gives a better overlap with hydrogen atomic orbital<sup>[37]</sup>, according to these observations it can be concluded that DTO is coordinated to the nickel through N and S atoms in the imide form. The  $\nu$ Ni-S fundamentals are to be expected in the region (435-333) $\text{cm}^{-1}$  and are depending on the following: (1) mass of the complexing agents (2) the coordination number and (3) the electronic configuration of the central metal ion<sup>[38]</sup>. In our work the Ni-S band was found at (410)  $\text{cm}^{-1}$ , this relatively high value refers to moderate Ni-S bond strength. The band due to  $\nu$ Ni-N bond was appeared at (588)  $\text{cm}^{-1}$ .

Two Ni-Cl stretching bands were observed at (275) and (318) $\text{cm}^{-1}$  belonging to symmetrical, and anti-symmetrical vibration respectively. According to the above experimental data, structure-II for Ni-complex can be suggested. PM7 theoretical IR calculation confirmed our finding that the bands (568), (426) and (352)  $\text{cm}^{-1}$  are belong to  $\nu$ Ni-N,  $\nu$ (Ni-Cl+Ni-S+Ni-N) and  $\nu$  (Ni-Cl+Ni-S) respectively.



Structure-II

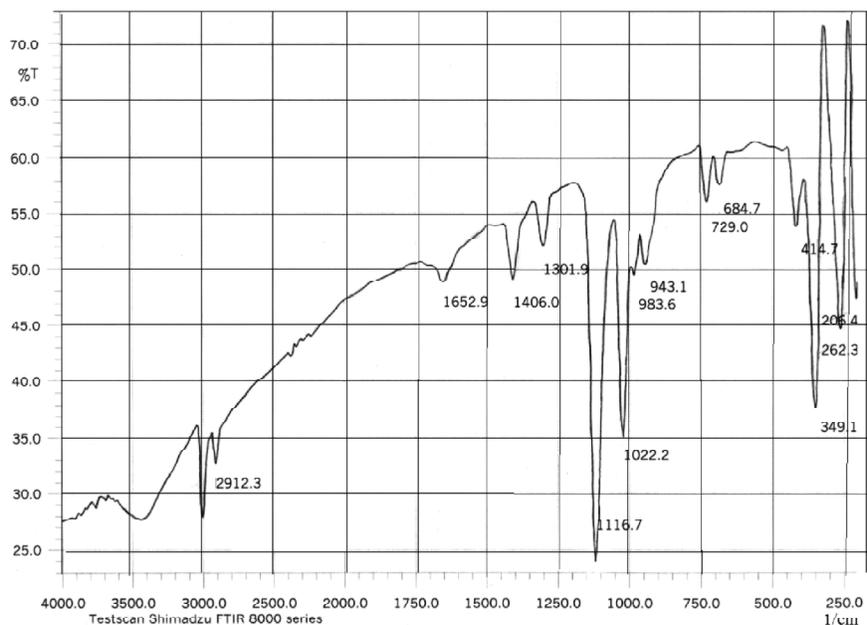
Table 2  
The Assignment of the most Diagnostic FT-IR Band

FTIR assignment	<i>Pd (PhCN)2Cl2</i>	<i>Pd(DMSO)2Cl2</i>
$\nu$ C-C Aromatic	1168	---
$\nu$ C=C Aromatic	1591	---
$\nu$ C $\equiv$ N Aromatic	2284	---
$\nu$ C-H Aromatic	3080	---
$\delta$ C-H out of plane	759	---
$\nu$ Pd-Cl	320	349
$\nu$ Pd-N	450	---
$\nu$ Pd-S	---	414
$\nu$ S-O	---	1116
$\delta$ C-S-C	---	729 as, 684s
$\nu$ (CH <sub>3</sub> )	---	3000as, 2912s
$\delta$ (CH <sub>3</sub> )	---	1406as, 1301s

