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SYNTHESIS, CHARACTERIZATION, BIOLOGICAL ACTIVITY, DFT AND HIRSHFELD SURFACE STUDIES OF Pd(II) AND Pt(II)-1-CYCLOHEXYL-3-PHENYLTHIOUREA AND AMINE LIGANDS

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ABSTRACT. A series of mixed ligand complexes of Pd(II) and Pt(II) of 1-cyclohexyl-3-phenylthiourea and diamine ligands {2,2'-bipyridyl (Bipy) and 1,10-phenanthroline (Phen)} were prepared and characterized by FT-IR, NMR spectroscopy, molar conductivity. Density functional theory (DFT) calculations and biological activity were carried out on the prepared complexes. In vitro antimicrobial activity was investigated against three pathogenic bacteria (*Staphylococcus aureus*, *Bacillus cereus* and *Escherichia coli*). The most active compound **6** was found more active than free ligand and other complexes. The crystal structure of the free ligand was determined by X-ray diffraction (XRD) analysis. Hirshfeld surface analysis was executed for the free ligand by finding and exploring the interatomic contacts that are important considering the supramolecular assembly of the crystal. The mechanical stability or response is prophesied by voids analysis. The supramolecular assembly is significantly uncovered by intermolecular interaction energies calculations performed at of the B3LYP/6-31G(d,p) electron density level.

KEY WORDS: Thiourea, Diamine, Crystal structure, DFT, Hirshfeld surface

INTRODUCTION

The coordination chemistry of thiourea has been attracting a lot of attention in the last decade due to its valuable applications. For example, thiourea metal complexes have been used as pharmaceutical agents, vulcanization accelerators, and herbicides [1-5]. Color complexes have been extremely useful in analytical chemistry [6]. Moreover, the thiourea group (-NH-CS-NH-) has played an essential role in metal complexes geometry. Many complex compounds that these derivatives formed with transition metal ions (i.e., Cu(II), Ni(II), Co(II), Pd(II) and Pt(II)) were used in different applications [2, 4-15]. For instance, it has been reported that thiourea can be coordinated through the thiolato sulfur as mono-anionic monodentate or bidentate complexes [7-10]. Also, it can be coordinated in a neutral form through the thione sulfur atom or as a doubly deprotonated di-anion form through NS atoms [11-14]. Furthermore, thiourea can form bridging compounds through their S and N atoms resulting in a di-nuclear complex. Other possibilities include metal-metal bond formation.

When bidentate ligand is introduced to the thiourea complexes, different geometries can be expected. For instance, in our previous work, tertiary phosphine ligands have resulted in the formation of the di-anion thiourea complex [15]. On the other hand, thiourea diamine ligands such as bipyridyl or phenanthroline have been poorly investigated in the literature. By keeping all the above facts in mind, this paper describes, the synthesis of 1-cyclohexyl-3-phenylthiourea (CyphSH) ligand and its Pd(II) and Pt(II) complexes with di-amine ligands, which were characterized using various techniques. Also, the nanostructure of the prepared complexes was studied using XRD and SEM. Furthermore, the antibacterial activity was screened, and Hirshfeld surfaces were studied.

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EXPERIEMENTAL

Materials and apparatus

All reactions were carried out in air using standard materials. isothiocyanate, cyclohexyl amine, Na_2PdCl_4, K_2PtCl_4, 2,2'-bipyridyl (Bipy) and 1,10-phenanthroline (Phen) were commercial products and used without further purifications. The molar conductivity measurements were recorded on digital conductivity meter model CD-2005. CHN analysis were recorded using the Elementary analyzer 1108 DC. IR spectra were recorded on a Shimadzu FT-IR 8400 spectrophotometer using KBr discs in the range 400–4000 cm^{-1}. The ^{1}H-NMR spectra were recorded on Bruker400 Advance 400 MHz spectrometer with DMSO-d_6 as solvent. Melting points were measured on a Stuarts SMP10 melting point apparatus and were uncorrected. The crystal structure of the collected X-rays data of the free ligand was solved by SHELXT-2014/7 [16] and refined by SHELXL 2018/3 [17].

Synthesis of ligand

The 1-cyclohexyl-3-phenylthiourea (CyphSH) ligand was prepared according to the method described in reference [4].

Synthesis of [Pd(CyphS)$_2$] (1)

An aqueous solution of Na_2PdCl_4 (0.120 g, 0.04 mmol) (10 mL) was added to a solution of **CyphSH** ligand (0.188 g, 0.08 mmol) in EtOH (15 mL) containing some drops of triethyl amine as a base, a brown ppt. was formed. The mixture was stirring for three hours, than filtered off, washed with distilled water and dried under vacuum (brawn powder, yield = 86%, m.p (°C) = 188-190). The [Pt(CyphS)$_2$] **(2)** complex was prepared and isolated in similar method.

