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PII: S0022-2860(19)30563-0

DOI: https://doi.org/10.1016/j.molstruc.2019.05.011

Reference: MOLSTR 26518

To appear in: Journal of Molecular Structure

Received Date: 15 January 2019

Revised Date: 30 April 2019

Accepted Date: 6 May 2019

Please cite this article as: M.Z. Mohd Zubir, N.S. Jamaludin, S.N. Abdul Halim, Hirshfeld surface analysis of some new heteroleptic Copper(I) complexes, *Journal of Molecular Structure* (2019), doi: https://doi.org/10.1016/j.molstruc.2019.05.011.

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# HIRSHFELD SURFACE ANALYSIS OF SOME NEW HETEROLEPTIC COPPER(I) COMPLEXES

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#### Abstract

Seven new coordination complexes namely, [Cu(T1)(I)(PPh<sub>3</sub>)<sub>2</sub>] (CT1), [Cu(T2)(I)(PPh<sub>3</sub>)<sub>2</sub>] (CT2),  $[Cu(T3)(I)(PPh_3)_2]$  (CT3),  $[Cu(T4)(I)(PPh_3)_2]$  (CT4),  $[Cu(T5)(I)(PPh_3)_2]$  (CT5),  $[Cu(T6)(I)(PPh_3)_2]$  (CT6) and  $[Cu(T7)(I)(PPh_3)_2]$  (CT7), were synthesized and characterized by using spectroscopic and crystallographic methods. The results from spectroscopic data and crystal structure analysis showed that in all complexes, the acylthiourea ligands coordinated as monodentate S-donor mode. All of the complexes displayed distorted tetrahedral geometry with one iodide anion, two triphenylphosphine ligands and one acylthiourea ligand (N-benzoyl-N'-(substituted phenyl)thiourea bearing different ortho/meta-substituents; R- H, 3-Me, 3-OMe, 3-OH, 3-Cl, 2-Me and 2-OMe, T1-T7 respectively) attached to the Cu(I) central metal atom. The acylthiourea ligands behaved as a monodentate S-donor ligand instead of its common O, S-bidentate nature due to the tetrahedrally favored geometry of the copper(I) metal and the presence of two bulky group of triphenylphosphine ligand as the co-ligand. Interestingly, CT1-CT4 and CT7 crystals are isostructural and crystallized in the monoclinic  $P2_1/c$  crystal system whereas **CT5** and **CT6** are also isostructurally crystallized in the triclinic  $P\overline{1}$  crystal system. Isostructural structures of these two crystal systems illustrated almost similar crystal packing but with significantly different interactions as determined by Hirshfeld surface analysis which is discussed herein.

Keywords: Copper(I) Complexes, Acylthiourea, Hirshfeld Surface Analysis, Crystallography.

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### 1. Introduction

Thiourea has interesting behavior because of their unique combinations of functional groups that include amino, imino, and thiol [1-2]. This series of ligands showed bonding to the metal centers via the S atom and is known to be favorable [3]. Thus, the chemistry of acylthiourea derivatives in coordination complexes has become an interest because of its interesting backbone of C(O)N(H)C(S)N, bearing O, N, N' and S donor atoms within it [1-3]. This has led to research far and wide on the study of the versatility of acylthiourea to form complexes of d-block elements with its remarkable applications in biological sciences [4, 5], luminescent studies [6], electrochemical investigations [7] and catalytic properties [8].

Theoretically, acylthiourea was expected to behave exclusively as a multidentate ligand yet it showed coordination through less than the maximum number of potential donor atoms. Hence, the term 'hypodentate' was used to describe this type of coordination behaviour [9, 10]. These hypodentate manners of acylthiourea were also observed with other metals such as platinum[9], palladium [11] and silver [12]. To observe this manner in detail, here we embark the challenge to conduct the Hirshfeld surface analysis apart from discussing the preparation, characterization and crystal structures of a series of new noble mixed copper(I) complexes of acylthiourea derivatives (Figure 1) with iodine and triphenylphosphine moiety as co-ligand.



R=H, 3-Me, 3-OMe, 3-OH, 3-Cl, 2-Me, 2-OMe

Figure 1: N-benzoyl-N'-(substituted phenyl)thiourea. (T1-T7).

The Hirshfeld surface analysis was developed to explain the space occupied by a molecule in a crystal structure by partitioning the crystal electron density into molecular fragments. Hirshfeld surfaces were named in honor of F. L. Hirshfeld, who proposed the stockholder partitioning scheme for defining atoms in molecules, consequently, lead to the extension of expressing a molecule in a crystal space [13, 14].

Hirshfeld surface has since become a unique tool in the prediction and study of crystal structure and its packing behavior. This method is so-called analysis; because it has proven to be a better method in uncovering the minute factors and features that contribute to a specific crystal characteristic, unlike by just examining the classical crystal packing diagrams [15]. Clearer rationale for distinguishing various types of non-bonding interactions (such as; van der Waals forces, hydrogen bonding, intermolecular contacts to halogen atoms,  $\pi \cdots \pi$  stacking interaction and so on [16]) and their impact within the crystal system can be understood. Each molecule has its own unique set of spherical atomic electron densities; thus, no two molecules have the same Hirshfeld surface. Spackman and coworker also stated that:

"... the Hirshfeld surface envelops the molecule and defines the volume of space where the promolecule electron density exceeds that from all neighboring molecules. It guarantees maximum proximity of neighboring molecular volumes, but the volumes never overlap because of the nature of the weight function." [13]