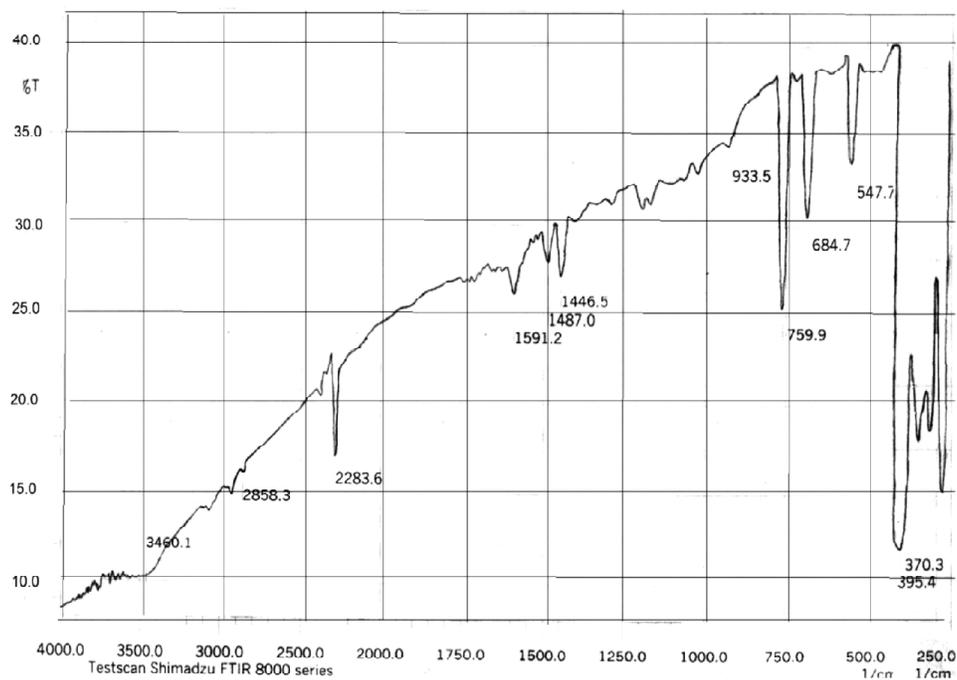
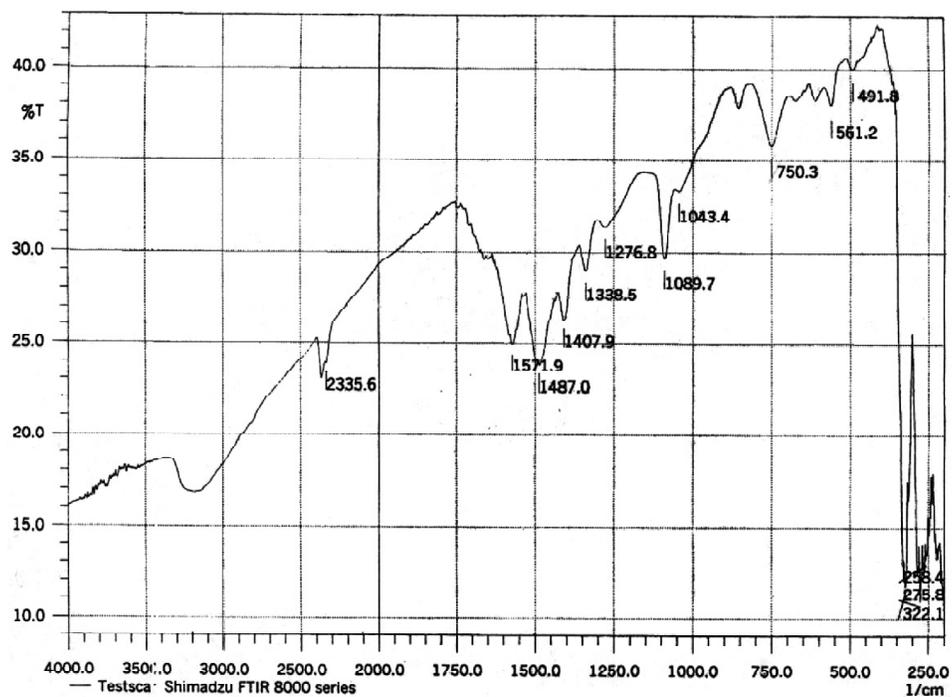
**Table 3**  
**The Assignment of the Most Diagnostic FT-IR Bands of DTO,  
 PdCl<sub>2</sub>(DTO), NiCl<sub>2</sub>(DTO) Complexes**