Synthesis of [Pd(CyphS)$_2$(Bipy)] (3)

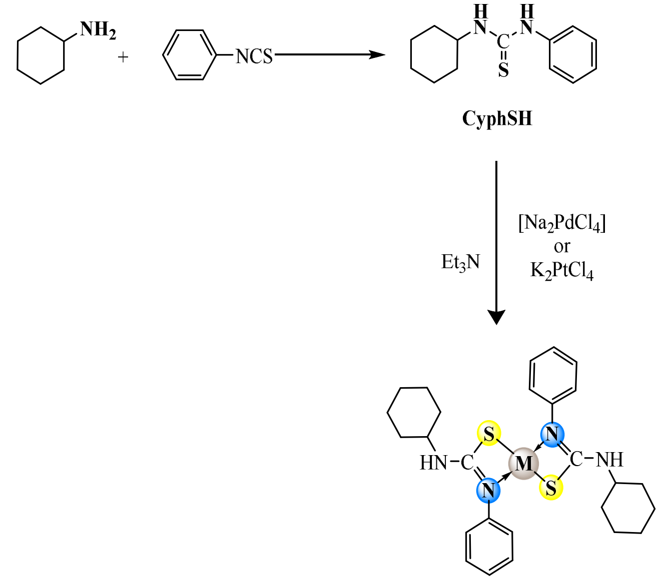
2,2'-Bipyridyl solution (0.120 g, 0.04 mmol) in chloroform (10 mL) was added to a solution of complex (**1**) (0.188 g, 0.08 mmol) in chloroform (10 mL) with stirring, and the color was change to an orange after addition. The mixture was stirring for three hours, than filtered off, and left aside to evaporate at room temperature. The orange ppt. formed was collected and washed with diethyl ether and dried under vacuum (orange solid powder, yield = 82%, m.p. (°C) = 145-148). The following complexes [Pt(CyphS)$_2$(Bipy)] (**4**), [Pd(CyphS)$_2$(Phen)] (**5**) and [Pt(CyphS)$_2$(Phen)] (**6**) were prepared and isolated in similar method.

RESULTS AND DISCUSSION

Synthesis

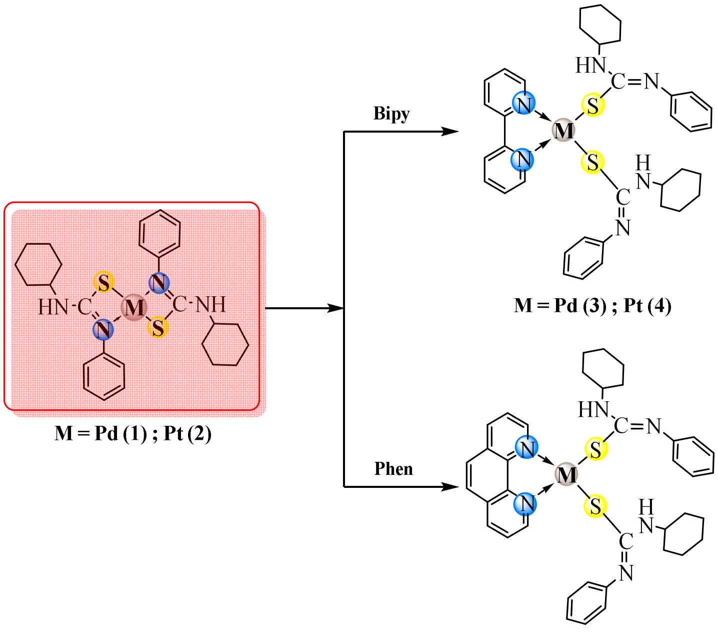
The 1-cyclohexyl-3-phenylthiourea (**CyphSH**) ligand prepared by the reaction of isothiocyanate with cyclohexyl amine as shown in Scheme 1. The reaction of two equivalent moles 1-cyclohexyl-3-phenylthiourea (**CyphSH**) ligand with one mole of Na_2PdCl_4 or K_2PtCl_4 in the presence triethylamine to afford new complexes of the formula [M(CyphS)$_2$] {M = Pd(**1**) and Pt(**2**)} as shown in Scheme 1.

Reaction of [M(CyphS)$_2$] {M = Pd(**1**) and Pt(**2**)} with diamine (Bipy or Phen) in equivalent molar ratio afforded complexes of the type [M(CyphS)$_2$(Bipy)] {M = Pd(**3**) and Pt(**4**)} and [M(CyphS)$_2$(Phen)] {M = Pd(**5**) and Pt(**6**)} in yield percentage (50-94 % yield) (Scheme 2). The prepared complexes were characterized using different spectroscopic and physical methods. The results data are listed in Tables 1 to 3.



