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DFT and MP2 Study of Pd(II) and Ni(II) PhCN, DMSO and Dithiooxamide Complexes- Part II: Theoretical

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ABSTRACT

The DFT and MP2 method at high level were used for calculating the relative energies of the 24 conformers of the prepared compounds $PdCl_2(PhCN)_2$, $PdCl_2(DMSO)_2$, $PdCl_2(DTO)$, $NiCl_2(DTO)$. *The DFT, MP2, PM7 and PM3 energy calculations help to predict the most stable structure among the other probable structures.Both quantum method showed that PD1-trans isomer was the most stable for* $PdCl_2(PhCN)_2$. *For* $PdC1_2(DMSO)_2$, *the PD9-DMSO-trans(S,S) was more stable than the other three isomers.The relative energy calculations for the six* $PdCl_2(DTO)$ *isomers, showed that, among the three amide isomers, the PD5-trans-A(N,S) was the most stable, and among the three imide isomers the PD6-cis-I-(N,N) was the most stable, among the total six amide and imide isomers, the PD5-trans-A(N,S) was more stable than PD6-cis-I(N,N).For Ni complexes, the results of relative energies calculated showed that, among amide and imide complexes, Ni5-trans-A(N,S) was the most stable complexes, while among the three imide isomers the Ni6-cis-I(N,N) was the most stable. The TD-DFT and Semi-empirical PM7 method were used for calculating the UV and IR spectra. The results of the vibrational calculations were in good agreement with those obtained from the energy calculations and the experimental UV and IR study came in accordance with the theoretical calculation.*

Keywords: Palladium DTO, DMSO complexes, Nickel DTO, DMSO complexes, IR, UV Spectra of Pd and Ni complexes, Theoretical DFT-IR and TD-UV.

INTRODUCTION

The dithiooxamide and its derivatives of N-substituted and N,N-disubstituted have been used extensively in many fields and especially in drug industry. 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 beside other applications[1].

Dithiooxamide has a long record of use as a reagent for the detection and determination of many metals, including Pd(II) and Pt(II)[2]. 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, isothiocynates or involved in a heterocyclic ring, e.g.[3] mercaptotriazole, mercaptooxadizole. The derivatives of these compounds are known to have an activity of antiviral, anti-infective and antineoplastic through binding to copper or iron in the cells.

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 antitumor 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.

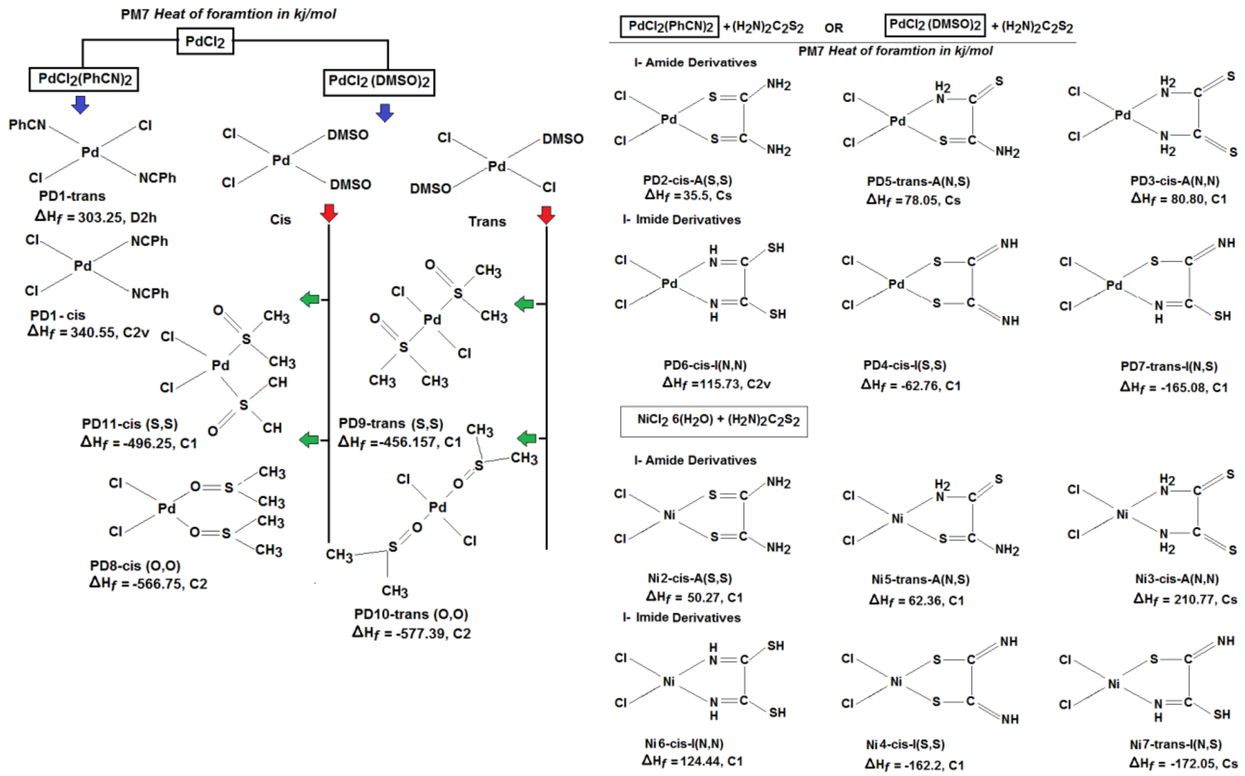
Dithiooxamide forms cationic complexes $[M(DTO)_2]X_2$ with Ni(II), Pd(II), Pt(II) and other metals. Also in these compounds the halogenide acts as a counter ion and is hydrogen bonded to the NH_2 group[4]. Consequently the NH_2 fundamentals, especially clear in the 3500-2500cm^{-1} region, exhibit strong ammonium character. Much of the attention that dithiooxamide has received in the chemical literature, however, 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 has 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[2].In 1973 Peryronel and co-workers[5] 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[6] reported on $M(HA)_2$ with M=Ni(II), Pd(II), and Pt(II). Also, other DTO-metals complexes such as Mn(II)[7], Co(II)[7,8], Zn(II)[9], Cu(I)[7,8,10-12], Cd(II)[7,10], Ir(III)[7] and Sb(III)[13,14] have been discussed. Several studies have been reported on platinum(II) complexes[7,8,15-19], palladium(II) complexes [7,8,15,16,21-29] and Ni(II) complexes[8,11,15,16,20,29-34]. In recent years, Desseyn and coworkers[29] have described three different kinds of Pd(II) polymers with dithiooxamide derivatives suggesting that 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_4 and MN_4 surrounding in polymeric structure[35].

Ray and Sathyarayana[30] proposed S,S-coordination for the cationic species $Ni(H_2A)_2Cl_2$ in analogy with dithiobiuret ($HN(C(S)NH_2)_2$) complexes. Two novel nickel(II) dinuclear complexes $[Ni(cyclam)_2(DTO)](CLO_4)_2$ and $Ni_2(TAA)_2(DTO)]$ $(CLO_4)_2$, (TAA= $N(CH_2Ch_2NH_2)_3$, cyclam=1,4,8,11-tetrazacyclotetradecanes have been proposed and studied by elemental analysis, IR, electronic spectra and magnetic measurements.

In 2002 we reacted DTO with both n-propyl chloride and p-nitrobenzaldehyde which gave the two new derivatives, PDTO and SDTO, respectively[36]. The reaction of copper chloride $CuCl_2$ 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. The Ab-initio method of high level was used for calculating the relative energies and IR spectra of the three compounds (DTO, PDTO, and SDTO). The *Ab initio* calculations indicated the tautomeric structure of DTO and helped to predict the most stable structures. Few theoretical studies have been carried out on DTO heavy metal complexes due to calculation complications. In 2012, Raul et al performed a structural analysis of Mo(VI)-DTO complex using DFT calculations (B3LYP/def2-TZVPP)[37].In this paper we used the theoretical calculation to compare the results with our previous experimental results to solve the debatable issue of linkage metal-ligand in addition to know the most stable configurations.

MATERIALS AND METHODS

Theoretical Part : In this present work, various theoretical MO methods, mounted in G09W[38], have been used for evaluation of relative quantum mechanical energies for 24 conformations for both Pd(II) and Ni(II) complexes with monodentate ligands DMSO and PhC≡N and the bidentate ligands DTO. Single-point calculations were performed using MP2/DGDZVP//RB3LYP/LANL2DZ/auto=all for Pd(II) and Ni(II) complexes.