FTIR assignment	DTO	Pd (DTO)Cl <sub>2</sub>	Ni (DTO) <sub>2</sub> Cl <sub>2</sub>
SH	2600	--	--
NH	3294as, 3215s, 3138 3290m, 3200m	3250 SH, 3135	3261, 3139 3264s, 3244s, 3210s (1) 3356m, 3308m, 3280s (2)
DTOA/I band (I)	1589 $\delta_s(\text{N-H})_A + \nu(\text{C=N})_I$	1571	1602, 1520 1504s (1), 1498m (2)
DTOA/I band (II)	1431 $\delta(\text{C-N})_A + \delta_s(\text{N-H})_A$	1487, 1407	1473, 1370
DTOA/I band (III)	1197 $\rho(\text{N-H})_A + \rho(\text{N-H})_I$	1276, 1089	1109
DTOA/I band (IV)	837 $\rho(\text{N-H})_A + \rho(\text{S-H})_I$	750	777
DTOA/I band (V)	708, $\omega(\text{S-H})_I$		
DTOA/I band (VI)	635, $\tau(\text{N-H})_A +$ $\delta(\text{N-H})_I + \delta_s(\text{S-H})_I$		
DTOA/I band (VII)	472, $\omega(\text{N-H})_A +$ $\delta(\text{S-H})_I \delta(\text{N-H})_I$		
DTOA/I band (VIII)	399 $\omega(\text{N-H})_A + \omega(\text{N-C-S})_I +$		
M-Cl	--	306, 322	275, 318
M-N	--	560	588
M-S	--	491	415

(1) [Ni<sub>2</sub>(cyclam)<sub>2</sub>-(DTA)](ClO<sub>4</sub>)<sub>2</sub> and (2) [Ni<sub>2</sub>(TAA)<sub>2</sub>(DTA)] (ClO<sub>4</sub>)<sub>2</sub><sup>[39]</sup>  
 (TAA .N(CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>3</sub>, cyclam . 1,4,8,11-tetra-azacyclotetradecane, DTA.dithiooxamide), see also<sup>[40]</sup>



**Figure 4:** FTIR Spectrum of PdCl<sub>2</sub>(DMSO)<sub>2</sub>

Figure 5: FTIR spectrum of  $\text{PdCl}_2(\text{PhCN})_2$ Figure 6: FTIR Spectrum of  $\text{Pd}(\text{DTO})\text{Cl}_2$