M = Pd
(1) ; Pt (2)

Scheme 1. Synthesis of the **CyphSH** ligand and complexes (**1** and **2**).



M = Pd (5) ; Pt (6)

Scheme 2. Preparation of complexes (**3** - **6**).

Table 1. Some of physical properties and elemental analysis of the free ligand and its complexes.

Compounds	Color	Yield (%)	m.p. (°C)	Molar conductivity (Ω^{-1} cm^{-1} mol^{-1})	%Elemental analysis calc.(found)		
					C	H	N
CyphSH	White	88	142-144	2.00	66.62 (66.70)	7.74 (7.83)	11.95 (12.13)
[Pd(CyphS)$_2$]	Brawn	86	188-190	14.77	54.68 (54.59)	5.65 (5.82)	9.81 (9.92)
[Pt(CyphS)$_2$]	Yellow	50	210-212	18.90	47.33 (47.48)	4.89 (5.01)	8.49 (8.71)
[Pd(CyphS)$_2$(Bipy)]	Orange	82	145-148	14.50	59.29 (59.31)	5.80 (5.89)	11.52 (11.67)
[Pt(CyphS)$_2$(Bipy)]	Yellow	83	165-167	17.60	52.86 (53.01)	5.18 (5.23)	10.27 (10.43)
[Pd(CyphS)$_2$(Phen)]	Red	69	148-150	14.04	60.26 (60.35)	6.12 (6.39)	11.10 (11.28)
[Pt(CyphS)$_2$(Phen)]	Yellow	73	95-97	8.63	53.95 (54.11)	5.48 (5.50)	9.93 (10.17)

From the data in the Table 1, the conductivity measurements of the prepared complexes (**1-6**) in DMSO solvent showed that complexes have a low conductivity value at 10^{-3} M (2.00–18.90) Ω^{-1} cm^{-1} mol^{-1} and fell within the range of non-electrolytic complexes [18]. Also, the CHN analysis of the prepared complexes were measured, and the results showed that the obtained experimental values agree with theoretical values, which is consistent with the proposed formulas for the prepared complexes

Spectroscopic data

^{1}H and ^{13}C NMR data

The ^{1}H NMR spectrum of the free 1-cyclohexyl-3-phenylthiourea (**CyphSH**) ligand displayed the protons of the NH groups as two singlet peaks at $\delta_H = 9.35$ ppm and $\delta_H = 7.61$ ppm, one of these peaks' disappearance suggests coordination of the thiourea derivative ligand to the metal center by the sulfur atom and nitrogen atom after abstraction of H^+ from the thiourea moiety. In the complexes (**2-6**), the phenyl ring protons undergo weak de-shielding and appear in the range of $\delta_H = 7.86–7.03$ ppm in all the complexes. Apart from the aromatic signals due to the phenyl moiety, the ring protons of 2,2'-bipyridyl in complexes (**3**) and (**4**) appear as a four separated peaks above $\delta_H = 7.45$ ppm. Complexes (**4**) and (**5**) also show signals above $\delta_H = 7.52$ ppm due to 1,10-phenanthroline. In all the adduct (**1-6**), the spectra showed the chemical shifts of the -CH-N and CH_2 groups of cyclohexyl group within $\delta_H = 4.21$-3.96 ppm and $\delta_H = 0.76$-2.00 ppm, range. Other chemical shifts of the carbons in the CyphSH and diamine ligands are listed in the Table 2.

The ^{13}C-{^{1}H} NMR spectrum of the free CyphSH ligand showed the chemical shifts of carbons of **C**=S(C5), **=C**-NH(C1), and **-C**H-N(C6) at $\delta_C = 179.66$ ppm, 140.06 ppm, and 52.57 ppm, respectively. The carbons of the CH_2 groups of cyclohexyl group displayed at $\delta_C = 32.35$ ppm, 25.02 ppm, and 25.65 ppm due to the C7, C8 and C9, respectively. The carbons of the phenyl rings displayed at $\delta_C = 128.88$ ppm, 124.20 ppm, and 123.10 ppm. The ^{13}C-{^{1}H} NMR spectra of [Pt(CyphS)$_2$(Bipy)] (**5**) and [Pt(CyphS)$_2$(Phen)] (**6**) displayed the chemical shift **C**=S(C5), at $\delta_C = 176.71$ ppm and $\delta_C = 178.70$ ppm, respectively, the chemical shift was shifted to lower value indicates the coordinated was take placed via the sulfur of carbonyl group. Also the spectra displayed the δ_C of **C**=N (C10) of diamine ligands at $\delta_C = 146.14$ ppm, and $\delta_C = 146.16$ ppm for the two complexes, respectively. Other chemical shifts of the carbons in the **CyphSH** and diamine ligands are listed in the Table 2.