#### 2. Experimental Section

### 2.1. Materials and Measurements

All the chemicals were obtained from commercial sources and used as received. The IR measurement was conducted via the attenuated total reflection (ATR) technique in the frequency range of 450-4000 cm<sup>-1</sup> using a Perkin Elmer FTIR-Spectrum 400. The <sup>1</sup>H NMR and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of ligand (**TI-T7**) were recorded in deuterated dimethyl sulfoxide, DMSO-d<sub>6</sub>. The <sup>1</sup>H NMR,

<sup>13</sup>C{<sup>1</sup>H} NMR and <sup>31</sup>P NMR spectra of the copper(I) phosphine complexes, **CT1-CT7** were recorded in deuterated chloroform, CDCl<sub>3</sub>. The <sup>1</sup>H NMR and <sup>13</sup>C{<sup>1</sup>H} NMR were referenced to internal tetramethylsilane (TMS) whereas the <sup>31</sup>P NMR was internally referred to 85 % phosphoric acid. All NMR experiments were conducted on a JEOL ECA 400 MHz instrument. The compositions of C, H, and N were analyzed on a Perkin Elmer CHN Analyzer 2400. The samples were packed in a standard size solid sample tin capsule. The melting point was measured with MEL-TEMP II melting point apparatus.

X-ray single crystal determinations of complexes (**CT1-CT7**) were carried out using the Agilent Oxford Supernova Single Crystal Dual Wavelength X-ray Diffractometer and XtaLAB Synergy, Dualflex, AtlasS2 Rigaku Oxford Diffractometer using CuK<sub>a</sub> ( $\lambda = 1.54184$  Å) radiation. High-quality crystals were chosen using a polarizing microscope and carefully mounted on glass fibers. Data processing and absorption correction were performed using a multi-scan method within CrysAlis PRO. Empirical absorption correction using spherical harmonics, as implemented in the SCALE3 ABSPACK scaling algorithm, [17] was carried out. The structures were solved by the direct method using SHELXS. All data were refined by full matrix least-squares refinement against  $|F^2|$  using SHELXL 2017, [18] and the final refinements include atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms, and isotropic thermal parameters for the hydrogen atoms. The programs Olex2 [19], PLATON, [20] and Mercury [21] were used to process the data. Hirshfeld surface analysis was conducted and their 2D fingerprint plots were obtained using CrystalExplorer17 software [22].

#### 2.2. Synthesis of Acylthiourea Ligands (T1-T7)

The acylthiourea ligand *N*-benzoyl-*N*'-phenylthiourea (**T1**), *N*-benzoyl-*N*'-(3-methylphenyl)thiourea (**T2**), *N*-benzoyl-*N*'-(3-methoxyphenyl)thiourea (**T3**), *N*-benzoyl-*N*'-(3-hydroxyphenyl)thiourea (**T4**), *N*-benzoyl-*N*'-(3-chlorophenyl)thiourea (**T5**), *N*-benzoyl-*N*'-(2-methylphenyl)thiourea (**T6**), and *N*-benzoyl-*N*'-(2-methoxyphenyl)thiourea (**T7**), were prepared by

reacting potassium isothiocyanate with benzoyl chloride in acetone and formed benzoyl isothiocyanate, followed by the addition of aniline or other substituted aniline to form the acylthiourea derivatives [23].

#### 2.3. Synthesis of Phosphanecopper(I) Complexes (CT1-CT7)

Seven novel phosphanecopper(I) complexes of N-benzoyl-N'-(substituted phenyl)thiourea (CT1-CT7) were synthesized by adapting previously described procedure [10, 24] by reacting acylthiourea derivatives (T1-T7) respectively with copper(I) iodide and triphenylphosphine (Scheme 1).



R= H, 3-Me, 3-OMe, 3-OH, 3-Cl, 2-Me, 2-OMe

#### Scheme 1: Preparation of phosphanecopper(I) complexes (CT1-CT7).

The **CT1** complexes were prepared by modifying a previously described procedure [8, 24]. Triphenylphosphine (20 mmol) was dissolved in acetonitrile (10 ml) and was stirred vigorously before copper(I) iodide solid (10 mmol) was added into the stirring solution. The reaction mixture was left to stirred for 1 hour and the solid formed (phosphanecopper(I) precursor) was isolated upon filtration with excess acetonitrile and methanol. The dried phosphanecopper(I) precursor, without any purification or characterization, was directly reacted with the solid thiourea (**T1**) (10 mmol) *in-situ* followed by addition of acetonitrile (5 ml) to give a yellow precipitate in a clear yellow solution. The clear yellow solution was allowed to stand at room temperature, for a day up to a week to form pure

yellow, prismatic crystals. A similar method was applied to obtained CT2-CT7.

### 3. Results and discussion

### 3.1. Synthesis

All complexes yielded yellow crystals and were structurally characterized and tabulated in Table 1. The crystals were air-stable, non-hygroscopic in nature, and soluble in common solvents such as dichloromethane, acetone, acetonitrile, dimethylformamide and dimethylsulfoxide. All compounds were characterized using FTIR and ( ${}^{1}$ H,  ${}^{31}$ P) NMR. Single crystal X ray diffraction crystallography studies revealed that complexes **CT1-CT7** contained one molecule of acylthiourea derivatives **T1-T7**, respectively, with two molecules of triphenylphosphine and one iodine. All acylthiourea ligands exhibited neutral monodentate coordination with copper(I) through the sulfur atom.