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

Other basis sets were also used such as DZVP for Pd(II) and QZVP for Ni(II) complexes to solve the debatable issue such that $PdCl_2$(DMSO) complexes regarding the linkage type i.e. SS or OO. The DFT energies including zero point energy, ZPE calculations were also performed using B3YLP/DGDZVP//B3YLP/LANL2DZ /auto=all for both Pd(II) and Ni(II) complexes. Generally, the energy and IR calculation of heavy metal complexes is a complicated, time-consuming and teddy. Semi-empirical method PM7 and PM3 were also used to calculate the heat of formation and IR frequencies. The theoretical unscaled vibrational frequencies have been calculated at B3YLP/LANL2DZ level for diagnosis of some debatable bands of the experimental FTIR spectra and to characterize the transition state structures. The calculation of UV/VIS spectra of Pd(II) and Ni(II) complexes using analytic time-dependent td(nstates=12) in addition to self-consistent reaction field key [scrf=(solvent=ethanol), Pop=Reg] at DFT level B3YLP/LANL2DZ. PM3 from HyperChem 7.52[39] was used for these calculations in addition to PM7 from MOPAC2012 program[40].

Infrared Spectroscopy study: The theoretical vibrational spectra of twenty four conformations of $Pd(PhCN)_2Cl_2$- two conformers (PD1-cis and PD1-trans), $Pd(DMSO)_2Cl_2$- four conformers (PD8-PD11), $Pd(DTO)Cl_2$- eight conformers (PD2-PD7, PD12, PD13), $Ni(PhCN)_2Cl_2$- two conformers (Ni1-cis and Ni1-trans), Ni $(DMSO)_2Cl_2$- four conformers (PD10-PD13) and $Ni(DTO)Cl_2$ – eight conformers (Ni2-Ni9) have been calculated using DFT and PM3. These theoretical spectra have been compared with our experimental FTIR spectra[43]. The results of the experimental and theoretical spectra represented as the most diagnostic vibrational modes, are shown in tables 7-13. Generally, the theoretically calculated frequencies of the studied twenty four conformers showed deviations from some well–documented experimental values due the basis sets function formula. The calculated frequencies were traced in the experimental spectra taking in account the deviations due to the main difference between the experimental measurements and the theoretical treatment of vibrational spectra, in order to select the most possible conformer for each complex and discuss the theoretical data. However, the theoretical vibrational spectra showed some assignment that has not been reported elsewhere**.** The theoretical spectra are superimposed on FTIR spectra of (PhCN), (DMSO) and (DTO) of Pd(II) and Ni(II) complexes are shown in figures 2-5.

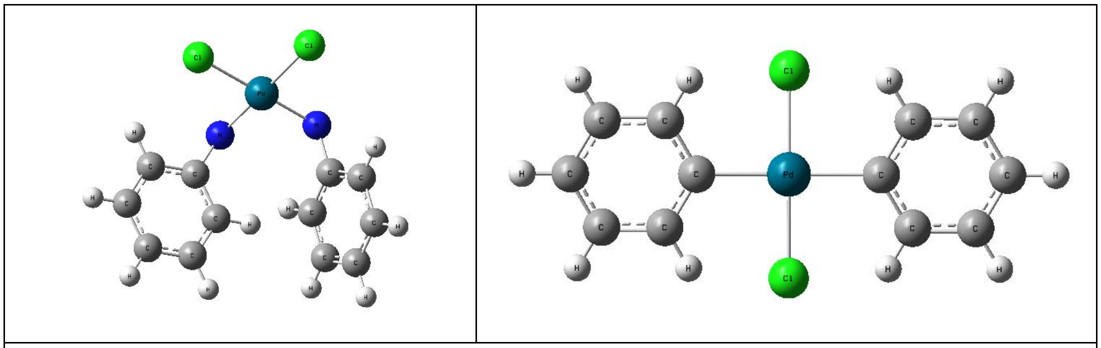
RESULTS AND DISCUSSION

Optimized Geometries and Energies : Twenty four theoretically probable square planar structures of **Pd(II)**; PD1-PhCN-cis-(N,N), PD1-PhCN-trans-(N,N), PD11-DMSO-cis-(S,S), PD9-DMSO-trans-(S,S), PD8-DMSO-cis-(O,O), PD10-DMSO-trans-(O,O), PD3-DTO-cis-A(N,N), PD2-DTO-cis-A(S,S), PD5-DTO-trans-A(N,S), PD4-DTO-cis-I(S,S)-(-2), PD7-DTO-trans-I(N,S)-(-1), PD6-DTO-cis-I(N,N), PD12-DTO-trans-I(NS), PD13-DTO-cis-I(SS) and **Ni(II)**; Ni1-PhCN-cis-(N,N), Ni1-PhCN-trans-(N,N), Ni2-DTO-cis-A(S,S), Ni3-DTO-cis-A(N,N), Ni5-DTO-trans-A(N,S), Ni4-DTO-cis-I(S,S)-(-2), Ni6-DTO-cis-I(N,N), Ni7-DTO-trans-I(N,S)-(-1), Ni10-DMSO-cis-(O,O), Ni11-DMSO-trans-(O,O), Ni12-DMSO-cis-(S,S), Ni13-DMSO-trans-(S,S) have been calculated to search for the most probable stable structure as shown in scheme-1 and figure-1.

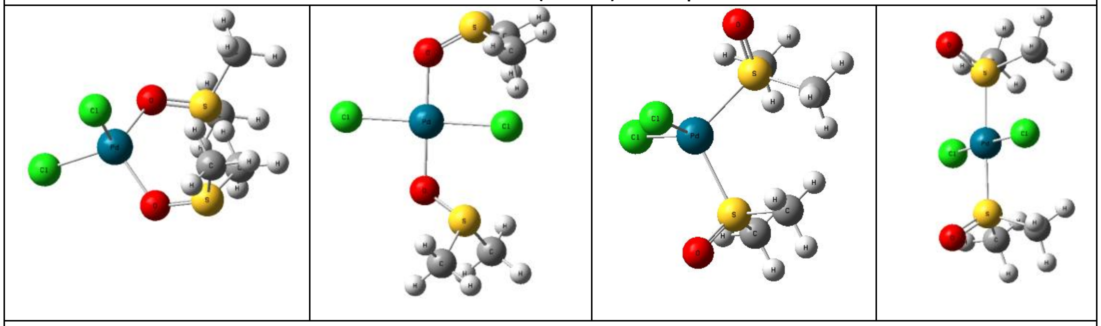
The modeled building structure includes various types of geometrical cis and trans isomers, linkage (N or S) cis and trans conformers. The DTO/A (A=Amide form) and DTO/I (I=Imide form) ligands are potentially capable of forming linkage isomers. Theoretically, all S and N atoms of the ligand contain unshared electron pairs. Thus the group C=S, C-N of DTO/A and C-S, C=N of DTO/I can attach itself to the palladium, or nickel ion through the nitrogen and sulfur atom.
For the NCS group, usually the first row transition elements prefer to attach through nitrogen, whereas the second and third row transition elements prefer to attach through sulfur, according to Pearson’s law[41]. All these facts are taken into consideration through model building.

Pd-Complexes: The total and relative energies and the heat of formation (ΔH_f) of the fourteen conformers belonged to DTO, DMSO, PhCN ligand complexes of Pd(II), which were calculated using DFT, MP2, PM7 and PM3 methods.

a. Benzonitrile Complexes: The results of the fourth quantum method calculations i.e. DFT, MP2, PM7 and PM3 in the gas phase showed that the PD1-PhCN-trans-(N,N) isomer of $Pd(PhCN)_2Cl_2$ was more stable than PD1-PhCN-cis-(N,N) isomer by 4.196 (MP2) or 5.741 (DFT) kcal/mol as shown in tables 1-3. It is known experimentally that cis vs. trans stability depend on the physical state of the complex, i.e. being in solid state or in solution. The results of our calculations support those of the vibrational measurements in solid state, which is expected considering the steric effect.



Cis and Trans conformation isomer of $PdCl_2(PhCN)_2$ complexes



The possible conformation isomers of $PdCl_2(DMSO)_2$ complexes

Figure-1: Conformation isomers of $PdCl_2$ complexes with PhCN and DMSO. Ni(II) complexes give identical configurations.

b. Dimethyl Sulphoxide Complexes: The four methods showed that the PD10-DMSO-trans-(O,O) conformer (0.00, MP2) of $Pd(DMSO)_2Cl_2$ was the most stable structure among PD8-DMSO-cis(O,O) (2.7, MP2), PD9-DMSO-trans-(S,S) (18.52, MP2) and PD11-DMSO-cis-(S,S) (21.0, MP2) as shown in Table-3, while MP2/DZVP showed that the PD9-DMSO-trans-(S,S) was the most stable structure among the others. Nakamoto[42] pointed out that palladium coordinates to the S-atom of DMSO in PdCl2$(DMSO)_2$ and this is indicated and confirmed by our infrared measurements[43]. Thus, only MP2/ DZVP theoretical calculations showed that Pd-S complexes are the more stable, see Table-1, while the high level DFT/DGDZVP, PM7 and PM3 failed. This inconsistency may be due to the improper mathematic formula of these basis sets that ignore the π-back donation phenomena between Pd↔S atoms. MP2/ DZVP showed that the stability energy due to π-back in Pd-S (PD9) and Pd-O (PD10) was 31.32 kcal/mol. On the other hand, the calculated stability of the sulfur bonded conformers showed the expected stability of the trans isomer over the cis considering the steric factor. For example, the MP2 calculation showed that the trans (PD9) was more stable than cis (PD11) in SS linkage while the cis (PD8) was more stable than trans (PD10) in case of OO linkage. Finally, we may conclude that the result of these four quantum methods were identical in determining the geometrical isomer but different in linkage (N or S) conformers regarding DMSO ligand.

