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PLATINUM(II) AND PALLADIUM(II) THIOLATE COMPLEXES; SYNTHESIS, CHARACTERIZATION, CRYSTAL STRUCTURE, DFT, HIRSHFELD SURFACE ANALYSIS AND ANTICANCER STUDIES

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ABSTRACT. The synthesis and characterization of platinum(II) and palladium(II) mixed ligand complexes, $[M(mtzS)_2(dppm)]$ (M = Pt or Pd), have been described. These complexes were synthesized through a one-pot reaction involving K_2MCl_4, KmtzS (prepared from HmtzS and KOH), and dppm. The prepared complexes **1** and **2** have been characterized by using various analytical techniques including conductivity measurements, IR spectroscopy, UV-Vis spectroscopy, ^{31}P and ^{1}H NMR spectroscopy and **1** by X-ray crystallographic studies. The in *vitro* anti-cancer activity of complexes **1** and **2** against breast cancer cells (MCF7 cell line), was evaluated using the MTT assay showed a moderate activity with an IC_{50} value of 27.59 µg/ml for **1** and 28.82 µg/ml for **2**. Additionally, the ligands and complexes underwent full geometry optimization using density functional theory (DFT). The calculated geometric and spectral data were found to be in good agreement with the experimental results. Theoretical calculations of molecular orbitals (HOMO-LUMO) and their energies suggested the occurrence of charge transfer within the complexes.

KEY WORDS: Platinum(II), Palladium(II), Thiolate, Diphosphine, X-ray crystallography

INTRODUCTION

The coordination chemistry of heterocyclic compounds become more interesting in the last decade [1-4]. Heterocyclic thiones which are recognized for their important exo-cyclic thione group have formed various metal complexes with different metals through either S or N atoms [5-9]. Thione groups (C=S) are mostly known for their contribution toward metal complexes due to their special pi-character. The pi-bonding in M-S=C contribution is 50-70% [10]. It is well known that thione groups to exhibit rich electron density, therefore it have the potential to form multiple coordination modes (Figure 1) [1, 9, 10]. Moreover, the bioactivity of sulfur-containing compounds especially thiones has interested more researchers [1].

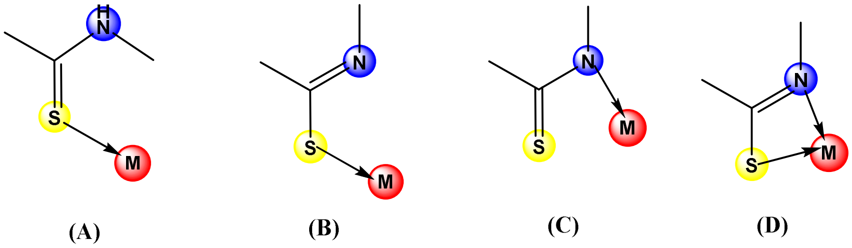

Figure 1. Some of the coordination modes of thione, and thiolate-metal complexes.

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2-Mercapto-5-methyl-1,3,4-thiadiazole (HmtzS) complexes have attracted several of research groups [11, 12]. This ligand is ambient, the non-deprotonated form can act as a monodentate bound to metal through the thione group) (Figure 1A) as in $[Pd(HmtzS)_4]Cl_2$ [12]. Bharati and co-workers [11] reported the synthesis of several of complexes in which the deprotonated thiol form adopted three different coordination modes; ionically or covalently bounded through the sulfur atom (Figure 1B), or through the deprotonating thiadiazole ring nitrogen adjacent to the thiol sulfur (Figure 1C) and as N,S chelating bidentate bonded through the thiolate sulfur and the thiadiazole ring nitrogen adjacent to it, forming a four membered chelate ring (Figure 1D).

Mixed ligand mercury(II) complexes of 2-meracpto-5-methyl-1,3,4-thiazdiazole (HmtzS) and phosphines or diamines have been recently reported [8]. The $mtzS^-$ ligand coordinated through the sulfur atom of thiol group. Platinum(II) or palladium(II) thione complexes have shown high anticancer properties [5, 6]. Literature has extensively reported mixed ligand complexes of palladium(II) thiols and tertiary phosphine ligands [13-15]. Also synthesis and characterization of palladium(II) mixed ligand complexes of the types $[Pd(mtzS)_2(dppf)]$, dppf = bis(diphenylphosphio)ferrocene and $[Pd(mtzS)_2(Ph_2P(CH_2)_nPPh_2)]$ n = 2-4 have been reported [5] as single linkage sulfur bounded (thiolate) isomers, except for n = 3 dppp for which a mixture of sulfur- and nitrogen- bounded linkage isomers were obtained. Unfortunately, palladium complex for n = 1, bis(diphenylphosphino)methane (dppm) did not prepared

As part of our interests in sulfur containing ligands [5, 7, 16-21], we herein report synthesis of paltnium(II) and palladium(II) mixed ligand complexes of 2-mercapto-5-methyl-1,3,4-thiadiazole (HmtzS) and bis(diphenylphoshino)methane (dppm). The prepared complexes were characterized by different spectroscopic techniques including x-ray crystallography for $[Pt(mtzS)_2(dppm)]$ **1**. Furthermore, the prepared complexes were studied for their anticancer activities and theoretical investigations.