Table 2. ^{1}H NMR and ^{13}C NMR (δ, dppm) data of the free ligand and its complexes.

Compounds	δ (dppm)
CyphSH	^{1}H NMR: 9.35 (s, 1H), 7.61 (s, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 4.11 (s, 1H), 2.02 – 1.85 (m, 2H), 1.76 – 1.51 (m, 3H), 1.30-1.23 (m, 5H). ^{13}C NMR: 179.66(C5); 140.06(C1); 128.88(C2); 124.20(C3); 123.10(C4); 52.57(C6); 32.35(C7); 25.65(C9); 25.02(C9).
1	^{1}H NMR: 9.34 (s, 2H), 7.45(d, *J* = 8.0 Hz, 4H), 7.30 (t, *J* = 8.0 Hz, 4H), 7.08 (t, *J* = 8.0 Hz, 2H), 4.09 (s, 2H), 1.90 (d, *J* = 14.0Hz, 4H), 1.77 (d, *J* = 13.5 Hz, 4H), 1.35-1.14 (m, 12H).
2	^{1}H NMR: 9.34 (s, 2H), 7.45 (d, *J* = 8.0 Hz, 4H), 7.30 (t, *J* = 8.0 Hz, 4H), 7.08 (t, *J* = 8.0 Hz, 2H), 4.09 (s, 2H), 1.90 (d, *J* = 14.0 Hz, 4H), 1.77 (d, *J* = 13.5 Hz, 4H), 1.35-1.14 (m, 12H).
3	^{1}H NMR: 9.91 (s, 2H), 9.91 (d, *J* = 7.8 Hz, 2H, H-Bipy), 8.61 (d, *J* = 7.7 Hz, 2H, H-Bipy), 8.38 (t, *J* = 8.0 Hz, 2H, H-Bipy), 7.82 (t, *J* = 8.0 Hz, 2H, H-Bipy), 7.53 (d, *J* = 7.8 Hz, 4H, H-phenyl), 7.28 (t, *J* = 7.7 Hz, 4H, H-phenyl), 7.05 (t, *J* = 7.8 Hz, 2H, H-phenyl), 4.13 (m, 2H), 1.72-1.14 (m, 20H, H-cyclohexyl).
4	^{1}H NMR: 9.60 (s, 2H), 8.70 (dd, *J* = 7.8, 1.8 Hz, 2H, H- Bipy), 8.40 (dt, *J* = 7.9, 1.8 Hz, 2H, H-Bipy), 7.96 (td, *J* = 7.8, 1.8 Hz, 2H, H-Bipy), 7.84 (d, *J* = 7.9 Hz, 2H, H-Bipy), 7.52-7.43 (m, 4H, H-phenyl), 7.29 (t, *J* = 7.9 Hz, 4H, H-phenyl), 7.06 (t, *J* = 7.4 Hz, 2H, H-phenyl), 4.21-3.96 (m, 2H), 2.00-0.76 (m, 20H, H-Cyclohexyl). ^{13}C NMR: 176.71(C5); 146.14(C10); 141.02(C14); 140.43(C1); 137.78(C13); 135.22(C12); 129.32(C11); 128.72(C2); 123.86(C3); 122.70(C4); 52.17(C6); 32.37(C7); 25.71(C9); 24.87(C9).
5	^{1}H NMR: 9.62 (s, 2H), 9.31 (t, *J* = 8.0 Hz, 2H, H-Phen), 8.97 (dd, *J* = 7.8, 1.6 Hz, 2H, H-Phen), 8.25(s, 2H, H-Phen), 8.11 (dd, *J* = 7.8, 1.6 Hz, 2H, H-Phen), 7.86 (d, *J* = 7.6 Hz, 4H, H-phenyl), 7.29 (t, *J* = 7.8 Hz, 4H, H-phenyl), 7.06 (t, *J* = 7.8 Hz, 2H, H-phenyl), 4.10 (s, 2H), 1.91-1.14 (m, 20H, H-cyclohexyl).
6	^{1}H NMR: 9.92 (s, 2H), 9.07 (d, *J* = 8.4 Hz, 2H, H-Phen), 8.30 (s, 2H, H-Phen), 8.10 (d, *J* = 8.3 Hz, 2H, H-Phen), 7.57-7.03 (m, 12H, H-phenyl), 4.11 (s, 2H), 1.93-1.13 (m, 20H, H-Cyclohexyl). ^{13}C NMR: 178.60(C5); 146.16(C10); 140.40(C1); 137.49(C14); 133.80(C13); 131.60(C12); 128.73(C2); 126.85(C11); 123.89(C4); 125.23(C3); 120.85(C15); 52.20(C6); 32.37(C7); 25.70(C9); 24.88(C9).