Compound	Chemical Formula	R	Molecular Weight (g/mol)	Yield (%)	Melting Point (□)	C	(%)	H	(%)	N	(%)
Compound		, it	Worecular Worght (g/mor)			Calc	Found	Calc	Found	Calc	Found
CT1	$C_{50}H_{42}CuIN_2OP_2S$	Н	971.36	81	154-156	61.82	61.53	4.36	4.37	2.88	2.87
CT2	$C_{51}H_{44}CuIN_2OP_2S$	3-Me	985.38	79	155-158	62.16	61.96	4.50	4.37	2.84	2.66
CT3	$C_{51}H_{44}CuIN_2O_2P_2S$	3-OMe	1000.09	82	152-154	61.25	61.38	4.43	4.29	2.8	2.71
CT4	$C_{50}H_{42}CuIN_2O_2P_2S$	3-OH	987.08	85	156-158	60.84	60.93	4.29	4.02	2.84	2.73
CT5	C <sub>50</sub> H <sub>41</sub> ClCuIN <sub>2</sub> OP <sub>2</sub> S	3-C1	1005.80	89	166-168	59.71	59.91	4.11	4.01	2.79	2.79
CT6	$C_{51}H_{44}CuIN_2OP_2S$	2-Me	985.38	75	172-174	62.16	62.30	4.50	4.48	2.84	2.65
CT7	$C_{51}H_{44}CuIN_2O_2P_2S$	2-OMe	1000.09	80	171-173	61.25	61.11	4.43	4.37	2.80	2.69

Table 1: Physical data of the phosphanecopper(I) complexes (CT1-CT7).

#### 3.2 IR Spectroscopic Characterization

The IR spectra for all the free ligands (**T1-T7**) presented strong vibrational bands in the wave number at around 3350-3200 cm<sup>-1</sup> regions, attributable to v(N—H) stretching modes [25]. The thiourea derivatives (**T1-T7**) can exist in the thiocarbonyl or thiol forms. In the solid state of these compounds, the absence of the v(S—H) band at about 2570 cm<sup>-1</sup> and the presence of the v(N—H) bands in the range of 3000-3300 cm<sup>-1</sup> in the IR spectra revealed the evidence for thiocarbonyl tautomer formation [26].

The coordination of the ligands (**T1-T7**) with phosphanecopper(I) was confirmed by comparing the IR spectra of the free ligands with those of the complexes (Table 2). The IR vibrational bands for the complexes show obvious changes of the v(C=S) bands at the region 1400-1200 cm<sup>-1</sup> [8]. This is a significant indication that the sulfur atom of the thiourea involved in coordination with copper(I). Another noticeable observation is that the IR bands at region 3300-3400 cm<sup>-1</sup> and 1670-1690 cm<sup>-1</sup> attributed to v(N—H) and v(C=O) respectively [27, 28], which are all similar in the IR spectra of the ligands and complexes. This ruled out the involvement of the thiocarbonyl nor the amine group in coordination with the copper(I) metal.

The four characteristic thioamide bands (I-IV) of the free ligands which contributed from the thioamide group HN-C=S, namely I;  $(v(C-N) + \delta(N-H))$  at about 1600-1500 cm<sup>-1</sup>), II; (v(C=S) + v(C-H)) at about 1400-1200 cm<sup>-1</sup>), III; (v(C-N) + v(C-S)) at about 1200-1050 cm<sup>-1</sup>) and IV; (v(C-S)) at about 800-700 cm<sup>-1</sup> [29, 30], have considerable changes in frequency upon coordination with copper(I). Based on the four (I-IV) thioamide bands, they indicated an exclusive S-coordination mode due to the coordination. Consequently, thioamide II, containing a contribution from the v(C=S) stretching vibration, generally appears to have reduced in intensity in the spectra of the complexes, compared to the spectra of the respective free ligands. The absorptions at 800-780 cm<sup>-1</sup> in the spectra of free ligands (**T1-T7**) was attributed to the v(C-S) stretching vibrations and it had shown some shifting consistently to the range of 741-743 cm<sup>-1</sup> in the spectra of the complexes. This slight changes

supported the coordination through the sulfur atom with the copper(I) metal center [29]. However, the bands of thioamide I and thioamide II, as expected, their changes in terms of the shifting and intensity are less significant [31].

Table 2: IR spectral assignments for the acylthiourea	( <b>T1-T7</b> )	and their	<sup>,</sup> phosphan	ecopper(I)

			Wavenumbe	$r, v (cm^{-1})$		
Compound	N-H	C-0		Thioamic	le bands	
	14-11	0	Ι	II	Ш	IV
T1	3257.25 (m)	1671.54 (m)	1526.39 (s)	1357.40 (s)	1141.92 (s)	793.27 (m)
CT1	3049.03 (w)	1669.47 (m)	1517.77 (s)		1143.89 (s)	741.63 (s)
T2	3323.81 (m)	1667.59 (m)	1519.09 (s)	1353.65 (s)	1137.99 (s)	792.57 (m)
CT2	3048.65 (w)	1667.60 (m)	1514.77 (s)	$\sim$	1139.24 (s)	741.79 (s)
T3	3270.57 (m)	1671.77 (m)	1522.07 (s)	1357.38 (s)	1140.08 (s)	784.87 (m)
CT3	3206.26 (w)	1668.63 (m)	1518.13 (s)	<u> </u>	1142.55 (s)	742.00 (s)
T4	3320.67 (m)	1670.54 (m)	1518.50 (s)	1327.19 (s)	1140.23 (s)	735.15 (m)
CT4	3051.29 (w)	1670.69 (m)	1514.88 (s)	-	1138.95 (s)	741.94 (s)
T5	3287.13 (m)	1668.87 (m)	1516.94 (s)	1344.28 (s)	1140.86 (s)	792.00 (m)
CT5	3051.11 (w)	1667.26 (m)	1508.62 (s)	-	1146.98 (s)	742.84 (s)
T6	3258.02 (m)	1668.63 (m)	1517.80 (s)	1337.59 (s)	1151.07 (s)	742.56 (s)
CT6	3053.36 (w)	1667.53 (m)	1510.84 (s)	-	1148.00 (s)	740.11 (s)
T7	3267.41 (m)	1674.35 (m)	1538.75 (s)	1353.68 (s)	1151.26 (s)	750.70 (s)
CT7	3047.42 (w)	1673.41 (m)	1503.31 (s)	-	1148.48 (s)	742.12 (s)

complexes (CT1-CT7) (cm<sup>-1</sup>).