EXPERIMENTAL

General methods and apparatus

All reactions were carried out in air using standard bench reagents. K_2PtCl_4, K_2PdCl_4, 2-mercapto-5-methyl-1,3,4-thiadiazol (HmtzS) and bis(diphenylphosphino)methane (dppm) were commercial products and used without further purifications**.** Molar electrical conductivity measurements were carried out using a Meter CON 700 Bench top conductivity meter. The NMR spectra were recorded at the University of Basra, College of Education, Iraq, using a Bruker 400 MHz ultra-shield ii DMSO-d_6 solvent. IR spectra were recorded on a Shimadzu CORP-A221375003225 spectrophotometer using KBr discs in the 400–4000 cm^{-1} range. The UV–Vis. spectra of the free ligands and their complexes were obtained in the DMSO solvent with a concentration of (10^{-3} M) using Shimadzu spectrophotometer (AEUV1609 (UK) CO.) within the 400–4000 cm^{-1} range. Melting points were measured on Melting Point-MPD-100 Pixel Technology CO., Limited melting point apparatus and were uncorrected. The cytotoxic effects of complexes **1** and **2** against human breast cancer cell (MCF7) were studied by MTT assay method.

*Synthesis of $[Pt(mtzS)_2(dppm)]$ (**1**)*

A solution of 5-methyl-1,3,4-thiadiazole-2-thiol (HmtzS) (0.0264 g, 0.2 mmol) and KOH (0.0 1 g, 0.2 mmol) in methanol (20 mL) was added to the a solution of K_2PtCl_4 (0.0326 g, 0.1 mmol) in water (5 mL) in mole ratio (1:2) of (M:L). The reaction mixture was heated under reflux for 2 h, during which the color of the solution changed to orange. A solution of bis(diphenylphosphino)methane (dppm) (0.0384 g, 0.1 mmol) in CH_2Cl_2 (5 mL) was added. The mixture of was stirred overnight at room temperature, to afford a clear yellow solution. The solution was filtrated off to remove any suspended particles to get good crystals and the filtrate was set aside for slow evaporation of solvent to give after one week yellow-needles crystals.

Yellow needles, 0.0630 g, 75% yield, IR (KBr): 3049 w, 2929 w, 1435 s, 1105 m, 736 s, 505 m, 328 s, and 278 s cm^{-1}. UV-Visible: (349 nm), (310 nm). Molar conductivity (DMSO, 10^{-3} M): 3.1 (ohm^{-1}cm^{2}mol^{-1}). ^{31}P-{^{1}H-NMR (DMSO–d$_6$, δppm): -48.17 (s, J$_{Pt-P}$ 2632 Hz). ^{1}H-{^{31}P}NMR (DMSO–d$_6$, δppm): 2.37(s, 6H, CH$_3$ -mtzS), 4.22 (s, 2H, CH$_2$ -dppm), 7.02–7.99 (m, 20H, H-Ph, dppm). m.p. (208-210 °C).

Synthesis of [Pd(mtzS)$_2$(dppm)] (2)

Complex (**2**) was prepared and isolated using a method similar to that used for (**1**) an orange powder. Orange color, 0.0432 g, 57% yield. IR (KBr): 3049 w, 2945 w, 1436 s, 1101 m, 731 s, 505 m, 308 s, and 327 m cm^{-1}. UV-Visible: (264 nm), (294 nm), (313 nm). Molar conductivity (DMSO, 10^{-3} M): 4.9 (ohm^{-1}cm^{2}mol^{-1}). ^{31}P-{^{1}H}NMR (DMSO–d$_6$, δ ppm): -52.28. ^{1}H-{^{31}P} NMR (DMSO–d$_6$' δppm): 2.45(s, 6H, CH$_3$ -mtzS), 4.98 (s, 2H, CH$_2$ -dppm), 7.14–8.02 (m, 20H, H-Ph, dppm). m.p. (189-191°C).