c. Dithiooxamide Complexes: The MP2/DGDZVP, PM7 and PM3 relative energies for the eight Pd-DTO complexes showed that, among the three amide isomers (DTOA), the following trend of stability was noticed:- PD5-DTO-trans-A(N,S)>PD2-DTO-cis-A(S,S)>PD3-DTO-cis-A(N,N) and among the three imide isomers (DTOI), the following trend of stability was noticed:- PD6-DTO-cis-I(N,N)> PD12-DTO-trans-I(N,S)>PD13-DTO-cis-I(S,S)> by MP2/DGDZVP and DFT only. Among amide and imide complexes, PD5-DTO-trans-A(N,S) was the most stable complexes. It means the trans linkage A-(N,S) was the most stable due to π-back bonding of sulfur atoms and trans configuration. The other two imide isomers i.e. PD4 and PD7 cannot be compared as they are charged and have different number of atoms. These results are confirmed by our infrared measurements[43].

Table-1: Single point energies (a.u.) for palladium complexes

Palladium (II) Complexes		**MP2/DZVP (HC752)** **MP2/ DGDZVP (G09W)**	**D.M. Debye**	**DFT/DGDZVP (G09W)**	**D.M. Debye**
PhCN	PD1-PhCN-cis-(N,N)	-6503.5834024 -6503.3780046	16.8802 16.1705	-6509.15386214	13.0720
	PD1-PhCN-trans-(N,N)	-6503.5925505 -6503.3846913	0.1161 0.0029	-6509.16234174	0.0004
Amide DTO	PD2-DTO-cis-A(S,S)	-6839.8430694 -6839.1852443	21.7910 21.2744	-6844.57729453	17.3942
	PD3-DTO-cis-A(N,N)	-6839.5082154 -6839.1666990	12.8799 11.7381	-6844.53751075	9.5399
	PD5-DTO-trans-A(N,S)	-6839.3503628 -6839.1905052	16.6217 15.9980	-6844.57216989	13.4496
Imide DTO	PD13-DTO-cis-I(S,S)	-6839.4531895 -6839.1230741	9.3514 10.3717	-6844.51135134	8.9772
	PD12-DTO-trans-I-(N,S)	-6839.3049565 -6839.1463143	12.9822 13.4698	-6844.53600399	11.0307
	PD6-DTO-cis-I(N,N)	-6839.3149663 -6839.1555973	15.2875 15.8198	-6844.54363873	12.3182
	PD7-DTO-trans-I(N,S)-(-1)	-6839.3233511 -6838.7039688	1222.07 10.0170	-6844.08583498	8.0118
	PD4-DTO-cis-I(S,S)-(-2)	-6837.8329697 -6838.0947933	1027.61 2.0091	-6843.46802952	1.8552
DMSO	PD8-DMSO-cis-(O,O)	-6960.8078389 -6960.6182046	10.0777 8.4410	-6966.47798885	7.3752
	PD10-DMSO-trans-(O,O)	-6968.4072506 -6960.6221771	4.4481 1.8298	-6966.48032579	1.5442
	PD11-DMSO-cis-(S,S)	-6960.7676517 -6960.5887079	12.4399 12.2151	-6966.45386872	10.3048
	PD9-DMSO-trans-(S,S)	-6968.4571597 -6960.5926579	9.1495 9.8994	-6966.46031504	8.4724

The DFT/DGDZVP calculation showed inconsistent results compared with MP2/DGDZVP. MP2/DZVP showed that PD13-DTO-cis-A(N,S) was more stable than PD6-DTO-cis-I(N,N) by 86.736 kcal/mole due to π-back bonding of sulfur atoms. It could be concluded the DZVP basis set is very sensitive to sulfur coordination chemistry. The preference of PD5-DTO-trans-A(N,S) (0.00) over PD12-DTO-trans-I-(N,S) (27.73 kcal/mol), i.e. amide over imide, according to theoretical treatment may be related to the electronegativity factor. Nitrogen is more electronegative than sulfur; therefore amide tautomer is expected to be more stable than imide tautomer.

Ni(II)-Complexes

a. Benzonitrile Complexes: The results of the fourth quantum method calculations i.e. DFT, MP2, PM7 and PM3 in gas phase showed that the Ni-trans isomer of $Ni(PhCN)_2Cl_2$ was more stable than Ni1-cis isomer by 8.130 (MP2) or 8.499 (DFT) kcal mol^{-1} as shown in tables 4-6.

b. Dimethyl Sulphoxide Complexes: The MP2 and DFT methods showed that the Ni11-DMSO-trans-(O,O) conformer (0.00, MP2) of $Ni(DMSO)_2Cl_2$ was the more stable structure than Ni10-DMSO-cis(O,O) (3.221, MP2) and (3.2942, DFT) as shown in table-6. The Ni13-DMSO-trans-(S,S) was unstable through the minimization energy, so it could not be compared with Ni12-DMSO-cis(S,S). More than 10 different basis set were used to achieve the convergence but all of them failed.

Table-2: Heat of formation for palladium complexes

Palladium (II) Complexes		**Heat of Formation**			
		ΔH_f PM7	**PG**	**ΔH_f PM3**	**PG**
PhCN	PD1-PhCN-cis-(N,N)	81.393	C_{2V}	-77.377	C_{2v}
	PD1-PhCN-trans-(N,N)	72.480	D_{2h}	-87.916	C_1
Amide DTO	PD2-DTO-cis-A(S,S)	10.397	C_S	-85.119	C_S
	PD3-DTO-cis-A(N,N)	19.313	C_1	6.677	C_1
	PD5-DTO-trans-A(N,S)	18.655	C_S	-108.930	C_1
Imide DTO	PD13-DTO-cis-I(S,S)	39.329	C_1	-86.628	C_2
	PD12-DTO-trans-I-(N,S)	25.145	C_1	-94.1273	C_1
	PD6-DTO-cis-I(N,N)	27.660	C_{2V}	-110.750	C_S
	PD7-DTO-trans-I(N,S)-(-1)	-39.455	C_1	-163.559	C_1
	PD4-DTO-cis-I(S,S)-(-2)	-15.000	C_1	-141.004	C_2
DMSO	PD8-DMSO-cis-(O,O)	-135.456	C_1	-281.390	C_2
	PD10-DMSO-trans-(O,O)	-137.999	C_2	-289.119	C_1
	PD11-DMSO-cis-(S,S)	-118.606	C_1	-264.865	C_1
	PD9-DMSO-trans-(S,S)	-109.024	C_1	-272.221	C_S

Table 3: The relative energies in kcal/mol for palladium complexes

Palladium (II) Complexes		**Relative Energy from Table-1**				**Relative ΔH_f From Table-2**	
		MP2/DZVP **MP2/ DGDZVP**		**DFT/DGDZVP**		**PM7**	**PM3**
PhCN	PD1-PhCN-cis-(N,N)	5.7405/4.1960		5.741		1.3	10.615
	PD1-PhCN-trans-(N,N)	0.000/0.000		0.000		0.000	0.000
Amide DTO	PD2-DTO-cis-A(S,S)	0.000/3.301		0.000		42.55	23.812
	PD3-DTO-cis-A(N,N)	210.124/14.939		21.749		45.3	115.608
	PD5-DTO-trans-A(N,S)	309.178/0.000		3.216		0.000	0.000
Imide DTO	PD13-DTO-cis-I(S,S)	0.000/20.409		20.261		14.184	24.122
	PD12-DTO-trans-I-(N,S)	93.018/5.825		4.791		0.00	16.6227
	PD6-DTO-cis-I(N,N)	86.736/0.000		0.000		2.515	0.000
	PD7-DTO-trans-I(N,S)-(-1)*	***		***		***	***
	PD4-DTO-cis-I(S,S)-(-2)*	***		***		***	***
DMSO	PD8-DMSO-cis-(O,O)	4800/2.49	4800/2.49	1.467	1.467	2.543	7.728
		0.00/0.00	31.32/0.00	0.000	0.000	0.000	0.000
	PD11-DMSO-cis(S,S)	4825/2.48	4825/21.00	4.045	16.60	19.393	24.254
	PD9-DMSO-trans-(S,S)	0.00/0.00	0.00/18.52	0.000	12.557	28.975	16.897

*They can't be compared as they have different number of atoms

c. Dithiooxamide Complexes: The MP2 and DFT relative energies for Ni-DTO complexes. Tables 4-6 showed that, among the three amide isomers (DTOA), the Ni5-DTO-trans-A(N,S) was the most stable, while PM7 and PM3 showed Ni3-DTO-cis-A(N,N) was the most stable. Among the three imide isomers (DTOI), the following trend of stability was noticed:- Ni6-DTO-cis-I(N,N)>Ni8-DTO-trans-I(N,S)>Ni9-DTO-cis-I(S,S)> by MP2 and DFT only. Among amide and imide complexes, Ni5-DTO-trans-A(N,S) was the most stable complexes. The other two imide isomers i.e. PD4 and PD7 cannot be compared as they are charged and have different number of atoms. Finally it was found that the Ni5-DTO-trans-A(N,S) was more stable than Ni8-DTO-cis-A(N,S) by 25.368 kcal/mol. Ni(II) ions is harder than Pd(II), so the trend of stability of the different conformers of $NiCl_2$ $(DTO)_2$, which show the S,S-bonded DTO in both amide and imide tautomers are less stable as seen in Ni2 and Ni9. This is consistence with Pearson's law of hard and soft argument where Ni(II) prefers to bond to polarizable ligands and forms square-planar coordination compounds[41].