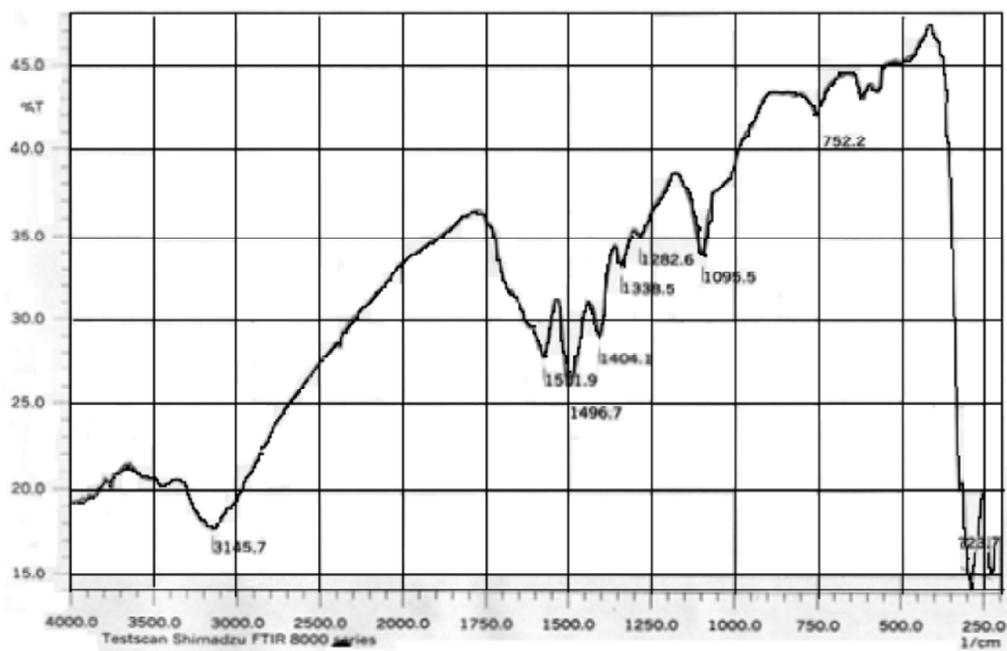


Figure 7: FTIR Spectrum of Pd(DTO)Cl<sub>2</sub>

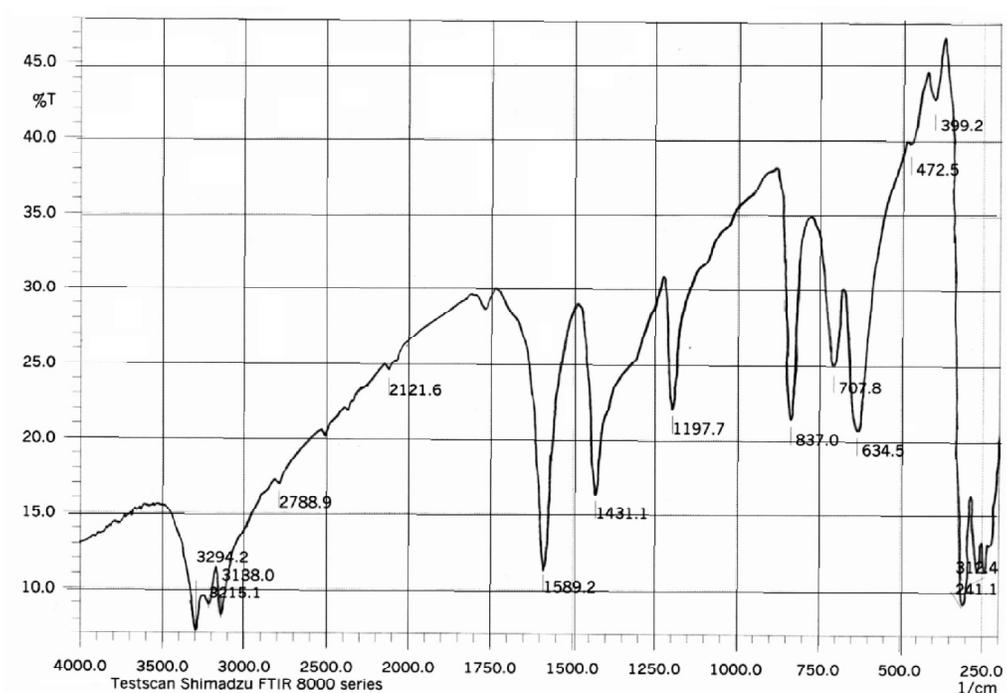


Figure 8: FTIR Spectrum of (DTO)