Infrared data

The 1-cyclohexyl-3-phenylthiourea ligand spectrum displayed four characteristic bands at 3242, 2935, 1543, and 1109 cm^{-1} namely those assigned to ν(N-H), ν(CH)$_{\text{aliphatic}}$, ν(C=N), and ν(C-S), respectively.

The IR spectra of the complexes (**1-6**) displayed a strong to medium band at (1541-1572) cm^{-1}, which may be due to ν(C=N), this band appeared in similar position or shifted towards higher side compared with free ligand (1643) cm^{-1}. A new strong band showed at (1587-1599) cm^{-1} in the spectra of complexes (**3-6**), assigned to ν(C=N) in diamine ligand, which shifted to lower frequencies in all complexes, indicating its involvement in coordination of ligand to metal ions through the nitrogen atoms of heterocyclic ring [19-21]. The stretching vibration of the N-H group of **CyphSH** ligand showed as a weak to medium bands, at (3149-3238) cm^{-1} in the spectra of complexes (**3-6**). Further the IR spectra showed the ν(C-H) stretching of the aliphatic and aromatic groups within the range (2850-2935) cm^{-1} and (3028-3059) cm^{-1}, respectively [19-21].

The IR spectra of complexes [Pd(CyphS)$_2$(Phen)] (**5**) and [Pt(CyphS)$_2$(Phen)] (**6**), displayed a strong band at 846 and 844 cm^{-1} assigned to the ρ(C-H) out of plane, indicating that the 1,10-phenanthroline ligand participate in complex structures [22]. Other bands are listed in Table 3.

Table 3. IR selected data of the free ligand and their complexes.

Compounds	νNH	νCH ar.	νCH aliph.	νC=N amine	νC=N CyphSH	νC=C	νC-N	νC-S or νC=S	ρC-H	νM-S νM-N
CyphSH	3242bs	3028w	2935s 2852s	-	1543s	1504s	1394s	1109m	740s 692s	
1	3209m	3053w	2929w	-	1564m	1481m	1435s	1095m	748s 694s	439w 470w
2	3180s	3059w	2928s 2850m	-	1541m	1491m	1359w	1070m	748s 694s	432w 453w
3	3188m	3049w	2929s 2854m	1599m	1572s	1498s	1419w	1070m	761s 692s	443w 474w
4	3238w	3053w	2928s 2850m	1587s	1550s	1494s	1357m	1070m	759s 694s	432w 462w
5	3186m	3051w	2929s 2852s	1597m	1568s	1496s	1342w	1030m	717s 694s	434w 464w
6	3149w	3049w	2931s 2854m	1595m	1568s	1498m	1365w	1072m	732m 692s	430w 489w

Single crystal XRD of CyphSH

The geometry of the molecule is described by the dihedral angles of the central thiourea group A (C1/N1/N2/S1) with the phenyl ring B (C2-C7) and cyclohexane ring C (C8-C13) which are far from the zero degree (Figure 1, Table 4). The dihedral angles A/B and A/C are 55.6 (5)° and 64.2 (4)° which represent non-planarity characteristic of the molecule. The lateral ring is not planar and adopted chair conformation with carbon atom (C8) shows maximum deviation from the root mean square plane. Such conformation of the cyclohexane ring is found in number of literature compounds [23-26]. The nearest neighboring molecules are interlinked in the form of dimers through N-H···S bonding and complete $R_2^2(8)$ loop (Figure 2a, Table 4). The neighboring dimers are interlinked by N-H···S bonding, where amino group that is not used in dimerization is employed for inter-linkage of dimers. C-S···π interaction provides further stability to the crystal packing or supramolecular assembly by forming molecular chains along *c*-axis. One such chain is shown in Figure 2b with the important distance of the interaction.

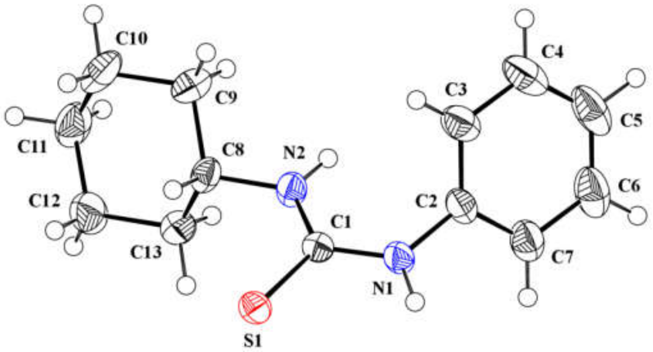


Figure 1. ORTEP diagram of **CyphSH** at 50% probability level.