\*w = weak, m = medium, s = strong

### 3.3 NMR Spectroscopic Characterization

The <sup>1</sup>H NMR spectrum of complex **CT1** showed multiplets at the aromatic region, which integrated as 40 hydrogens at 8.04-7.19 ppm due to the aromatic protons of two phenyl rings of the ligand and the aromatic protons of two triphenylphosphine molecules attached to the metal. Similar multiplicities were also observed in the <sup>1</sup>H NMR spectra of complexes **CT2-CT7**, which integrated as 39 hydrogens at the range of 8.52-6.80 ppm, as presented in Table 3. In the <sup>1</sup>H NMR spectra of complexes, the N(1)H appeared at the range of 10.00-9.60 ppm and has shifted downfield compared

to the free ligands at the range of 11.70-11.40 ppm. This is due to the changes in the molecular environment as a result of complexation with the metal, based on consistent observation of all the complexes [32].

The <sup>13</sup>C{<sup>1</sup>H} NMR spectra of these complexes showed the presence of 13 carbon signals in complex **CT1** and 17 carbon signals in complexes **CT2**, **CT3**, **CT6** and **CT7**, while complexes **CT4** and **CT5** only had 16 carbon signals. These data are coherent with the formulation of each complex containing one acylthiourea ligand molecules and two triphenylphosphine molecules in accordance with the proposed structure of the mixed ligand copper(I) iodide complexes. The C=S carbon atom resonance was observed in the farthest low field at a range between 178.49-180.56 ppm in the <sup>13</sup>C{<sup>1</sup>H} spectrum of the free ligands, resultant of the conjugative effect of the thiourea skeleton. This signal underwent a slight upfield shift to 176.58-179.15 ppm in all complexes. This is possibly due to the electron delocalization induced from the coordination of copper(I) with the ligand through the thiourea sulfur [10]. The carbon atoms of the phenyl rings in triphenylphosphine are observed in the aromatic region with a higher abundance. It was also noticed that the signals split into doublets by the magnetic field of phosphorus atoms. This splitting occurred even in the proton-decoupled spectrum, this is expected because the carbon-phosphorus coupling is not turned off [33]. Meanwhile, the other signals observed in the aromatic region were carbons due to the acylthiourea ligands.

The <sup>31</sup>P NMR spectrum of the complexes in CDCl<sub>3</sub> exhibited only one signal at around -5.00 ppm indicating the presence of the triphenylphosphine [34]. A single resonance signal was observed because the chemical environment of the phosphorus atom from all of the triphenylphosphine are similar [35]. These results are in good agreement suggesting that the nitrogen is not involved in coordination with Cu(I) for all of the complexes. Hence, leaving the coordination occur only through the sulfur atom.

						Chemical shifts, $\delta$ (ppm)			
Compound		$^{1}\mathrm{H}$				<sup>13</sup> C{ <sup>1</sup> H}			<sup>31</sup> P
Compound	N(1)H	Aromatic	Others	C=S	C=O	Aromatic due to acylthiourea	Aromatic due to PPh3	Others	PPh3
CT1	9.86	8.04-7.19 (m,	_	178.24	168.01	137.36, 133.88, 133.32, 133.06, 131.31, 127.12,	134.18, 129.69,	_	-5.38
	(s, 1H)	40H)	-	170.24	100.01	124.67	128.94, 128.47	-	-5.50
CT2	9.92	8.04-7.18 (m,	2.34 (s, 3H)	178.00	168.00	138.92, 137.22, 133.85, 133.36, 133.09, 131.30,	134.18, 129.68,	21.49 -	5 4 1
C12	(s, 1H)	39H)	-Me	176.09	100.09	128.99, 127.93, 125.20, 121.77	128.74, 128.56	Me	-5.41
СТ3	9.81	8.03-6.80 (m,	3.76 (s, 3H)	177.02	168.06	159.93, 138.43, 133.90, 133.25, 132.99, 131.31,	134.17, 129.72,	55.51 -	53
CT3	(s, 1H)	39H)	-OMe	177.92	106.90	129.64, 116.60, 113.18, 109.74	129.05, 128.58	OMe	-5.5
CT4	9.61 (s,	7.98-6.74 (m,	5.14 (s, 1H)	177.01	167 73	155.95, 138.51, 133.16, 132.89, 131.35, 130.01,	134.16, 129.78,		5.00
014	1H)	39H)	-OH	1//.91	107.75	128.25, 116.52, 114.14, 111.37	129.13, 128.63	-	-5.09
CT5	9.93 (s,	8.05-7.19 (m,		179.22	169 15	138.44, 134. 43, 133.29, 133.03, 131.09, 129.89,	134.16, 129.71,		5 29
015	1H)	39H)	-	1/0.55	108.15	128.61, 127.14, 124.64, 122.71	129.06, 128.57	-	-5.56
СТб	9.95 (s,	8.05-7.19 (m,	2.28 (s, 3H)	170 15	168 10	136.00, 133.91, 133.63, 133.08, 132.79, 131.19,	134.22, 129.76,	18.09 -	5 33
CT6	1H)	39H)	-Me	1/9.13	100.10	130.86, 127.91, 126.61, 126.48	128.94, 128.57	Me	-5.55
CT7	9.61 (s,	8.52-7.21 (m,	3.92 (s, 3H)	176.58	167 63	151.16, 134.05, 133.12, 132.85, 131.58, 128.21,	134.19, 129.76,	56.07 -	-5.41
CT7	1H)	39H)	-OMe	170.30	107.05	127.14, 126.88, 123.73, 120.20	128.99, 128.58	OMe	-5.41