Table 4: Single point energies for nickel complexes

Nickel (II) Complexes		**MP2/ DGDZVP**	**D.M. Debye**	**DFT/DGDZVP**	**D.M. Debye**
PhCN	Ni1-PhCN-cis-(N,N)	-3072.61592254	16.8621	-3077.551194	13.1351
	Ni1-PhCN-trans-(N,N)	-3072.62887905	0.0001	-3077.564738	0.0012
Amide DTO	Ni2-DTO-cis-A(S,S)	-3408.41079946	20.9627	-3412.96544886	16.6491
	Ni3-DTO-cis-A(N,N)	-3408.40847811	11.0815	-3412.93994229	8.7459
	Ni5-DTO-trans-A(NS)	-3408.42352147	15.6160	-3412.96586246	12.6944
Imide DTO	Ni9-DTO-cis-I(S,S)	-3408.34142218	10.6621	-3412.89449860	8.8707
	Ni8-DTO-trans-I-(N,S)	-3408.38309450	12.8718	-3412.93589837	10.2468
	Ni6-DTO-cis-I(N,N)	-3408.40071127	15.1664	-3412.95040649	11.4097
	Ni7-DTO-trans-I(N,S)-(-1)	-3407.93851838	9.7960	-3412.47863394	7.8540
	Ni4-DTO-cis-I(S,S)-(-2)	-3407.31101444	1.2536	-6843.46802952	1.8552
DMSO	Ni10-DMSO-cis-(O,O)	-3529.86411214	8.9074	-3534.87677227	8.0302
	Ni11-DMSO-trans-(O,O)	-3529.86924479	2.1949	-3534.88202187	1.7925
	Ni12-DMSO-cis-(S,S)	-3529.80008311	12.5142	-3534.83153101	10.0260
	Ni13-DMSO-trans-(S,S)	++++	++++	-3534.84673932	8.3555

Table 5: Heat of formation for nickel complexes

Nickel (II) Complexes		**Heat of Formation**			
		ΔH_f PM7	**PG**	**ΔH_f PM3**	**PG**
PhCN	Ni1-PhCN-cis-(N,N)	304.55	C_{2V}	-61.4647	C_1
	Ni1-PhCN-trans-(N,N)	303.25	D_{2h}	-73.46887	C_2
Amide DTO	Ni2-DTO-cis-A(S,S)	12.01385	C_1	-48.3649	C_s
	Ni3-DTO-cis-A(N,N)	50.37622	C_S	-94.9079	C_1
	Ni5-DTO-trans-A(NS)	14.88129	C_1	-79.8398	C_1
Imide DTO	Ni9-DTO-cis-I(S,S)	24.87038	C_2	-53.270	C_2
	Ni8-DTO-trans-I-(N,S)	22.31979	C_1	-86.5173	C_1
	Ni6-DTO-cis-I(N,N)	29.74222	C_1	-124.533	C_2v
	Ni7-DTO-trans-I(N,S)-(-1)	-41.12203	C_S	-157.976	C_1
	Ni4-DTO-cis-I(S,S)-(-2)	-38.76006	C_1	88.0639	C_1
DMSO	Ni10-DMSO-cis-(O,O)	-138.22692	C_2	-266.1196	C_2
	Ni11-DMSO-trans-(O,O)	-132.75818	C_2	-274.0356	C_1
	Ni12-DMSO-cis-(S,S)	-122.61724	C_1	-191.6857	C_1
	Ni13-DMSO-trans-(S,S)	-126.54861	C_{2v}	-197.1817	C_s

$PdCl_2(PhCN)_2$ – PD1-cis and PD1-trans : The theoretical vibrational modes which were followed are those of C≡N and Pd-Cl moieties, these can reflect the structure and bonding in complexes which are explained in table-7 and figures 2 and 3. They show the frequencies of the two conformers, the *v*C≡N of both conformers were close to each other. On the other hand, PD1-PhCN-cis-(N,N) gave two stretching modes for Pd-Cl (347 and 339cm^{-1}), while PD1-PhCN-trans-(N,N) gave only one at (278cm^{-1}) closer to the experimentally chosen value at (320cm^{-1}). This makes PD1-PhCN-trans-(N,N) the preferred structure which is in accordance with the relative energy results. The FTIR spectrum of (PhCN) complex of Pd(II) shows the geometry to be trans-isomer, this is due to the appearance of one PdCl band stretching frequency in the range (300-330cm^{-1}) i.e. at 320cm^{-1}. On the other hand, the cis-isomer should give two bands in the above range. These assignments were based on the argument of Nakamoto[42]. This result was more indicated by the appearance of the *v*C≡N at 2284cm^{-1}, which came at a higher frequency compared to 2230cm^{-1} of the free benzonitrite. The theoretical spectrum of PD1-PhCN-trans-(N,N) was superimposed on the experimental FTIR to show the degree of the accuracy of the theoretical calculation as seen in figure-2.

Table 6: The relative energies in kcal/mol for palladium complexes.

Nickel (II) Complexes		**Relative Energy from Table-4**		**Relative ΔH_f from Table-5**	
		MP2	**DFT**	**PM7**	**PM3**
PhCN	Ni1-PhCN-cis-(N,N)	8.130	8.499	1.3	10.615
	Ni1-PhCN-trans-(N,N)	0.000	0.000	0.000	0.000
Amide DTO	Ni2-DTO-cis-A(S,S)	7.983	0.259	45.3	115.608
	Ni3-DTO-cis-A(N,N)	9.439	16.265	0.000	0.000
	Ni5-DTO-trans-A(NS)	0.000	0.000	42.55	23.812
Imide DTO	Ni9-DTO-cis-I(S,S)	37.204	35.083	2.551	71.263
	Ni8-DTO-trans-I-(N,S)	11.055	9.104	0.000	38.016
	Ni6-DTO-cis-I(N,N)	0.000	0.000	7.423	0.000
	Ni7-DTO-trans-I(N,S)-(-1)*	*****	*****	*****	*****
	Ni4-DTO-cis-I(S,S)-(-2)*	*****	*****	*****	*****
DMSO	Ni10-DMSO-cis(O,O)	3.221	3.2942	0.000	7.916
	Ni11-DMSO-trans-(O,O)	0.000	0.000	5.46874	0.000
	Ni12-DMSO-cis(S,S)	++++	9.5434	3.93137	5.496
	Ni13-DMSO-trans-(S,S)	++++	0.0000	0.000	0.000

*They can't be compared as they are charged and have different number of atoms

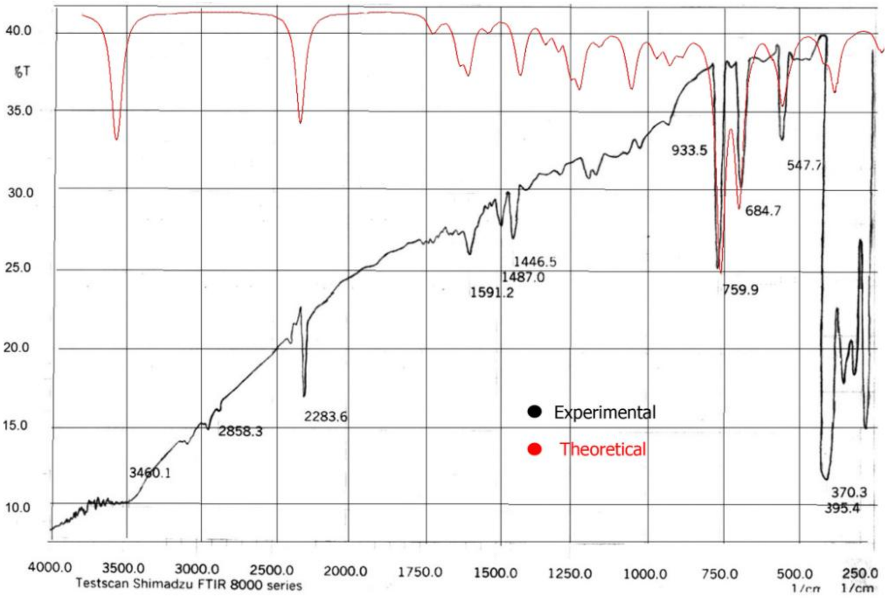


Figure 2. Theoretical DFT-IR and FTIR spectrum of $Pd(PhCN)_2Cl_2$

$PdCl_2$ $(DMSO)_2$-(PD8→ PD11) : The three selected diagnostic bands were *v*S=O, *v*Pd-Cl and *v*Pd-S, as seen in Tables 7, 9 &10 and Figure-3, showed the frequencies of these modes of vibrations in PD9-DMSO-trans (S,S) i.e. *v*S=O (PM3/DFT 1002/795cm^{-1}), *v*Pd-S (PM3/DFT 436/330cm^{-1}) and *v*Pd-Cl (PM3/DFT 469/364cm^{-1}) to be closest to the experimental values (1116, 414, 349cm^{-1} respectively) among the other conformers (i.e. PD8, PD10 and PD11), so it can be chosen as the preferred one,