Single X-ray crystal structure of [Pt(mtzS)$_2$(dppm)] (1)

Yellow needle crystals suitable for X-ray crystallographic study were obtained by slow evaporation of CH_2Cl_2 solution. Suitable crystal was mounted on glass fibers and all geometric and intensity data were taken from these samples using a Bruker SMART APEX CCD diffractometer using graphite-monochromatic Mo-K radiation **(**ν = 0.71073 Å**)** at 293 ±2 K. Absorption corrections were made using the OLEX2 software package [22]. All structures were solved by direct methods with SHELXT [23] and refined using full-matrix least-square routines against F2 with Diamond. Non-hydrogen atoms were refined with anisotropic displacement parameters. Table 1 shows these data.

Table 1. Crystal and structure refinement data of complex **1**.

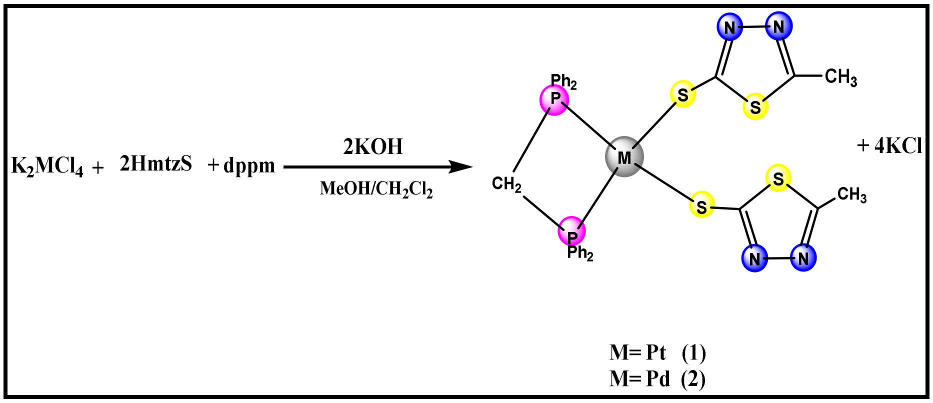
Crystal data	
Deposition No. Chemical formula ρcalcg/cm3	2248175 $C_{31}H_{28}N_4P_2PtS_4$ 1.713
μ/mm^{-1}	4.680
Formula weight	841.84
Colour	yellow
Size/mm^3	0.40×0.24×0.08
T/K	293(2)
Crystal system	monoclinic
Space group	*P21/n*
a/Å	8.4552(7)
b/Å	46.093(3)
c/Å	9.3212(8)
α/°	90
β/°	115.997(6)
γ/°	90
Volume/Å^3	3265.1(5)
Z	4
F(000)	1656.0
Wavelength/Å	0.71073
Radiation type	Mo K$_a$

2θ range for data collection/°	1.768 to 39.016
Index ranges	$-7 \leq h \leq 7$, $-40 \leq k \leq 42$, $-8 \leq l \leq 8$
Reflections collected	9503
Independent reflections	2803 [Rint = 0.0655, Rsigma = 0.0432]
Data/restraints/parameters	2803/0/381
Largest peak	0.75
Deepest hole	-0.30
Goodness-of-fit on F2	1.096
Final R indexes [I>=2σ (I)]	R1 = 0.0276, wR2 = 0.0670

RESULTS AND DISCUSSION

*Synthesis of [M(mtzS)$_2$dppm] (**1**) and (**2**)*

We have previously been developed three-steps synthesis of diphosphine-thionate complexes [ML$_2$(diphosphine)] [16, 17, 24-26]. This involves the treatment of thiol LH with palladium(II) or platinum(II) precursors to give complexes of the type [MCl$_2$(LH)$_2$]. These can be converted to [ML$_2$] by treatment with base, which in turn is converted to the final product on treatment with diphosphine. This method was only partially successful leading to a mixture of products. Then we used another synthetic route to synthesize the desired products by treatment of [MCl$_2$(diphosphine)] with two equivalents of potassium thiolates which afford clean products [5]. Now we developed a one-pot synthesis of **1** and **2** by treatment of K$_2$MCl$_4$ (M = Pt or Pd) with two equivalents of KmtzS (prepared in situ from HmtzS and KOH) followed by one equivalent of dppm to afford [Pt(mtzS)$_2$dppm] (**1**) and [Pd(mtzS)$_2$dppm] (**2**) in 75 and 57% yield ,respectively (Scheme 1).



Scheme 1. Synthesis of complexes **1** and **2**.