**N** 

## Table 3: <sup>1</sup>H NMR assignments of acylthiourea (T1-T7) and their phosphanecopper(I) complexes (CT1-CT7) (ppm).

\*s= single, d= doublet, t= triplet, m=multiplet

#### 3.4 X-ray Crystallography

The single crystal X-ray diffraction studies of phosphanecopper(I) complexes with substituted acylthiourea ligand have been conducted to evaluate the coordination behavior of these polyfunctional group ligands when forming complexes with copper(I) metal center. The steric effect of the bulky phosphine co-ligands, which can modify the compound geometry and behavior was also explored [36].

Prismatic yellow-colored crystals of **CT1-CT7** were grown from its acetonitrile solution by slow evaporation method at ambient atmosphere and collected to conduct the SCXRD analysis. The crystallographic data and structural refinement details and parameters obtained from X-ray diffraction analysis for all the crystals **CT1-CT7** are listed in Table 4. The result revealed that all the phosphanecopper(I) complexes, **CT1-CT7** are isostructural, adopting the geometry of a distorted tetrahedral geometry with one monodentate acylthiourea ligand, an iodine atom and two PPh<sub>3</sub> moieties. Compounds **CT1**, **CT2**, **CT3**, **CT4**, **CT7** shows isomorphism as they crystallized in the monoclinic system with space group  $P2_1/c$ , while **CT5** and **CT6** crystallized in the triclinic system with space group  $P\overline{1}$ . Significant bond lengths and angles are shown in Table 5 and Table 6 respectively.

#### 3.4.1 Crystal Structure of CT1- CT7

The molecular structure obtained for complex **CT1** and **CT5** is depicted in Figure 2 and Figure 3 respectively, the H atoms of the PPh<sub>3</sub>were omitted for clarity. **CT1** is a monomeric compound, crystallizes in the monoclinic space group  $P2_1/c$ , that consists of four independent [Cu(**TI**)(I)(PPh<sub>3</sub>)<sub>2</sub>] molecular units accommodated per cell. Whereas **CT5** crystallizes in the triclinic space group  $P\overline{1}$ , that consists of two independent [Cu(**T5**)(I)(PPh<sub>3</sub>)<sub>2</sub>] molecular units accommodated per cell. The asymmetric unit of complex **CT1** showed that it is a mononuclear and four-coordinated with one iodine, two triphenylphosphine units and one acylthiourea ligand, that is *N*-benzoyl-*N*'-

phenylthiourea (**T1**), as a monodentate ligand coordinating via the sulfur, (S1) atom to the copper(I), (Cu1) atoms. Again, **CT1** is isostructural with **CT2**, **CT3**, **CT4** and **CT7**, while **CT5** is isostructural with **CT6**.

Parameter	CT1	CT2	CT3	CT4	CT5	CT6	CT7
CCDC No	1865948	1865949	1875061	1874984	1865944	1865945	1865946
Empirical formula	$C_{50}H_{42}CuIN_2OP_2S$	C <sub>51</sub> H <sub>44</sub> CuIN <sub>2</sub> OP <sub>2</sub> S	$C_{51}H_{44}CuIN_2O_2P_2S$	$C_{50}H_{42}CuIN_2O_2P_2S$	$\frac{C_{50}H_{41}Cl_1CuIN_2OP_2S}{C_{50}H_{41}Cl_1CuIN_2OP_2S}$	$C_{51}H_{44}CuIN_2OP_2S$	C <sub>51</sub> H <sub>44</sub> CuIN <sub>2</sub> O <sub>2</sub> P <sub>2</sub> S
Formula weight	971.30	985.32	1005.75	987.30	1976.03	985.33	1001.32
Temperature/ K	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Wayalangth	CuK <sub>α</sub>	CuK <sub>α</sub>	CuK <sub>α</sub>	CuK <sub>a</sub>	CuK <sub>a</sub>	CuK <sub>a</sub>	CuK <sub>α</sub>
wavelength	$(\lambda = 1.54178)$	$(\lambda = 1.54178)$	$(\lambda = 1.54178)$	$(\lambda = 1.54178)$	$(\lambda = 1.54178)$	$(\lambda = 1.54178)$	$(\lambda = 1.54178)$
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_{1}/c$	$P2_{1}/c$	$P2_{1}/c$	P21/c	<i>P</i> -1	<i>P</i> -1	$P2_{1}/c$
a/ Å	10.4262(3)	10.7295(5)	10.2510	10.3834(10)	11.7876(10)	11.6335(6)	10.4317(5)
b/ Å	22.6541(6)	22.7196(10)	22.8713(10)	22.3572(10)	12.7342(12)	12.5117(6)	22.8237(12)
c/ Å	18.8774(6)	18.6290(8)	19.0029(10)	18.7591(10)	17.6274(15)	18.0259(8)	19.1489(10)
α/ °	90.000	90.000	90.000	90.000	79.475(7)	88.279(4)	90.000
β/°	90.491(3)	91.489(4)	91.230	91.400	74.273(7)	71.833(4)	90.266(5)
γ/ °	90.000	90.000	90.000	90.00	65.999(9)	67.611(5)	90.000
Volume/ Å <sup>3</sup>	4458.60(2)	4539.70(4)	4454.44(3)	4353.51(5)	2318.8(4)	2293.3(2)	4559.1(4)
Z	4	4	4	4	2	2	4
$\rho_{calc}, g/cm^3$	1.536	1.536	1.495	1.506	1.412	1.395	1.459
$\mu/ \text{ mm}^{-1}$	7.583	7.583	7.585	7.753	7.790	7.324	7.411
F (000)	2088	2088	2036	2000	995	980	2032
20 range for data collection/°	7.80 to 148.02	7.78 to 148.34	6.04 to 153.08	6.16 to 153.2	7.62 to 147.78	7.68 to 148.044	7.74 to 147.66
Reflections	19369	19651	57755	56828	16134	15880	11884