The bond lengths and bond angles of **CyphSH** (Table 5) are consistent with the corresponding ones in literature compounds with reference codes ACIZET (trifluoromethyl-substituted phenyl ring) [27], FEPMIX (2,4-trifluoromethyl-substituted phenyl ring) [28], ZAMQIN (methyl-substituted phenyl ring) [29].

Table 4. Experimental details of **CyphSH**.

CCDC	2285307
Chemical formula	$C_{13}H_{18}N_2S$
M_r	234.35
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	170
a, *b*, *c* (Å)	12.0899 (4), 11.2885 (4), 10.2058 (3)
β (°)	113.858 (2)
V (Å^3)	1273.84 (7)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.23
Crystal size (mm)	0.25 × 0.21 × 0.18
Diffractometer	STOE *IPDS* 2T
Absorption correction	Multi-scan
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11310, 3377, 3201
R_{int}	0.050
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.685
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.111, 1.06
No. of reflections	3377
No. of parameters	145
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.30, −0.24

Table 5. Main geometry parameters and hydrogen bond geometry (Å, °) and C-S···π interaction.

Bond lengths (Å)		Bond angles (°)		
C1—N1	1.3503 (14)	N1—C1—S1	119.03 (9)	
C1—N2	1.3405 (15)	N2—C1—N1	117.52 (10)	
C1—S1	1.6988 (12)	N2—C1—S1	123.45 (9)	
C8—N2	1.4671 (14)	C3—C2—N1	120.86 (13)	
C2—C7	1.385 (2)	C7—C2—N1	118.24 (12)	
C2—N1	1.4229 (15)	N2—C8—C9	110.37 (11)	
		N2—C8—C13	110.92 (10)	
D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***<(D*—H···*A)*°**
N1—H1···S1^{i}	0.88	2.68	3.5026 (11)	155
N2—H2···S1^{ii}	0.88	2.88	3.6301 (11)	144
C*—S···*π	***C*—S**	**S···*π***	***C*···*π***	***<(C*—S···*π)*°**
C1—S1···*Cg1*^{iii}	1.6988 (12)	3.9868 (8)	4.1354 (13)	82.88 (4)

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $x, -y+1/2, z-1/2$; (iii) $x, -y+1/2, z+1/2$. Cg1 is centroid of the phenyl ring.

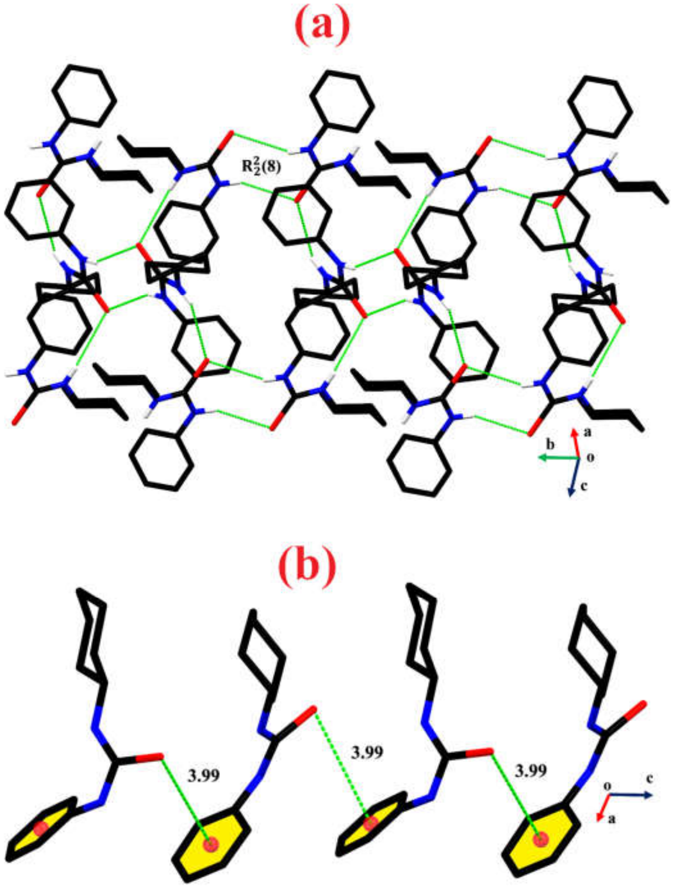


Figure 2. (a) Packing diagram exhibiting dimerization and linkage of dimers by H-bonding. (b) Illustration of C-S···π interaction.