*Characterization of [M(mtzS)$_2$dppm] (**1**) and (**2**)*

The newly prepared complexes **1** and **2** were characterized based on spectroscopic and analytical data. The IR spectra of complexes **1** and **2** showed no ν(SH) band which typically appears within the 2600-2500 cm^{-1} range [5] indicating the deprotonating of the HmtzS ligand. The strong absorption bands appeared in complexes (**1**), (**2**) within 1108-1101 and 736-731 cm^{-1} ranges, attributed to ν(N-N) and ν(C-S) [5, 27]. Furthermore, the spectra exhibited two distinctive bands of phosphine at 1435 and 505 cm^{-1} attributed to ν(P–Ph) and ν(P–C), respectively. While the IR spectra are less informative, the NMR spectra are more informative. The ^{31}P-$\{^{1}H\}$-NMR spectra of **1** and **2** each showed a single phosphorus resonance at δ_P = -48.17 and -52.26 ppm, respectively indicating a single isomer formation for each. The negative chemical shifts indicate that dppm behaves as chelate in both complexes [28, 29]. The small phosphorus-platinum coupling constant for [Pt(mtzS)$_2$dppm] (**1**) of 2632 Hz as compared to [PtCl$_2$(dppm)] ($J_{Pt\text{-}P}$ 3083 Hz) [30] suggests the ligand mtzS bind through the sulfur atom. The ^{1}H-$\{^{31}P\}$-NMR spectra were as expected each displaying multiples between δ 7.02-7.99 and 8.02-7.02 ppm assigned to the phenyl protons, a singlet at δ 4.22 and 4.96 ppm assigned to the aromatic and methylene protons of dppm ligands respectively and a singlet at δ 2.36 and 2.45 ppm assigned to the methyl group of the mtzS ligand. Clearly, ^{31}P, and ^{1}H-NMR spectra indicated that two mtzS and one dppm ligands are incorporated in each complex. The low molar conductivity 3.1 and 4.1 $ohm^{-1}cm^{2}mol^{-1}$ (for10^{-3} M in DMSO) and negative $AgNO_3$ test indicate a non-electrolyte behavior of complexes **1** and **2** and suggest that they are neutral.

The electronic spectra of free ligands (HmtzS) and (dppm) exhibited two bands in the 249-319 nm range attributed to π-π* and n-π* transitions of the aromatic ring [31, 32]. The bands within 349-264 nm range in the spectra of complexes **1** and 2 were assigned to C.T. transitions, respectively. These electronic spectral data, indicated that both complexes **1** and **2** pose square planner geometry [17, 27].

X-ray crystal structure of [Pt(mtzS)$_2$(dppm)] (1)

In order to ascertain the precise arrangement of ligands around the platinum(II) center and confirm thiodiazole binding mod in this complex, a crystallographic study was carried out on [Pt(mtzS)$_2$(dppm)] (**1**), the results of which are displayed in Figure 2 and Tables 1 and 2. Bond angles, bond lengths and hydrogen bonding for (**1**) are displayed in Table 2. The Pt(II) is coordinated to two phosphorus atoms of the dppm ligand and two sulfur atoms of thiodiazole adopting square planar geometry. The Pt-P bond lengths range [2.2571(17) and 2.2751(18) Å] and Pt-S bond lengths range [2.3527(18) and 2.3539(18) Å are within the expected range found in related complexes [33-35]. The diphosphine bit angle of 74.22(6) is slightly larger than those found in [Pt(tsac)$_2$(dppm)] of 73.82(5° [36] while the S-Pt-S angle of 80.42(7)° being smaller than that found in [Pt(tsac)$_2$(dppm)] of 86.24(4)°. The C(21)- H(21)…. S(31), C(12)- H(12)**….** S(21), C(6)- H(6B**)….**S(42), and C(6)- H(6C)**….**N(43) intramolecular hydrogen bonds stabilize the square planner crystal structure of **1** (Table 2).

DFT studies

The Gaussian 09 package's B3LYP correlation function computation method has been used to further understand the electronic structure of the ligands (dppm), (HmtzS) and complexes **1** and **2**, The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were calculated for both ligands and complexes. The E_{HOMO}, E_{LUMO}, and ΔE energy gaps of (HmtzS), (dppm) and complexes **1** and **2** are exhibited in Table 3 and Figure 3. The energy gap ΔE of the free bis(diphenylphosphino)methane (dppm) and (HmtzS) ligands are 1.0680 and 6.2160 eV respectively, while that of complexes **1** and **2** are 0.6525 and -3.058 eV, respectively. The energy gap that splits the HOMO and LUMO orbitals is associated with the reactivity and stability of compounds. Compounds with a small energy gap (ΔE) are more reactive than ones with a big energy gap (ΔE). In addition, compound with a high-energy gap is more stable than one with a low-energy gap. Calculations illustrated that the ligand dppm has a lower energy gap (1.0680 eV) than that of (HmtzS) (6.2160 eV), which means that dppm is more reactive than

HmtzS, towards metal ions [37]. In comparison with dppm and (HmtzS) ligand. The synthesized Pt(II) complex **1** is higher energy gap (0.6525 eV) than Pd(II) complex **2** (-3.058 eV), then complex Pt(II) is more stable that complex Pd(II) [31].