## Table 4: Crystal data and refinement details for phosphanecopper(I) complexes (CT1-CT7).

collected							
Independent	7863	8943	9308	9073	9097	8904	7312
reflections	[Rint = 0.0385,	[Rint = 0.0525,	[Rint = 0.0287,	[Rint =0.0320,	[Rint = 0.0918,	[Rint = 0.0859,	[Rint = 0.0292,
Tenections	Rsigma = 0.0365]	Rsigma = 0.0558]	Rsigma = 0.0179]	Rsigma = 0.0194]	Rsigma =0.0827]	Rsigma = 0.0789]	Rsigma =0.0417]
Data/ restraints/ parameters	7863/0/524	8943/0/534	9308/0/542	9073/0/529	9097/0/533	8904/0/534	7312/0/543
Goodness-of-fit on F2	1.023	1.021	1.046	0.990	1.033	1.136	1.028
Final R indices	R1 = 0.0557,	R1 = 0.0588,	R1 = 0.0207,	R1 = 0.0274,	R1 = 0.0745,	R1 = 0.0782,	R1 = 0.0457, wR2 =
[I>=2σ (I)]	wR2 = 0.1480	wR2 = 0.1529	wR2 = 0.0517	wR2 = 0.0738	wR2 = 0.1848	wR2 = 0.2036	0.1249
Final R indices	R1 = 0.0592,	R1 = 0.0649,	R1 = 0.0212,	R1 = 0.0283,	R1 = 0.0819,	R1 = 0.0858,	R1 = 0.0504, wR2 =
(all data)	wR2 = 0.1535	wR2 = 0.1622	wR2 = 0.0520	wR2 = 0.0747	wR2 = 0.1982	wR2 = 0.2221	0.1319
Largest diff. peak/ hole/ e.Å-3	1.20/-1.94	1.31/-1.98	0.28/-0.89	1.44/-1.23	2.45/-1.91	2.12/-2.80	1.10/-1.18

Atom	Atom Length/Å							
Atom	Atom	CT1	CT2	CT3	CT4	CT5	CT6	CT7
Cu1	S1	2.3745(9)	2.3588(9)	2.3266(4)	2.3426(5)	2.4089(14)	2.4095(16)	2.3550(10)
Cu1	I1	2.6350(6)	2.6369(6)	2.6106(2)	2.6520(3)	2.6462(8)	2.6349(8)	2.6330(6)
Cu1	P1	2.2883(9)	2.2886(10)	2.2912(4)	2.2786(5)	2.2836(13)	2.2870(15)	2.3061(10)
Cu1	P2	2.2840(9)	2.2833(9)	2.2801(4)	2.2730(5)	2.2989(13)	2.2915(16)	2.2966(10)

## Table 5: Selected bond lengths (Å) for phosphanecopper(I) complexes (CT1- CT7).

 Table 6: Selected bond angles (\*) for phosphanecopper(I) complexes (CT1- CT7).

Atom	Atom	Atom				Angle/°					
7 Hom	7 HOIL	7 tom	CT1	CT2	CT3	CT4	CT5	CT6	CT7		
P1	Cu1	S1	99.71(3)	101.52(3)	99.93(15)	99.77(2)	108.50(5)	106.69(6)	99.62(4)		
P1	Cu1	I1	104.93(3)	105.92(3)	105.03(13)	103.73(17)	104.02(4)	101.49(4)	106.16(3)		
P1	Cu1	P2	123.46(4)	123.37(4)	124.24(16)	124.12(2)	123.42(6)	122.53(6)	123.52(4)		
P2	Cu1	S1	104.14(4)	103.73(4)	106.88(16)	104.75(2)	102.19(6)	103.75(6)	106.87(4)		
P2	Cu1	I1	109.07(3)	108.63(3)	107.83(12)	108.85(16)	110.62(4)	115.58(5)	107.50(3)		
S1	Cu1	I1	115.84(3)	113.75(3)	112.88(12)	116.06(16)	107.26(4)	115.58(5)	113.18(3)		

It is noted that the angle between the phenyl rings of the acylthiourea ligands shows some differences i.e. the phenyl ring appeared to be planar in CT5 and CT6, while perpendicular in the others. The presence of intramolecular hydrogen bond N—H···O=C (with the formation of a '6-membered ring'), explained the stability of the complex in forming a monodentate S behaviour of the acylthiourea ligand [37].



Figure 2: Three-dimensional structure of CT1 complex.