especially if we consider the Pearson's law of softness and hardness. This result did come in accordance with that obtained results from relative energy calculations of MP2/DZVP (See Table 3).
The FTIR spectrum of (DMSO) complex of Pd(II) show clearly the formation of trans isomer, since a strong sharp band appeared at 1116cm^{-1} for a single S-O stretch, and single Pd-S and Pd-Cl stretching frequencies at 414 and 349cm^{-1} respectively. These data also indicate the coordination with S-atom rather than O-atom[42]. The theoretical unscaled IR spectrum of PD9-DMSO-trans-(S,S) was superimposed on the FTIR spectrum of Pd(DMSO)$_2$Cl$_2$ as shown in figure 3.

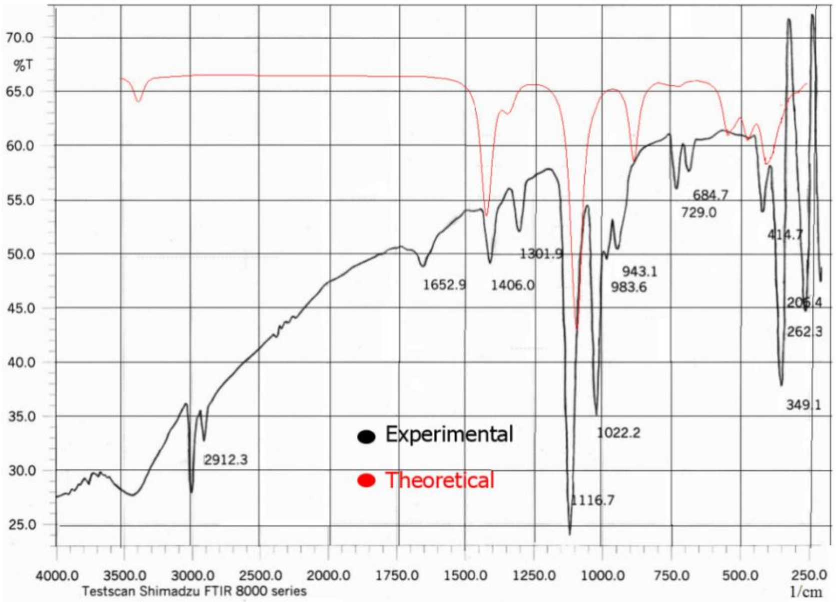


Figure 3: Theoretical DFT-IR and FTIR Spectrum of Pd(DMSO)$_2$Cl$_2$

Table7: The assignment of the most diagnostic FTIR band of PdCl$_2$(PhCN)$_2$ and PdCl$_2$(DMSO)$_2$ complexes

FTIR assignment	Pd (PhCN)$_2$Cl$_2$	Pd(DMSO)$_2$Cl$_2$
υC-C Aromatic	1168	---
υC=C Aromatic	1591	---
υC≡N Aromatic	2284	---
νC-H Aromatic	3080	---
δ C-H out of plane	759	---
νPd-Cl	320	349
νPd-N	450	---
νPd-S	---	414
νS-O	---	1116
δ C-S-C	---	729 as, 684s
ν(CH$_3$)	---	3000as, 2912s
δ (CH$_3$)	---	1406as, 1301s

PdCl$_2$ (DTO)$_2$-(PD2→ PD7, PD12 and PD13) : On comparison of the calculated frequencies of (PD2→ PD7), tables 7, 9 &10, Figure-4,with those experimentally determined, it was found that the theoretical frequencies of *v*NH, *v*CS, *v*PdN, *v*PdS, and *v*PdCl of PD5-DTO-trans-A (N,S) were closet to the experimental values. Also it was found that two separate frequencies of *v*NH were found; first one at 3463cm^{-1} for bonded NH$_2$, and the second at 3402cm^{-1} for the terminal non-bonded NH$_2$. These results are consistence with those obtained from experimental results. The spectra of both DTO complexes, prepared from either PdCl$_2$(PhCN)$_2$ or PdCl$_2$(DMSO)$_2$, were nearly identical, indicating the formation cis-dichloro complexes of the chelating DTO scheme-1 in both cases. Two bands were observed at 306 and 322cm^{-1} assigned as νPd-Cl symmetrical and asymmetrical frequencies respectively, were shown in figure 5, table 8.