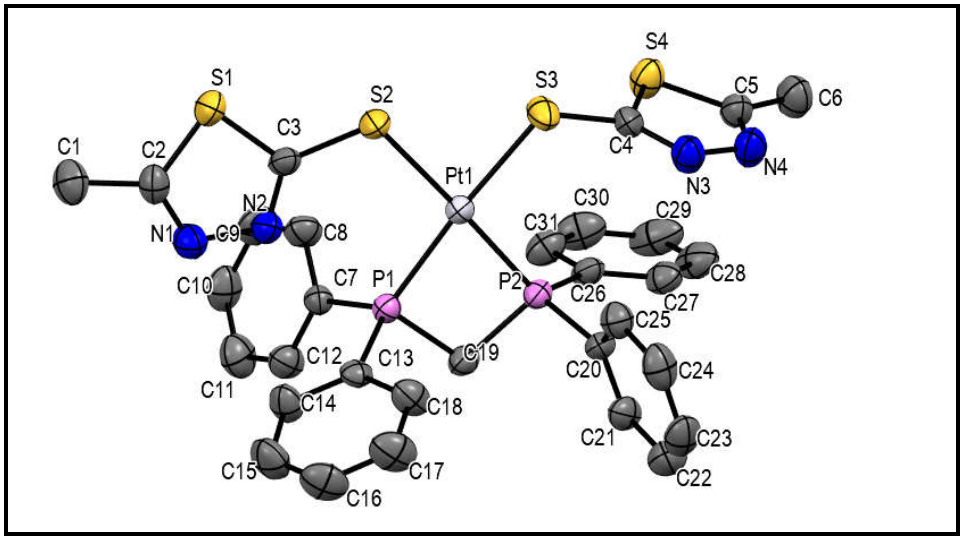


Figure 2. Single-crystal X-ray molecular structure of complex **1**. Ellipsoids with a 20% of probability, (H atoms are omitted for clarity).

Table 2. Selected bond lengths (Å), bond angles (°) and hydrogen bonding of the complex.

Atoms	Bond length	Atoms	Bond angle
Pt1-P1	2.2751(18)	P1- Pt1-S2	103.62(6)
Pt1-P2	2.2571(17)	P1- Pt1-S3	175.79(6)
Pt1-S2	2.3539(18)	P2-Pt1-P1	74.22(6)
Pt1-S3	2.3527(19)	P2 -Pt1-S2	177.72(7)
P1-C13	1.819(6)	P2- Pt1-S3	101.76(6)
P1-C19	1.863(6)	S3- Pt1-S2	80.42(7)
P1-C7	1.816(7)	C13 -P1-Pt1	120.1(2)
P2-C26	1.825(7)	C19- P1-Pt1	94.4(2)
P2-C19	1.842(7)	C7- P1-Pt1	120.2(2)
P2-C20	1.804(6)	C13- P1-C19	102.5(3)
S-C	1.702(7)- 1.749(7)	C7- P1-C19	102.0(3)
N-C	1.268(9)- 1.308(8)	C7- P1-C13	111.6(3)

Hydrogen-bond geometry (Å, °)

Hydrogen bonding	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C(21)- H(21)**….** S(31)	0.93	3.00	3.774(9)	141.6
C(12)- H(12)**….** S(21)	0.93	2.97	3.834(8)	155.1
C(6)- H(6B)**….**S(42)	0.96	3.02	3.837(8)	144.3
C(6)- H(6C)**….**N(43)	0.96	2.57	3.388(10)	143.5

Symmetry code:1-1+X,+Y,+Z; 2-1/2+X,3/2-Y,-1/2+Z; 31/2+X,3/2-Y,1/2+Z.