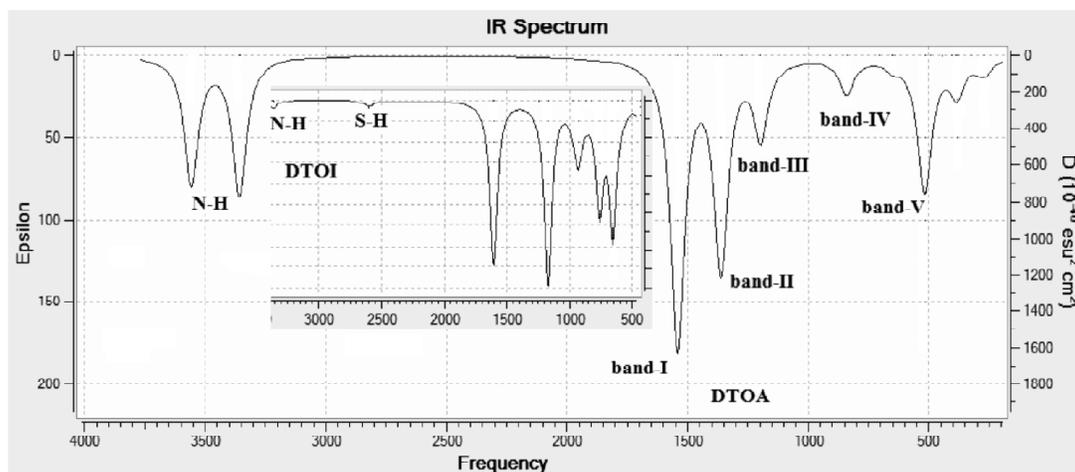


Figure 9: Theoretical Spectrum of DTOA/I

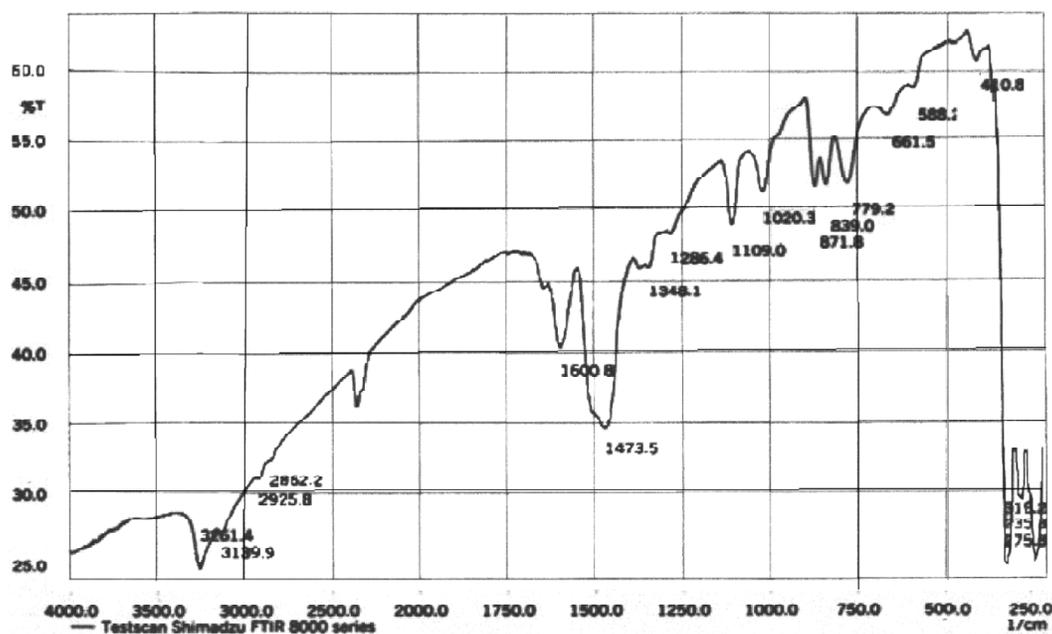


Figure 10: FTIR Spectrum of  $\text{NiCl}_2(\text{DTO})$

## 3.2. Electronic Spectra and Magnetic Properties

### 3.2.1. Pd(II) complex of DTO

Almost all 4-coordinated Pd(II) complexes are diamagnetic and most of them are square planar<sup>[41-43]</sup>. In some cases they may have a distorted octahedral geometry because of the coordination of more than one type of ligands or solvent molecules in the vacant axial position<sup>[44]</sup>.

In the present work, the value of magnetic moment measured at 25°C, was zero BM, which indicates a square planar geometry of low spin  $dsp^2$  hybridization.

The electronic spectrum of  $PdCl_2(DTO)$  in ethanol as shown in Figure 11, two well defined bands at 417nm ( $23981\text{ cm}^{-1}$ ) of low intensity and at 309nm ( $32362\text{ cm}^{-1}$ ) of higher intensity. The first band can be considered as d-d transition<sup>[45]</sup>. The second band suggests that it may be (M→L) a charge-transfer in character rather than ligand field. These data may confirm the previously suggested structure-I.

### 3.2.2. Ni(II) Complex of DTO

The electronic spectrum of Ni(II) complex, Figure 12, shows two distinguishable weak d-d transition bands in octahedral field, the first one appeared as a broad band at 630nm ( $15873\text{ cm}^{-1}$ ), while the second band appeared as a shoulder at 375nm ( $26666\text{ cm}^{-1}$ ), these bands can be suggested as  $v_2(^3 A_{2g} \rightarrow ^3 T_{1g}(F))$  and  $v_3(^3 A_{2g} \rightarrow ^3 T_{1g}(p))$ , respectively in octahedral field<sup>[27,46]</sup>. The first transition  $v_1(^3 A_{2g} \rightarrow ^3 T_{2g}(F))$  did not appear in the spectrum. Fitting the values of  $v_2$  and  $v_3$  to the Tanabe-Sugano diagram of  $d^8$  configuration, Figure 11, it was possible to calculate the first band ( $v_1$ ) and the ligand field parameters (racah parameter  $B'$ , nephelauxetic  $\beta$ , and ligand field splitting parameter