Hirshfeld surface analysis

Now, the era of the supra-molecular chemistry paying special attention to the inspection of crystal in terms of intermolecular interactions because that knowledge is directly related with the properties that a crystal has. Crystal Explorer version 21.5 [30] is employed for study of the contacts in **CyphSH**. Figure 3a exemplifies the Hirshfeld surface over normalized distances (d_{norm}) that contained red spots representing short contacts which signifies that the thiourea group is active in forming short contacts. White spots symbolize the contacts with distance equal to sum of the Van der Waal radii and blue spots showed longer contacts [31-33]. The regions of uninterrupted trigular shaped of red and blue color around the rings is the sign for π···π interaction in **CyphSH** (Figure 3b) but that interaction is weedy with inter-centroid separation of 5.2986 (10) Å.

The fragments of the crystal packing can be prepared by 2D plots for the in-depth inspection of supra-molecular behavior [34-36]. The vital contacts in are H···H, H···S and H···C with percentage contribution of 69%, 14.1% and 13% in the crystal packing, respectively. The blue regions on the surface of Figure 3 stand for H···H contacts which showed that all H-atoms form contacts. The H-atoms of amino group are more prominent in forming contacts with S-atom as compare to H-atoms of rings (Figure 3). The pair having highest probability to make contacts can be calculated by enrichment ratio [37]. The results showed that hydrogen-sulfur pair has highest above-mentioned probability with enrichment ratio 1.13.

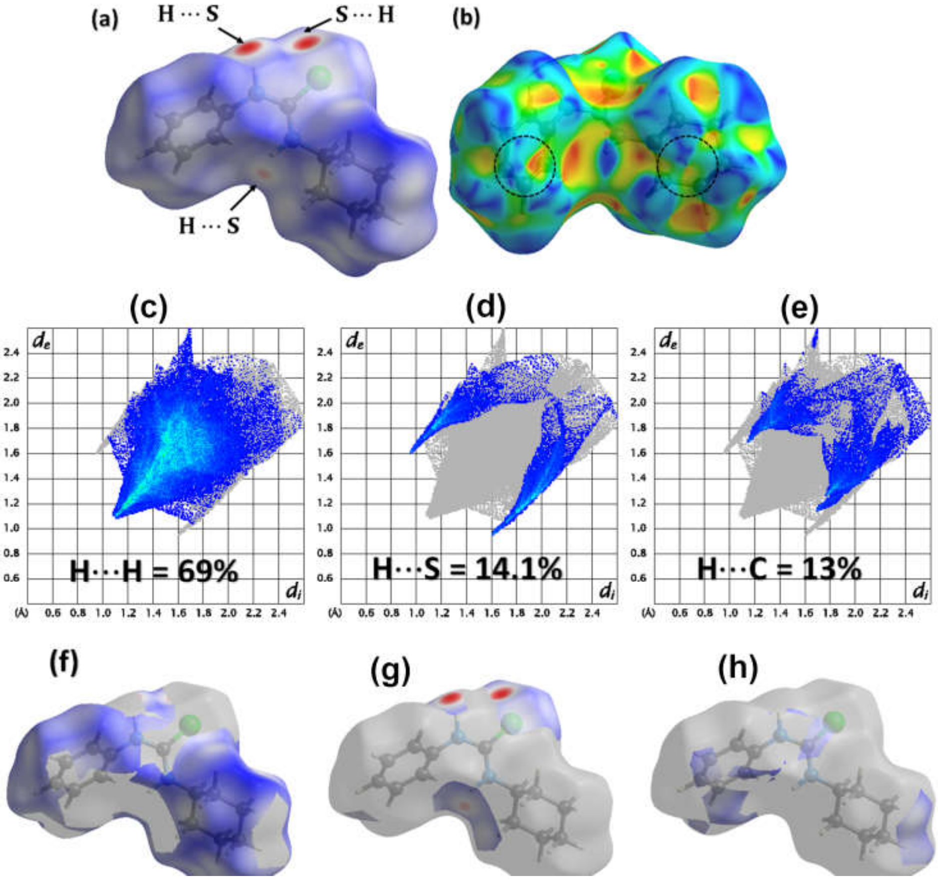


Figure 3. **(a)** Hirshfeld surface formed by using d_{norm}, **(b)** shape index, **(c-e)** vital 2D plots and **(f-h)** their associated Hirshfeld surface.

The curiosity of the researchers in finding voids is increasing as the voids are important regarding the properties of crystals. Voids are figured out by summing up the electron density of the atoms [14, 38, 39]. No gigantic cavity is observed as the voids occupy just 11.4% space in **CyphSH** and crystal at present study is expected to have good mechanical response.