We used the natural bond orbital (NBO) approach to calculate the atomic charge distribution on each complex atom. From the NBO analysis, we can predict electron delocalization, atomic charge distribution, and intra-atomic interaction of atoms within a compound [38]. The calculated natural atomic charges of ligands and complexes **1** and **2** are listed in Figure 4. The natural charge on Pt(II) and Pd(II) ions (+2.0 e) changed lowered on complex formation to (-0.45975 and -0.58567 e) respectively, showing that electron transfer occurred from (3s, 3p) orbitals of S and P atoms to Pt(II) and Pd(II) (5d and 4d) orbitals of central metal atoms. However, the atomic charge on the sulfur atom change from (S7(0.02577e) in the free ligand to a higher positive charge (S7(0.13344),S8(0.18627),S6(0.09777)and S7(0.28897) in complexes **1** and **2** respectively, this is an evidence that the sulfur atom of (HmtzS) ligand is more strongly bounded to Pd(II) and Pt(II) in complexes [5, 39].

Table 3. HOMO-LUMO orbital energies (eV) and NBO charges (e) of dppm, (HmtzS) ligands and complexes **1** and **2**.

Parameter	dppm		HmtzS		Complex **1**	Complex **2**	
E_{HOMO}	-5.2756		-7.603		-4.8530	-1.4169	
E_{LUMO}	-4.2076		-1.387		-4.2005	-4.4757	
ΔE	1.0680		6.2160		0.6525	-3.058	
The NBO charge of dppm, HmtzS ligands and complexes **1** and **2**							
Atom	dppm	Atom	HmtzS	Atom	Complex (**1**)	Atom	Complex (**2**)
P45	0.04408	N1	-0.33040	Pt1	-0.45975	Pd70	-0.58567
P46	0.31114	N2	-0.21712	P21	0.96707	P20	1.03611
		S5	0.37280	P23	1.12661	P22	1.12528
		S7	0.02577	S5	1.94969	S6	0.09777
				S6	0.42062	S7	0.28897
				S7	0.13344	S4	1.95982
				S8	0.18627	S5	0.43579
				N2	-0.28754	N1	-0.31117
				N3	-0.86582	N2	-0.82010
				N4	-0.78822	N3	-0.77237
				N59	-0.31051	N58	-0.30722

Hirshfeld surfaces analysis (HAS)

The Hirshfeld surface analyses (HSA) and the fingerprints of complex **1** were attained using Crystal Explorer 21.5 program.22. Surfaces that were mapped through d_{norm}, shape index, and curvature are presented in (Figure 5) the shape index and curvedness were mapped across ranges of -1.0000 to 1.0000 and -4.0000 to 0.4000, respectively, while the d_{norm} surface has been mapped across a range of -0.0490 to 1.3232. As demonstrated in (Figure 5), the 2D fingerprint plots disclose that the chief intermolecular interactions in complex (**1**) are C…C, H...C/C...H, C...S/S...C, H…H, H...N/N...H, N...C/C…N, Pt...H/H...Pt., S…N/N…S, and S…H/H…S. The highest contribution to the overall Hirshfeld surface occurs due to H...H close contacts with 44.9%. The percentages of C…C, H...C/C...H, C...S/S...H, H...N/N...H, N...C/C…N, Pt...H/H...Pt, S…N/N…S, and S…H/H…S. interactions are 0.2, 19.9, 1.5, 9.4, 0.5, 1.1, 0.8, and 21.7, % of the complex surface, respectively [40]. The d_{norm} Hirshfeld surface shows red, blue and white spots, which indicate the presence of N-H…H, H…H, and C-H...H, intermolecular interaction (respectively) in the crystal structure of complex **1**. The shape index of Hirshfeld surfaces with blue triangles denoting convex portions of the compound inside the surface and red triangles denoting concave regions above the surface. As a result of the stacking compound's phenyl carbon atoms can be used to investigate $\pi \cdots \pi$ interactions [41]. The existence of interaction in the complex is also shown by green flat areas on the curvedness (HS) [42].