$10Dq$ ),  $\frac{v_2}{v_3} = \frac{26666}{15873} = 1.68$ . This ratio fits the diagram at  $\frac{Dq}{B'} = 1.2$ . Considering the value of

the second transition  $(v_2) \frac{E(v_2)}{B'} = 20$ , therefore,  $B' = \frac{E(v_2)}{20} = \frac{15873}{20} = 794$ . So,  $10Dq$  can be calculated as follows:

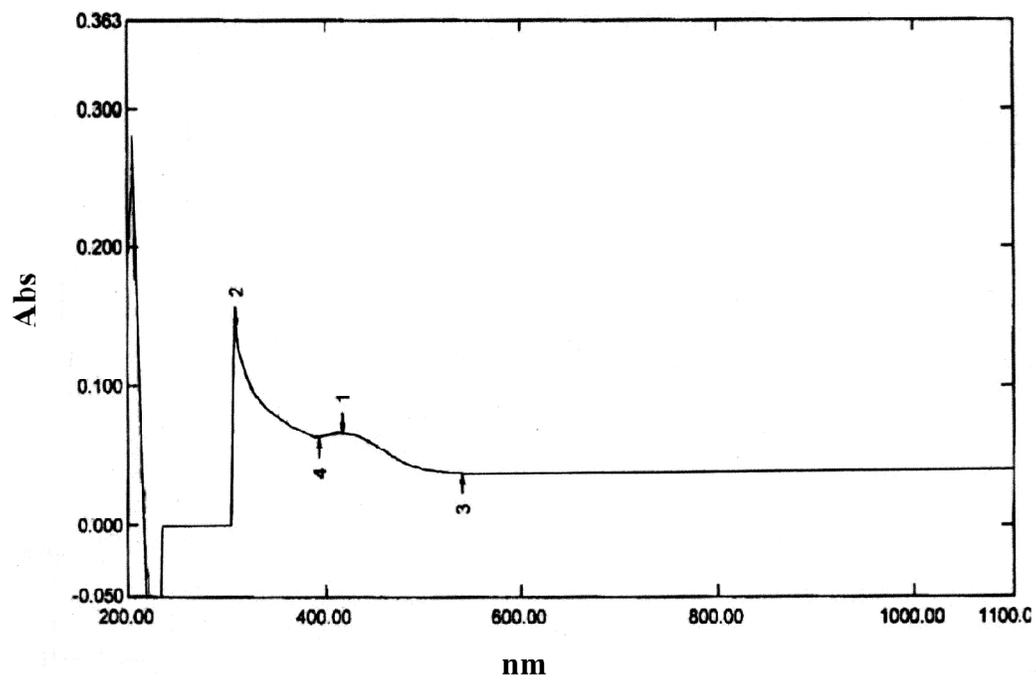
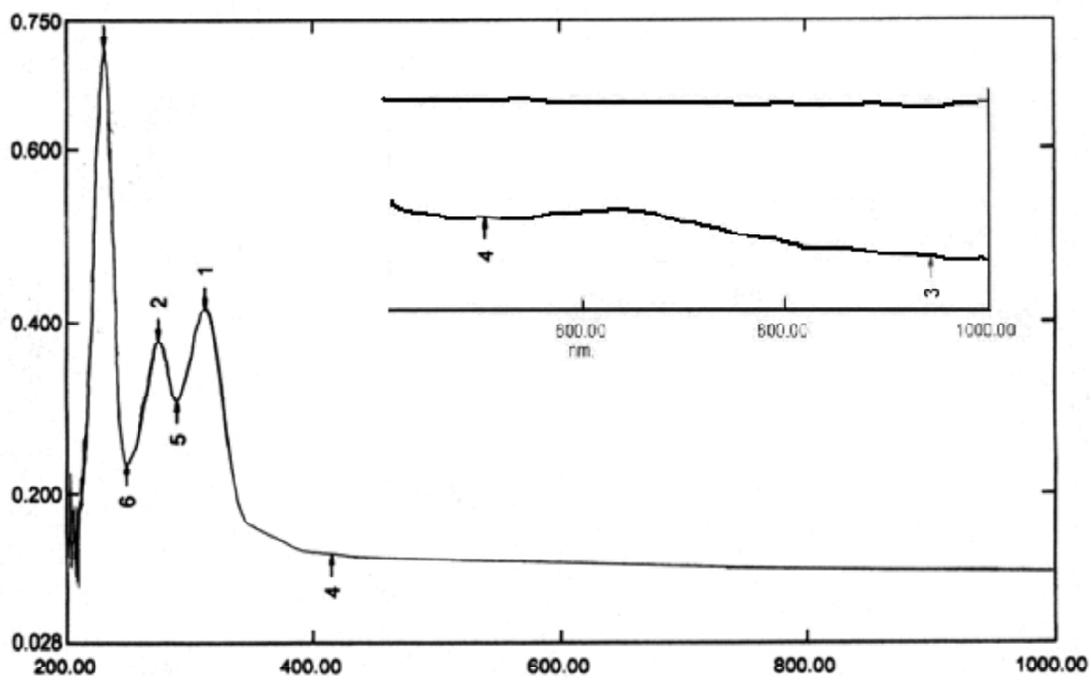
Since  $Dq = 1.2 \cdot B'$ , then  $Dq = 1.2 \cdot 794$ , or  $=952.4\text{ cm}^{-1}$