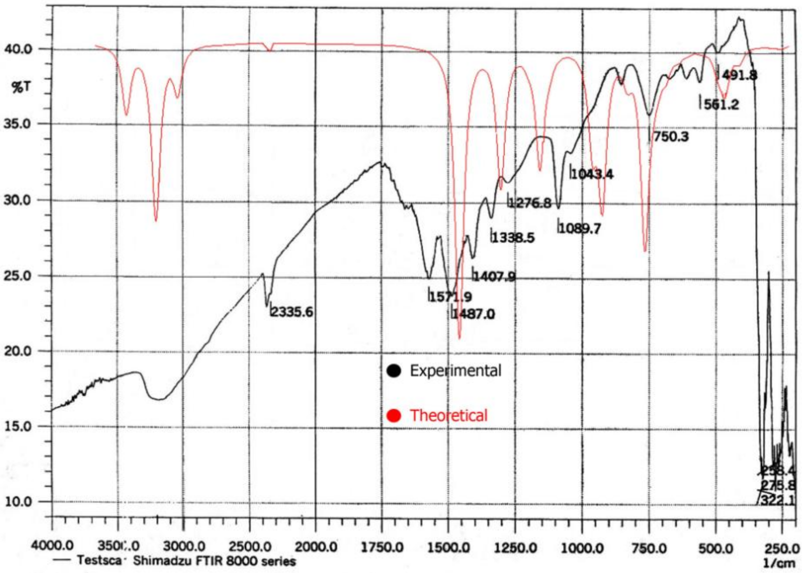


Figure 4: Theoretical DFT-IR and FTIR Spectrum of $Pd(DTO)_2Cl_2$

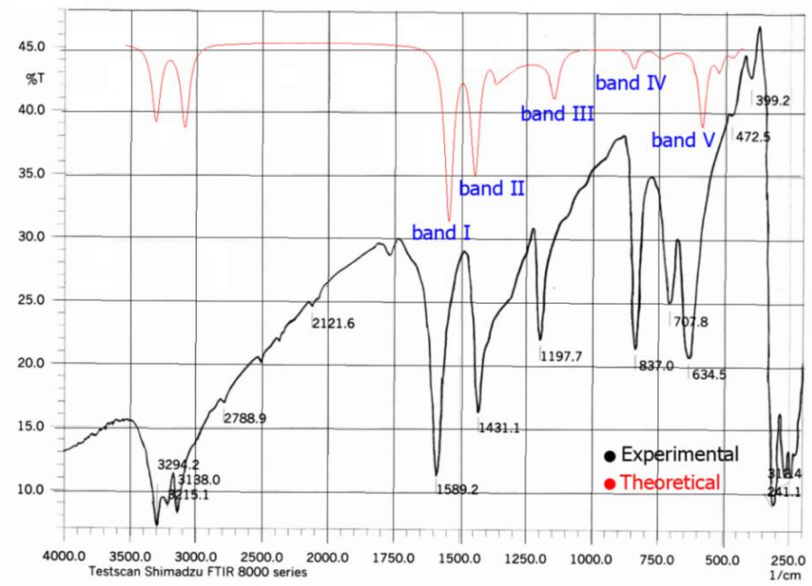


Figure 5: Theoretical DFT-IR and FTIR Spectrum of DTO

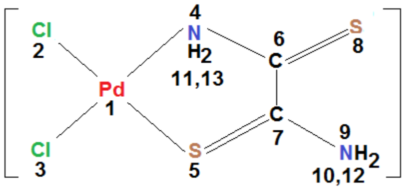
The theoretical DFT-IR and FTIR spectrum of free DTO as shown in Figure-5, shows νN-H bands at 3294cm^{-1} and 3215cm^{-1} which are representing, respectively, the "free" asymmetrical and symmetrical vibration modes of primary amine; νN-H of secondary amine appears at 3138cm^{-1}, the appearance of these three νN-H band in the spectrum of DTO mean that thione-thiol tautomerism can be suggested to take place[44]. These three bands were reduced in intensity in the formation of the Pd and Ni complexes. Thioamide band (I) appeared at 1589cm^{-1} in the spectrum of DTO, Figure-5 which was shifted to lower frequency and appeared at 1571cm^{-1} in the spectra of both Pd complexes as shown in figure 5.Thioamide band (II) was found at 1431cm^{-1}, this band was split into two bands of higher and lower frequencies in both complexes as reported in table 8. Thioamide band (III) found at 1197cm^{-1} in free DTO, has a 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 νC-N+C=S vibrations respectively[45], as seen in figure 5 and reported in table 8. More fact DOTA/DTOI are discussed in our previous work[46]. Thioamide band (IV), which is due to νCS, was found at 837cm^{-1} in the case of free DTO and observed at 750cm^{-1} for $PdCl_2$(DTO), which was prepared from $PdCl_2$ $(PhCN)_2$ and at 752cm^{-1} for $PdCl_2$(DTO), which was prepared from $PdCl_2$ $(DMSO)_2$. The red shift can be attributed to reduced bond order of the C=S bond upon complexation[47]. These results are in good agreements with Berdan[34], Desseyn[48], Pastorek[49] and Fouad[50] IR measurements.

Table 8. The assignment of the most diagnostic FTIR bands of DTO, $PdCl_2$(DTO)

FTIR assignment	DTO	Pd(DTO)Cl_2	Ni$(DTO)_2Cl_2$
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 $\delta_S(N\text{-}H)_A + \upsilon(C{=}N)_I$	1571	1602, 1520 1504s (1), 1498m (2)
DTOA/I band (II)	1431 C=N and also $\delta(C\text{-}N)_A + \delta_S(N\text{-}H)_A$	1487, 1407	1473, 1370, 1422 (3)
DTOA/I band (III)	1197 N-C-S and also $\rho(N\text{-}H)_A + \rho(N\text{-}H)_I$	1276, 1089	1109, 1105.5 (3)
DTOA/I band (IV)	837 C=S and also $\rho(N\text{-}H)_A + \rho(S\text{-}H)_I$	750, (716-34)(4)	777
DTOA/I band (V)	708, $\omega(S\text{-}H)_I$	680	661
DTOA/I band (VI)	635, $\tau(N\text{-}H)_A +$ $\delta(N\text{-}H)_I + \delta_S(S\text{-}H)_I$	630	
DTOA/I band (VII)	472, $\omega(N\text{-}H)_A +$ $\delta(S\text{-}H)_I\ \delta(N\text{-}H)_I$	470	470
DTOA/I band (VIII)	399 $\omega(N\text{-}H)_A + \omega(N\text{-}C\text{-}S)_I +$		
M-N	---	560	588
N-C=S	281,334,396,416,458 δ and ρNCS	492, (475-555)(4)	411
M-Cl	---	306, 322	275, 318
M-S	---	322, (227-269)(4)	275

$NiCl_2$(DTO) complexes. (1) $[Ni_2(cyclam)_2\text{-}(DTA)](ClO_4)_2$ and (2) $[Ni_2(TAA)_2(DTA)]$ $(ClO_4)_2$[49] (TAA. N(CH2CH2NH2)3, cyclam. 1,4,8,11-tetra-azacyclotetradecane, DTA. dithiooxamide), see also[50] (3)$[(Ni(II)(oxamide)_2)^{2-}]$ [34], (4) $[Pd(II)(thioacetamide)_4Cl_2]$[48]

No band was observed due to νS-H in the spectrum of the complexes, which indicate that the ligand became only in the thione form in the complex[51]. Two new bands were observed at 560 and 491cm^{-1} in both Pd complexes spectra, which may assigned as *ν*Pd-N and *ν*Pd-S frequencies[42]. According to the above theoretical and experimental data, the following structure for the Pd-complex can be suggested:-



Structure 1

Three new bands were observed at 560, 491 and 322cm^{-1} in both Pd complexes spectra, which may be assigned as *ν*Pd-N, *ν*Pd-S and *ν*Pd-Cl frequencies[52]. According to the above experimental data, structure-I for the Pd-complex can be suggested. PM7 theoretical IR showed three bands 561, 445 and 315cm^{-1}, which belong to *v*Pd-N, *v*Pd-S and *v*Pd-Cl respectively.

Table 9: The assignment of the most diagnostic theoretical vibrational frequencies for $Pd(PhCN)_2Cl_2$ and $Pd(DMSO)_2Cl_2$ at B3YLP/LANL2DZ level

Compounds	C≡N	Pd-Cl	Pd-N	Pd-S	Pd-O	S=O
PD1-PhCN-cis-(N,N)	2360	339 s. 347 as.	519 522	-	-	-
PD1-PhCN-trans-(N,N)	2359	278	538 544	-	-	-
PD8-DMSO-cis(O,O)	-	324 as. 326 s.	-	-	411 442	691 701
PD10-DMSO-trans-(O,O)	-	317 as. 333 s.	-	-	428 490	678 698
PD11-DMSO-cis(S,S)	-	323 as. 358 s.	-	323 335	-	763 790
PD9-DMSO-trans-(S,S)	-	364	-	330	-	585 795

Table 10. The assignment of the most diagnostic theoretical vibrational frequencies for $Pd(PhCN)_2Cl_2$ and $Pd(DMSO)_2Cl_2$at PM3 level.

Compounds	C≡N	Pd-Cl	Pd-N	Pd-S	Pd-O	S=O
PD1-PhCN-cis-(N,N)	2452	547 s. 535 as.	428 446	-	-	-
PD1-PhCN-trans-(N,N)	2469	462	447	-	-	-
PD8-DMSO-cis-(O,O)	-	548 as. 545 s.	-	-	873	963
PD10-DMSO-trans-(O,O)	-	488 s.	-	-	871	965
PD11-DMSO-cis-(S,S)	-	588 as. 570 s.	-	436	-	777
PD9-DMSO-trans-(S,S)	-	469 s.	-	486	-	1002

Table 11 The assignment of the most diagnostic theoretical vibrational frequencies for $Pd(PhCN)_2Cl_2$ and $Pd(DMSO)_2Cl_2$ at B3YLP/LANL2DZ level

Compounds	C≡N	Ni-Cl	Ni-N	Ni-S	Ni-O	S=O
Ni1-PhCN-cis-(N,N)	2339 2332	198s. 204as.	307 335	-	-	-
Ni1-PhCN-trans-(N,N)	2362	272	115 321 353	-	-	-
Ni10-DMSO-cis(O,O)	-	362as. 348s.	-	-	438 362	718 708
Ni11-DMSO-trans-(O,O)	-	253 372	-		527 432	715 703
Ni12-DMSO-cis-(S,S)	-	407 365	-	324	-	782 758
Ni13-DMSO-trans-(S,S)	-	286 419	-	342	-	782 784

$Ni(PhCN)_2Cl_2$ – Ni1-cis and Ni1-trans : The frequencies of the two conformers, Ni1-PhCN-cis-(N,N) and Ni1-PhCN-trans-(N,N), showed the *v*C≡N of both conformers were close to each other 2332 and 2362 cm^{-1} respectively as shown in table 11. On other hand, Ni1-PhCN-cis-(N,N) gave two asymmetrical modes for Ni-Cl 198 and 204cm^{-1}, while Ni1-PhCN-trans-(N,N) gave only one stretching at 272cm^{-1}. No FTIR spectra had been done for this complex.

Ni(DMSO)$_2$Cl$_2$-(Ni10→ Ni13) : The main four diagnostic bands were listed *v*S=O, *v*Ni-Cl, *v*Ni-N, *v*Ni-O and *v*Ni-S, as seen in table 11 and figure 6. The absorption bands for these four conformers are approximately equal. No FTIR spectra had been done for this complex.

Ni(DTO)Cl$_2$-(Ni2→ Ni9) : Among the calculated amide conformers Ni2-DTO-cis-A(S,S), Ni3-DTO-cis-A(N,N) and Ni5-DTO-trans-A(NS), the Ni5-DTO-trans-A(NS) spectra data for nearly all the studies frequencies were found closer to the experimental results. Ni5-DTO-trans-A(NS) was also found to be more stable according to the relative energy calculations. It is worthy to mention that the theoretical treatment show that DTO coordinate to Ni^{+2} through S and N-atoms. These findings confirm the experimental predictions which suggest that the coordination through N-and S-atoms.
The FTIR spectrum of the Ni(II) complex of DTO, Figure-6, Tables 8,11&12, shows the *v*N-H at 3261 and 3139cm^{-1} to be assigned as asymmetrical, and symmetrical vibrations respectively. The thioamid band (I) (σNH+*v*C=N) is situated in the range 1561-1477cm^{-1} in the present Ni complex. It was split into two bands; 1602 and 1520 cm^{-1}. Band (II) was found split into two bands; 1473 and 1370cm^{-1}.From the increased double bond character of C=N group and decreased C=S bond character, in addition to the appearance of the δN-H mode at higher wave number, in analogy with C-H vibration, as the increased S-character in the hybridized N-orbitals gives a better overlap with hydrogen atomic orbital[42], 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 *v*Ni-S fundamentals are to be expected in the region 435-333cm^{-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[53].