Coordination bonds are listed in Table 5. It shows that the range for Cu—S bond distance are from (2.2832(14)-2.6456(9)) Å, are consistent with the distances usually found for tetrahedrally coordinated copper(I) complexes with S-donors ligands [8, 31, 34]. The Cu—P distances ranges from (2.2730 (5)-2.3061 (10)) Å are similar to Cu—P distances in previous reported analogous complexes [10, 36]. The Cu—I bond ranges from (2.6106 (2)-2.6520 (3)) Å is less than the sum of the ionic radii of Cu and I, that is 2.97 Å, agrees to other reported copper(I) halide complexes [24, 38-40].

The bond angles around the copper(I) atom is in the range of  $(99.62 \ (4)-124.24 \ (16))^{\circ}$  deviated from the ideal tetrahedral bond angle of  $109.5^{\circ}$  as shown in Table 6. It is significant to

observe the P1—Cu1—P2 angle, that is above 120°; (122.53–124.24)°, subtended by the bulky triphenylphosphine ligands [24]. This reveals a distorted tetrahedral coordination environment around each copper(I) atom in the phosphanecopper(I) complex. The distorted tetrahedral geometry is also reported in the copper(I) halide complexes with mixed PPh<sub>3</sub>/sulfur-based ligands [24, 41, 42]. This demonstrated that the two triphenylphosphine ligands exerted significant steric effects on the coordination geometry of the complexes [24].



Figure 3: Three-dimensional structure of CT5 complex.

#### 3.5 Hirshfeld Surface Analysis

In order to exemplify the interactions of the crystal structures in this series of closely related molecules, the Hirshfeld surface analysis was conducted and their 2D fingerprint plots were established using CrystalExplorer17 software [22]. All the Hirshfeld surfaces were generated for all the structure of the phosphanecopper(I) complexes **CT1-CT7**. There were four different Hirshfeld surfaces obtained, namely;  $d_{norm}$ , shape index, curvedness and electrostatic potential. Since the complex **CT1-CT7** are all closely related structures (where they only differ by a few atoms or a small

group of atoms), their Hirshfeld surface analysis results in a somewhat analogous but still differ considerably. All the Hirshfeld surfaces were elucidated as transparent to permit visualization of the molecular structure and the positioning of each of the complexes was set individually in accordance with the specific and significant orientation of interest. Such information is crucial to fully understand and appreciate the interaction based on the crystal packing of the entire molecule [15].

#### 3.5.1 The Hirshfeld Surface Maps



Figure 4: Relevant complementary patches and the neighboring molecule on the shape index surface of CT5

The Hirshfeld surface mapped with shape index function illustrated the consistent pattern of adjacent blue and red triangles for complexes **CT5** as in Figure 4 respectively. They showed a planar stacking arrangement of the molecules, a typical characteristic for a planar geometry aromatic hydrocarbon rings arranged in such a way. This is obvious when associated to the  $d_e$  and  $d_i$  range, which is within the van der Waals radii separation (clearly seen as the large white region in the  $d_{norm}$  mapping surrounding the planar surface of the ligand) [13]. The alternating red and blue region represented the concave and convex structure correspondingly, indicating that the neighboring molecule participated in a  $\pi \cdots \pi$  stacking interaction in these crystal structures [43]. Complex **CT6** exhibits similar properties whereas, there is no such existence of participation in complexes **CT1**,

#### CT2, CT3, CT4 and CT7.



Figure 5: Curvedness mapping of CT6

This is further proven by the evidence observed on the of the Hirshfeld surface. This gives insight into the different acylthiourea surface geometry resulting in different crystal packing. Complexes **CT5** and **CT6** (Figure5) showed relatively large green plane at the region of the acylthiourea ligand and **CT5** was observed to be more planar than **CT6**. This deduction is based on the fine blue lines on the **CT6** surface around the acylthiourea ligand. This is due to the presence of the tetrahedral methyl group on the acylthiourea ligand. Instead, obvious sharp edges were observed on the surface surrounding the acylthiourea in **CT5** because the chlorine atom is planar to the aromatic ring. The curvedness mapping provided a convincing suggestion of the planarity of **CT5** and **CT6** and that give rise to the  $\pi$ ··· $\pi$  stacking interaction between the crystal molecules resulting in a triclinic crystal packing [44]. Whereas all the complexes **CT1**, **CT2**, **CT3**, **CT4**, and **CT7** showed many sharp edge faces and no such flat surfaces on the aromatic rings of the acylthiourea ligand. The differences between these phosphanecopper(I) complexes were due to their distinctive conformations affected by the small different substituent groups [13].

The molecular electrostatic potentials mapped on Hirshfeld surfaces is over the range of -0.09 to 0.04 au for all the molecules. In specific, the blue (electropositive) and red (electronegative) mapping provided a very strong indication of the theory of electrostatic complementarity. The

complexes presented a rather dramatic fashion and clear distinction can be observed between them. This proved how small substituent groups on the acylthiourea affected the electrostatic potential of the complexes. The intermolecular hydrogen bonding of N—H···O=C interaction that was observed in **CT3**, **CT4** and **CT7** is signified based on the electrostatic environment on the surface that resulted in the dipole moments of the molecule. For instance, Figure 6 illustrated the electrostatic potential mapping of complex **CT4**. The presence of a hydroxy group (dominated with a blue surface) on the acylthiourea ligand consequently involved in electrostatic complementary interaction with the iodine (enveloped with a red surface) of the adjacent molecule. Thus, forming a polymeric crystal chain interaction. Observing at the electrostatic potential mapping of complexes **CT1** and **CT2**, it indicates similar electrostatic potential distribution. This is where the area enveloping the triphenylphosphine group appeared to be blue and the region for the acylthiourea ligand is overall red. Therefore, in the complexes (**CT1-CT2**) crystal packing, they arranged themselves accordingly by obeying the electrostatic complementarity.