$\therefore 10Dq = 9524\text{ cm}^{-1}$ <sup>[27,47]</sup>

This value of  $10Dq$  represents the first transition  $v_1$ . The value of  $v_1$  can also be recalculated taking  $\frac{E(v_2)}{B'} = 12$

$v_1 = 12B' = 9528\text{ cm}^{-1}$ . The similarity of the value of  $v_1$  obtained by the two approaches indicate the accuracy of the calculations, the nephelauxetic factor  $\beta$ , was calculated taking the value of racah parameter for the free ion to be  $1030\text{ cm}^{-1}$ . This relatively high value refers to appreciable ionic character of the bonds between nickel and donor atoms, i.e., relatively weak field, this can also be shown by the low value of  $10Dq$ . The measured magnetic moment of solid Ni complex was zero BM which refer to diamagnetic, square planar geometry of  $dsp^2$  hybridization, but when this dark-blue complex was dissolved in ethanol it became octahedral as characterized above due to coordination of the ethanol molecules to the vacant axial positions.

In order to show the complex to be regular or distorted  $v_3/v_2$  was calculated and found to be (1.67) this value came in the range of distorted octahedral complexes (1.66-1.78)<sup>[27,48]</sup> these finding came in accordance with the previously suggested structure-II.

Figure 11: Electronic Spectrum of PdCl<sub>2</sub> (DTO)Figure 12: Electronic Spectrum of NiCl<sub>2</sub> (DTO)

## Conclusions

The conclusions that could be derived from the data of this research may be summarized in the following steps:-

1. Complexation reaction of Pd(II) chloride with benzonitrile gave  $\text{PdCl}_2(\text{PhCN})_2$  which reacted with DTO to give  $\text{PdCl}_2(\text{DTO})$ . The reaction of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  with DTO gave  $\text{NiCl}_2(\text{DTO})$ . Both of these two complexes were confirmed by UV, FTIR spectra and quantum calculations.
2. The presence of two donor atoms (N and S) of DTO enhanced different complexing behaviors and geometries using the studied metal ions.
3. The semi-empirical PM7 methods were used for the calculation of the total relative energies for Pd complexes. They showed that PD1- trans isomer was more stable than PD1-cis for  $\text{PdCl}_2(\text{PhCN})_2$  complexes. In experimental results of FT-IR also showed that the PD1-trans was the more stable expected isomer.
4. For  $\text{PdCl}_2(\text{DMSO})_2$ , the PD10-DMSO-trans (O,O) was the more stable than the other three isomers, the experimental results of FT-IR showed that the PD9-DMSO-trans(S,S) was the most stable isomer.
5. For the complex of  $\text{PdCl}_2(\text{DTO})$ , the results of relative energy calculation showed that, the PD5-trans A-(N,S) was the most stable among the three amide isomers, and among the three-imide isomers, the PD6-cis I-(N,N) was more stable.

The PD-5trans-A (N, S) was more stable than PD6-cis I- (N, N) among the total amide and imide isomers.

For the results of experimental values of vibrational spectra we find the PD5-trans-A (N, S) was the most stable.

6. For Ni complexes the results of relative energy, which were calculated by semi-empirical PM3 method, show that the Ni6-cis-I (N, N) to be more stable than Ni-3-cis-A (N, N).

The experimental vibrational data also showed that Ni6-cis-I (N, N) was the most stable expected isomer.

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