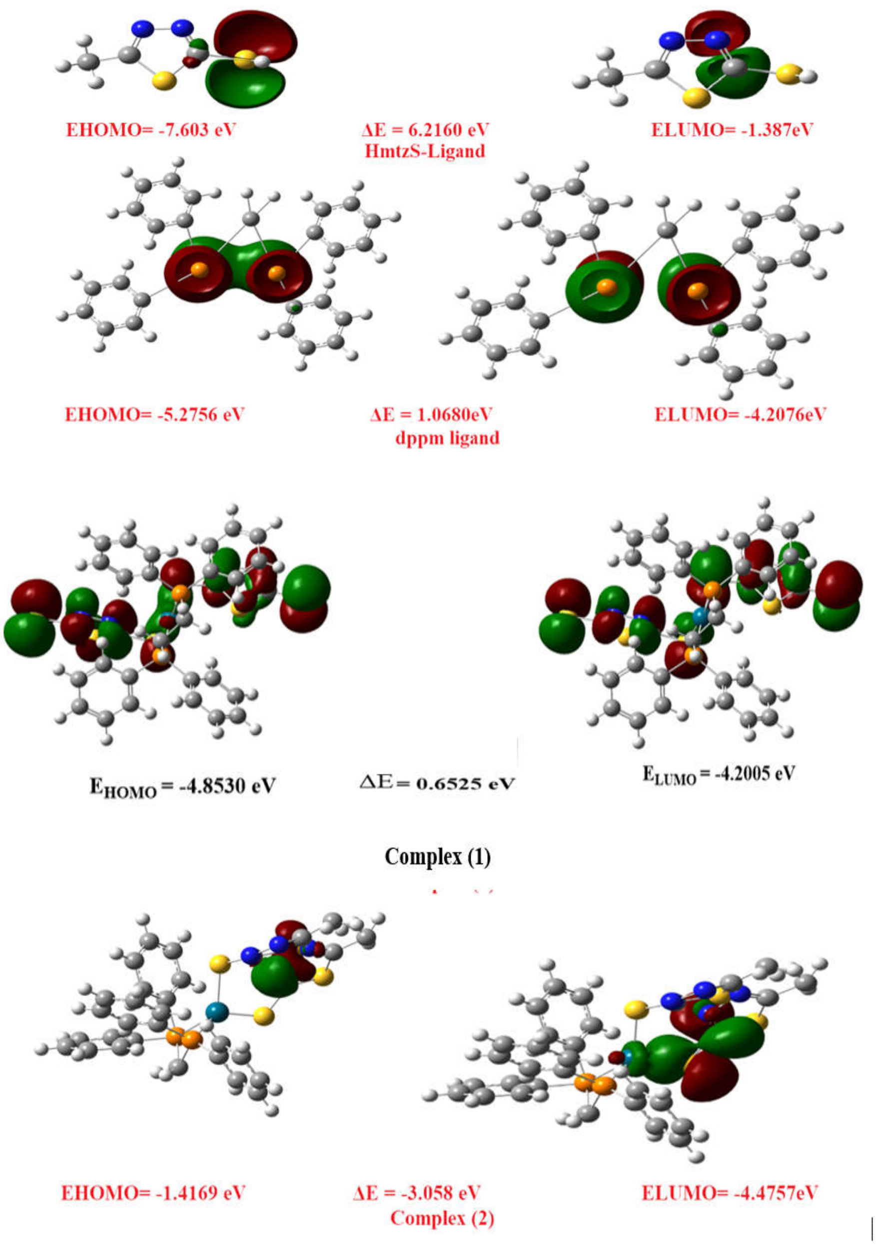
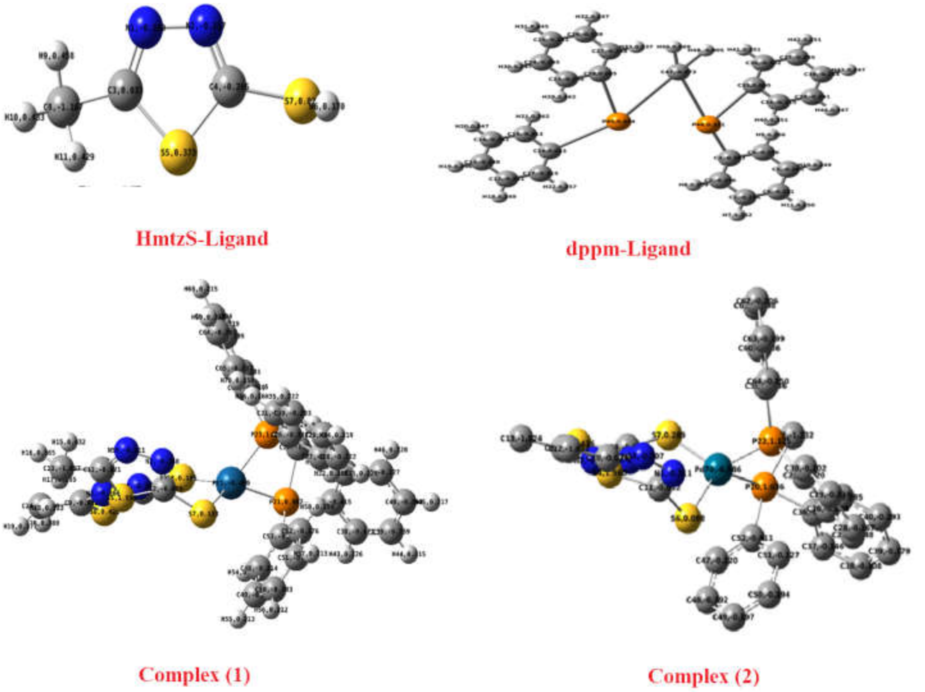


Figure 3. Surface plots of HOMO and LUMO orbitals of dppm, HmtzS ligands and complexes **1** and **2**.