In our work the Ni-S band was found at 415cm^{-1}, this relatively high value refers to moderate Ni-S bond strength. The band due to νNi-N bond appeared at 588cm^{-1}. Two Ni-Cl stretching bands were observed at 275 and 318cm^{-1} belonging to symmetrical and asymmetrical vibration respectively. Based on the above data the following structure for Ni-complex can be suggested:

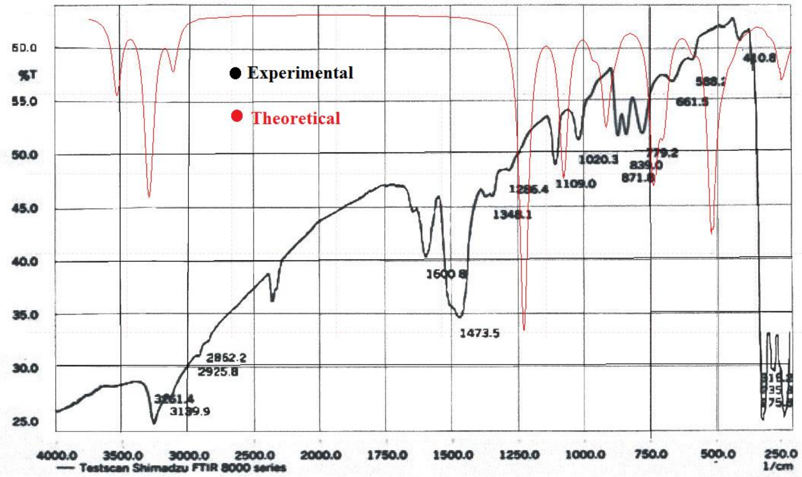
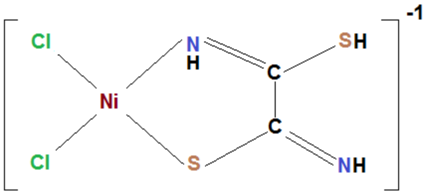


Figure 6: Theoretical and FTIR Spectrum of Ni(DTO)Cl$_2$



Structure-2, Ni7

Table 12 The assignment of the most diagnostic theoretical vibrational frequencies for $Pd(DTO)_2Cl_2$ and $Ni(DTO)_2Cl_2$ at B3YLP/LANL2DZ level

Compounds	N-H	C=S	C=N	M-Cl	M-N	M-S
PD3-DTO-cis-A(N,N)	3542as. 3437s.	1159	-	351as. 345s.	515 673	-
PD2-DTO-cis-A(S,S)	3707as. 3574s.	1429as. 1296s.	1378as. 1297s.	344as. 340s.	-	438as. 366s.
PD5-DTO-trans-A(N,S)	3696as. 3552s.	1269	1466	348as. 336s.	378	328
PD4-DTO-cis-I(S,S)(-2)	3357as. 3353s	1544as. 1290s.	1591as. 1544s.	285as. 271 s.	-	448as. 308s.
PD7-DTO-trans-I(N,S)(-1)	3490as. 3454s.	1310as. 1211s.	1624as. 1580s.	258as. 242 s.	626	366
PD6-DTO-cis-I(N,N)	3535as. 3532s.	1321	1566as. 1530s.	361 as. 376 s.	586as. 616s.	-
Ni2-DTO-cis-A(S,S)	3709 as. 3706 s.	1297	1440as. 1386s.	390as. 383s.	-	353
Ni3-DTO-cis-A(N,N)	3519as. 3518 s.	1076	1258as. 1163s.	383 as. 388 s.	548	-
Ni5-DTO-trans-A(N,S)	3697as. 3541s	1263	1474 1473 (exp)	386,364 318 (exp)	544 588 (exp)	396 411 (ex
Ni4-DTO-cis-I(S,S)(-2)	3357 as. 3354 s.	804	1587as. 1543s.	200 217 290 314	-	331 332 391
Ni6-DTO-cis-I(N,N)	3543as. 3540s.	910	1580as. 1541s.	374 263 413	616 269	-
Ni7-DTO-trans-I(N,S)(-1)	3490as. 3454s.	754	1624as. 1580s	375as. 329s.	626	754

Electronic Spectra and Magnetic Properties

Pd(II) complex of DTO : The theoretical UV-Vis absorption spectra of $Pd(DTO)Cl_2$ calculated using time-dependent at DFT level B3LYP/LANL2DZ/auto=all scrf=(solvent=ethanol, check) with two keys; the first red spectra calculated at td(nstates=12) and the second blue spectra calculated at td(nstates=18). Both gave a similar absorption bands as listed in table 14 and shown in figure 7. The calculated bands helped in explanation of our experimental UV-Vis spectra of the $Pd(DTO)Cl_2$. The theoretical results were in good agreement with the experimental spectra. The ratio of the oscillator strength is expressed as intensity.

Almost all 4-coordinated Pd(II) complexes are diamagnetic and most of them are square planar[54-56]. 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[57]. In our experimental 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-7, showed two well defined bands at 417nm of low intensity and at 309nm of higher intensity. The first band can be considered as d-d transition[58]. The second band suggests that it may be a ligand-Metal charge-transfer LMCT. These data may confirm the previously suggested structure-I, PD5 (sec. 3.2.3). Halder *et. al.*[59] found three bands 310, 410 and 550nm in UV spectra of Pd(II) complexes. The theoretical spectra indicated that the bands above 477nm are due to metal-ligand charge-transfer MLCT. Mishra[60] and others[23,24] observed the d-d transition $A_{1g} \rightarrow A_{2g}$ in Pt(II) planar field around 410nm and charge transfer ${}^1A_{1g} \rightarrow {}^1B_{1g}$ at 390nm. Transition metal complexes usually show three types of electronic bands cover a wide range: d-d (crystal-field) transitions (300-1500nm); charge-transfer transitions (200-500nm) and transitions localized on the ligands. The last are n→π* or π→π* and regularly occur in the ultraviolet region which affected by type of coordination.

Table 13 The assignment of the most diagnostic theoretical vibrational frequencies for $Pd(DTO)_2Cl_2$ and $Ni(DTO)_2Cl_2$ at PM3 level

Compounds	N-H	C=S	C=N	M-Cl	M-N	M-S
PD3-DTO-cis-A(N,N)	3479 as. 3476s.	810	-	579 as. 532 s.	715	-
PD2-DTO-cis-A(S,S)	3506 as. 3418 s.	831	-	578 as. 558 s.	-	468
PD5-DTO-trans-A(N,S)	3463 3402	781	-	574 s. 538 as.	658	451
PD4-DTO-cis-I(S,S)(-2)	3431	-	1780	576 s. 571 as.	-	460
PD7-DTO-trans-I(N,S)(-1)	3467 3399	736	1771 1714	551 as. 534 s.	658	462
PD6-DTO-cis-I(N,N)	3436	918	1640	556 as. 516 s.	629	-
Ni2-DTO-cis-A(S,S)	3507 as. 3423 s.	843	-	646 as. 585 s.	-	441
Ni3-DTO-cis-A(N,N)	3498 as. 3495 s.	984	-	619 as. 556 s.	631	-
Ni5-DTO-trans-A(N,S)	3511 3495	976,811	1226	643 s. 592 as.	621	372,302
Ni4-DTO-cis-I(S,S)(-2)	3483 as. 3482 s.	-	1852	612 600	-	485
Ni6-DTO-cis-I(N,N)	3481	927	1703	620 as. 539 s.	539	-
Ni7-DTO-trans-I(N,S)(-1)	3467 3427	-	1790 1772	600 s. 589 as.	589	483