The solid state assembly or crystal packing is explored further by finding interaction energy between molecular pairs at B3LYP/6-31G(d,p) electron density level [40] by employing Crystal Explorer version 21.5. The outcomes of the study inferred that coulomb energy is non-positive for all the pairs and total energy is largest for the pair with smallest intermolecular distance. The contribution of coulomb energy to the total attractive energy is maximum for the pair mentioned above but the corresponding contribution of dispersion energy is maximum for pair with R =

11.07 Å. In order to show which type of the energy dominant over the other kind of energies, energy frameworks are created in which width of cylinders is proportional to the strength of the corresponding energy [41]. Although, the width of some cylinders are larger in case of coulomb energy but overall, when we look at all the cylinders at the same time, we found that the dispersion energy is the most dominating one regarding the supra-molecular assembly of **CyphSH**.

Biological activity

The anti-bacterial studies were tested using the agar disc diffusion method [42]. Four pathogenic bacteria (*Staphylococcus aureus*, *Bacillus cereus* and *Escherichia coli*) were used. The diameter of the inhibitory zone (DIZ) results are showed in Figure 5, and were compared with commercial antibiotic (ciprofloxacin) as a positive control at 10^{-3} M in DMSO. The standard error for the experiment was ± 0.03%, and the experiments were repeated three times under the same conditions. $[Pt(CyphS)_2(Phen)]$ (**6**) complex display the highest activity than the free salts and other complexes and the highest inhibition zone against *Escherichia coli* compared with other species and standard antibiotic. Whereas the $[Pd(CyphS)_2(Bipy)]$ (**1**) shows the least activity than the other complexes but more than the free metal ions.

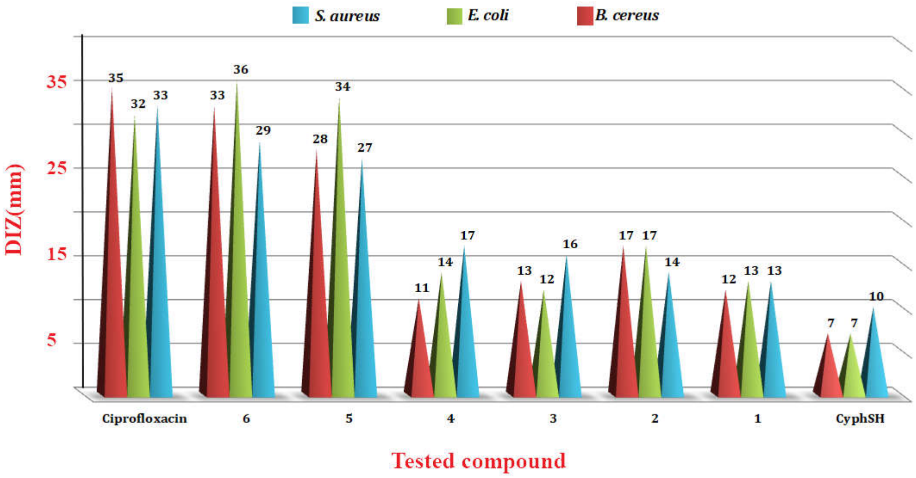


Figure 4. Anti-bacterial activity diagram of the free ligand and its complexes and standard antibiotic at 10^{-3} M.

CONCLUSION

Two of Pd(II), and Pt(II) complexes were synthesized through the reaction of the metal salts with the thiourea derivative **CyphSH** ligand in a of 1:2 molar ratio. Also, mixed ligand complexes of the $[M(CyphS)_2]$ (M^{II} = Pd and) with diamine ligands (Bipy and Phen) were prepared and characterized by various physicochemical techniques. The spectroscopic data showed that the **CyphSH** ligand acted as a monobasic bidentate ligand via nitrogen and sulfur atoms in complexes (**1**) and (**2**), while behaving as a monodentate ligand via sulfur atom of CS group. The crystal structure of **CyphSH** ligand was confirmed by X-ray technique which showed that the molecule was non-planar and a chair conformation is adopted by cyclohexane ring. Supra-molecular assembly investigation inferred that C-H···S bonding played leading role in stabilization of the crystal packing. Hirshfeld surface analysis showed that H···H, H···S and H···C contacts were the significantly important than other contacts. Intermolecular interaction energies calculations showed that the dispersion energy was the most dominant one in stabilization of the supramolecular assembly as compared to other types of energies. The molar conductivity values confirmed that Pd(II), and Pt(II) were nonelectrolytes All novel compounds demonstrated considerable antimicrobial activity when compared to standard drug.

Supplementary material

CCDC <2285307> contain the supplementary crystallographic data for < **CyphSH**>. This 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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