HmtzS-Ligand

dppm-Ligand

Complex (1)

Complex (2)

Figure 4. NBO Charges (e) of HmtzS, dppm ligands and complexes **1** and **2**.

*Cytotoxicity study of complexes **1** and **2***

Using the MTT assay, the cytotoxicity of **1** and **2** was evaluated against the breast cancer (MCF-7 cancer cells) line to determine the IC_{50} value (IC_{50} is the concentration that inhibits 50% of the proliferation of MCF-7 cells) [43]. The results were potted in Table 4. From these data, the following characteristics were noted. The complex with a lower IC_{50} value is more active compound and has better anticancer activity. Complexes **1** and **2** exposed moderate activity to MCF-7 cell lines with an IC_{50} value of 27.59 µg/mL 28.82 µg/mL respectively in comparison with the published value of IC_{50} of the anticancer drug (*cis*platin) *(* IC_{50} = 24.67-94.00 µg/mL at 6.25, 12.5, 25.50 and 100 µg/mL concentrations incubated for 72 hours on MCF-7 cells) [27, 44].

Table 4. Percentage cell viability, concentration (µg/mL) and IC_{50} values of complexes 1 and 2 against MCF7 cell line.

Complexes	Concentrations (µg/mL)/ Relative Cell Viability (%)							Control	IC_{50}
	500	250	125	62.5	31.25	15.625	7.8125		
[Pt(mtzS)$_2$(dppm)] (**1**)	14.1569	33.6273	45.79837	47.0423	58.35185	67.67136	93.3316	100	27.59
Pd(mtzS)$_2$(dppm)] (**2**)	11.79742	28.02275	38.16531	37.53525	50.29321	79.72614	95.27633	100	28.82

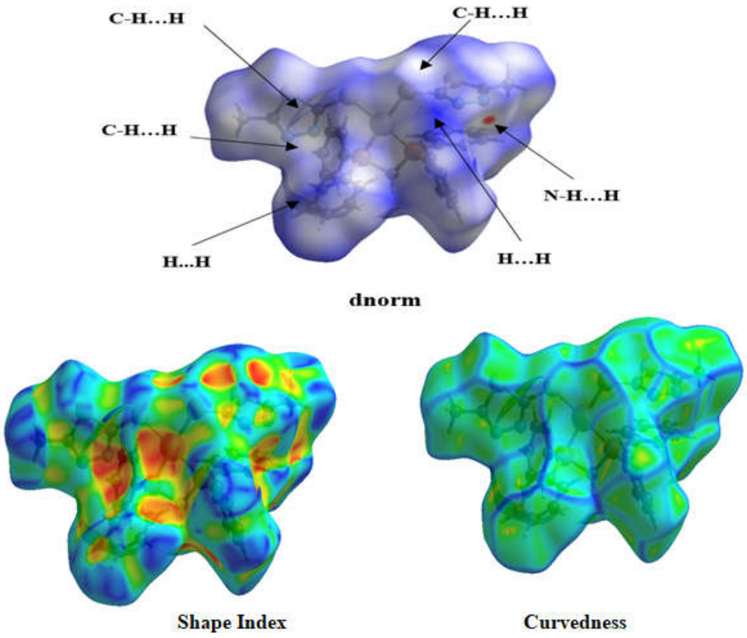


Figure 5. Hirshfeld surfaces mapped with d_{norm}, shape index, and curvedness of complex **1**.

CONCLUSION

In this work, that palladium(II) and platinum(II) complexes, [Pd(mtzS)$_2$(dppm)] (**1**) and [Pt(mtzS)$_2$(dppm)] (**2**) have been shown, in good yield via a one-pot reaction involving K_2MCl_4, KmtzS, and bis(diphenylphosphino)methane (dppm). Spectroscopic data and the single X-ray crystal of complex **1** showed a square planner arrangement in which dppm ligand bonded in a bidentate chelate fashion, while the two mtzs ligands bonded in a monodentate fashion through the sulfur atom. Complexes **1** and **2** showed good cytotoxicity against Breast cancer (MCF-7) cell lines with IC_{50} Mention at which concentration of the complexes **1** and **2** have showed that value within (27.59-28.82) µg/mL range.

Supplementary data

CCDC (2244269) contain the supplementary crystallographic data for complex **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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