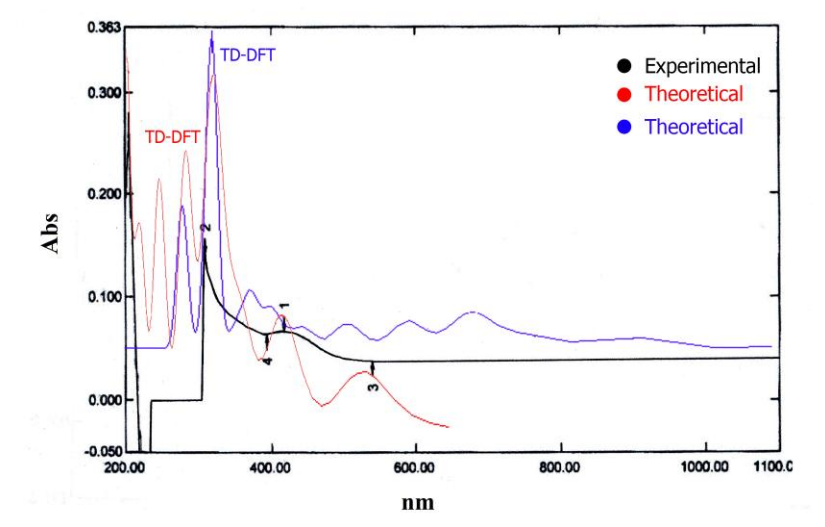


Figure7 Theoretical and electronic spectrum of $Pd(DTO)Cl_2$

Table 14 Theoretical UV-Vis absorption bands Pd(DTO)Cl_2

Band No.	Theoretical bands Band (intensity)	Transitions (HOMO→LUMO)	Experimental
1	781.65(13.79%)	Pd(d), Cl(p_z) →C(p_z), N(p_z), S(p_z)	700
2	766.21(1.15%)		570
3	618.15(29.89%)		480
4	530.78(32.18%)		
5	477.38(93.103%)	Pd(d) → Pd(d)……………... 90%	417
6	425.79(10.35%)	Cl(p_z) →C(p_z), N(p_z), S(p_z) …10%	
7	421.63(63.22%)		
8	376.93(13.39%)	Pd(d), Cl(p_z) → Pd(d)	417
9	366.52(52.87%)	Pd(d), Cl(p_z) → Pd(d) Pd(d), Cl(p_z) →C(p_z), N(p_z), S(p_z)	
10	333.37(39.08%)	Pd(d), → Pd(d)	309
11	320.50(29.89%)	Pd(d), Cl(p_z) → Pd(d)	309
12	301.57(100.0%)	N(p_z), S(p_z), Cl(p_z) → N(p_z), S(p_z), Cl(p_z)	

Ni(II) Complex of DTO : The theoretical UV-Vis absorption spectra of Ni(DTO)Cl_2 calculated using time-dependent at DFT level B3LYP/LANL2DZ/auto=all scrf=(solvent=ethanol, check). The red spectrum calculated using these keys: td(nstates=12), Pop=Reg. It gave absorption bands listed in table 15 and shown in figure 8. The blue spectrum was computed using time-dependent at DFT level with B3LYP functional, LANL2DZ for Ni, 6-311+G(d,p) basis set for H, C, N, S, and Cl in the G09W program package. The calculated bands helped in explanation of our experimental UV-Vis spectra of the Pd(DTO)Cl_2. The theoretical results were in good agreement with the experimental spectra. The ratio of the oscillator strength is expressed as intensity.

The theoretical and electronic spectrum of Ni(II) complex, figure 8, shows two distinguishable weak d-d transition bands in octahedral field, the first one appeared as a broad band at 630nm (15873 cm^{-1}), while the second band appeared as a shoulder at 375nm (26666cm^{-1}). These bands can be suggested as v_2 ($^3A_2g \rightarrow ^3T_1g(F)$) and v_3 ($^3A_2g \rightarrow ^3T_1g(p)$), respectively in octahedral field[61,62].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 ν_3/ν_2 was calculated and found to be (1.67) this value came in the range of distorted octahedral complexes (1.66-1.78)[61,63]. These findings came in accordance with the previously suggested structure-II, Ni7. A recent computational study on UV-Vis using DT-DFT on Ni(II) Schiff base gave several absorption bands i.e. 716, 516, 407 and 550,409, 356 for two Ni(II) complexes[64] were very close to our results.

Table 15: Theoretical UV-Vis absorption bands Ni(DTO)Cl_2

Band No.	Theoretical bands Band (intensity)	Transitions (HOMO→LUMO)	Experimental
1	665.68(0.19%)	Ni(d) → Ni(d), d-d	630
2	646.17(0.00%)	Ni(d), Cl(p_z) → Ni(d), LMCT	
3	595.19 (0.00%)		
4	303.67 (0.00%)		
5	504.23 (14.5%)	Cl(p_z) → Ni(d), LMCT	500
6	322.79 (27.0%)		315
7	393.77(6.50%)	Ni(d), Cl(p_z) → N(p_z), C(p_z), S(p_z)	430
8	350.25 (1.50%)		
9	376.81(0.19%)	Ni(d), Cl(p_y,p_z) → N(p_z), C(p_z), S(p_z)	375
10	370.20 (100%)		
10	311.56 (0.00%)	Ni(d), Cl(p_x) → N(p_z), C(p_z), S(p_z)	
12	293.96 (14.5%)	Ni(d), Cl(p_x), C(p_z) → N(p_z), C(p_z), S(p_z)	

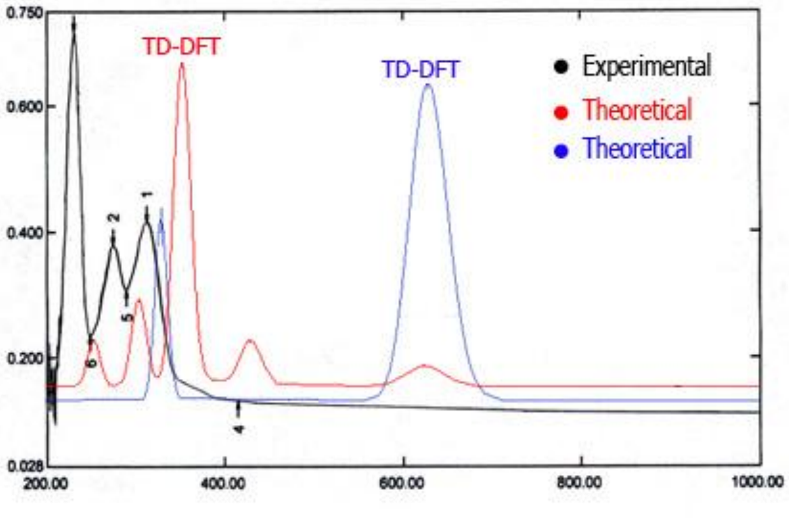


Figure 8: Theoretical and electronic spectrum of Ni(DTO)Cl_2

APPLICATIONS

The results of the vibrational calculations were in good agreement with those obtained from the energy calculations and the experimental UV and IR study came in accordance with the theoretical calculation. So this method is more useful.

CONCLUSIONS

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

Pd(II) Complexes :

1. The DFT and ab initio MP2/DGDZVP//RB3LYP/LANL2DZ/auto=all, semi-empirical PM3, PM7 and DFT energies including zero point energy, ZPE calculations, B3YLP/DGDZVP //B3YLP/ LANL2DZ/ auto=all were used for the calculation of the total relative energies for Pd and Ni complexes. They showed that PD1-PhCN-trans isomer was more stable than PD1-PhCN-cis for $Pd(PhCN)_2Cl_2$ complexes by 4.196 (MP2) or 5.741 (DFT) kcal/mol. The experimental results of FTIR also showed that the PD1-trans was the more stable expected *isomer.*

2. For Pd(DMSO)2Cl2, the MP2/QZVP//B3YLP/LANL2DZ/auto=all showed that PD9-DMSO-trans(S,S) was the more stable than the other three isomers. This results confirmed the experimental results of FTIR which showed that the PD9-DMSO-trans(S,S) was the most stable isomer.

3. Regarding the complexes of Pd(DTO)Cl_2, 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 preference of PD5-trans-A(N,S) (0.00) over PD12-trans-I(N,S) was by (27.73 kcal/mol). The PD-5-trans-A(N,S) was more stable than PD6-cis-I(N,N) among the total amide and imide isomers by 21.9 kcal/mol due to π-back bonding of sulfur atoms in the trans configuration A(N,S). For the results of experimental values of vibrational spectra we find the PD5-trans-A(N,S) was the most stable. In solution, the experimental vibrational data also showed that the PD5-trans-A(N,S) conformer was the most stable expected isomer. The TD-DFT UV spectra were identical to the experimental spectrum and helped in assigning the type of the bands.

Ni(II) Complexes:

4. The DFT and *ab initio* calculation showed that Ni1- trans isomer was more stable than Ni1-cis for $Ni(PhCN)_2Cl_2$ complexes by 8.130 (MP2) or 8.499 (DFT) kcal/mol.

5. Concerning the $Ni(DMSO)_2Cl_2$ complexes, the *ab initio* calculations showed that Ni11-DMSO-trans-(O,O) conformer was the most stable structure among the others.

6. Among amide and imide complexes, Ni5-trans-A(N,S) was the most stable complexes. It was also found that the trans form i.e. Ni5-trans-A(N,S) was more stable than the cis form i.e. Ni8-cis-A(N,S) by 25.368 kcal/mol. In solution the experimental vibrational data also showed that the cationic Ni7-trans-I (N,S) conformer was the most stable expected isomer. The TD-DFT UV spectra were similar to the experimental spectrum and assisted in assigning the type of the bands.

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