Figure 6: Electrostatic potential mapping and the polymeric neighboring molecules of CT4

The  $d_{norm}$  (-0.5 to 1.5) Å mapping of the Hirshfeld surface revealed several red spots with different sizes and intensity. The red spots proved that the intramolecular distance to be notably shorter than the sum of the van der Waals radii. Larger and more intensify red spots noticed on complex **CT3** (Figure 7) and **CT7**, corresponding to a close and strong intermolecular hydrogen bonding and they are consistent with the crystal structures. They showed the dominant interactions at the thiourea backbone between the hydrogen of the amine and its adjacent oxygen of the carbonyl atoms (N—H···O=C), forming a dimeric arrangement in the crystal packing. Thus, it built the stability of the unit cell packing. For complex **CT4**, apart from the N—H···O=C interaction, there is also additional intense red spot representing the intermolecular hydrogen bonding due to the presence of hydrogen of the hydroxy group and the iodine atom (O—H···I—Cu). In the case of **CT1**, **CT2**, **CT5** and **CT6**, they were only dotted with smaller and paler red spots representing weaker close contacts [7].



Figure 7: Neighboring molecules associated with intermolecular hydrogen bonding on a  $d_{\text{norm}}$  of

СТ3.

### **3.5.2 2D Fingerprint Plot**

The full colored, 2D fingerprint plots of the Hirshfeld surface was plotted over the range 0.4-

2.8 Å in each of  $d_i$  and  $d_e$ . Each fingerprint plot was decomposed into specific pairs of atom-types contributions to highlight all their interactions (including H····H, H···C, H···O, H····I, H···S, H···N, C···C and other), allowing the relationship and their contributions towards the different intermolecular interaction types within the crystal packing [16]. For each plot, the outline of the original fingerprint plots is represented as a grey shadow and the reciprocal contacts were included.

Each Hirshfeld surface of the complexes does not generate the same 2D plotting and there are distinguishable likenesses and differences that could be discussed. For all the complexes (**CT1-CT7**), they showed a large number and a great spread of points ( $d_e$  and  $d_i$ ) displayed as tailed structures; as seen at the top right of the plots where they nearly filled up all the available plotting area (Figure8). These regions also described that  $d_e$  is generally greater than  $d_i$ , indicating that voids exist around the molecule in the crystal packing are very small. This type of points distribution was observed and reported in other benzene and phenyl-containing compounds, showing both  $d_e$  and  $d_i$  points covering much greater ranges in the fingerprint plots [15, 45, 46]. This also supported the large blue areas surrounding the aromatic rings in the  $d_{norm}$  mapping, corresponding to the longer contact distances contributed by the bulky phosphine group.



Figure 8: 2D fingerprint plots of CT1 (Full), CT3 (H···H contacts) and CT2 (H···C contacts)

The intermolecular H···H contacts (Figure 8) is in accordance with the Hirshfeld surface analysis for all the molecules, containing from 52.6 to 67.3 % of the total number of contacts. They are major contributors to the crystal packing. The characteristic spikes representing the shortest H···H contacts are converging along the diagonal line in the fingerprint plots at  $d_e + d_i \approx 2.2-2.4$  Å.

Accordingly, it showed obvious short head-to-head H···H contacts [15]. The structures of all molecules are also dominated by H···C contacts, including from 20.4 to 34.5 % of the total Hirshfeld surface areas. The presence of 'wings' at the bottom right and top left of each plot in the fingerprint plots are a typical representation of a C···H contact (Figure 8). In all the complexes, the shortest  $d_e + d_i \approx 2.6-2.7$  Å are documented as characteristic of a C···H unteraction. The wing at the top left representing  $d_i < d_e$  relates to points on the surface around the C···H donor. While the bottom right plotting where  $d_e < d_i$  corresponds to the surface throughout the  $\pi$  acceptor [15]. All plots contain one or more C···H··· $\pi$  interactions because of the presence of the multiple aromatic rings [46].



Figure 9: 2D fingerprint plots of CT7 (H···O contacts), CT4 (H···I contacts) and CT5 (C···C contacts)

The spikes of H···O and H···I contacts corresponded to the presence of interactions in all of the complexes. However, throughout the series, only **CT3**, **CT4** and **CT7** showed a higher contribution of H···O contacts which is above 4 %. The sharpest point featured a closer contact of  $d_e + d_i \approx 2.2-2.4$  Å which is in the range that is in agreeable to the intermolecular hydrogen bonding between N—H donor and O=C acceptor (N—H···O=C) [16] as in Figure 9. All the complexes showed a trend for the H···I contact in the range of 3-4 % of the surface area. **CT4** (Figure 9) showed the shortest contact of  $d_e + d_i \approx 2.8-3.0$  Å that allowed intermolecular hydrogen bonding. This is expected for interaction engaged between strong hydrogen bond donor O—H and a strong hydrogen bond acceptor I—Cu (O—H···I—Cu) [47].

A particular observation worth discussing from the fingerprint plots is the interests in the

relative areas associated with C···C contacts and correlated with the presence of planar stacking arrangement of aromatic  $\pi$ ··· $\pi$  interaction [15]. This is observed in complexes **CT5** (Figure 9) and **CT6** with the contribution of 3.7 % and 2.9 % respectively but there is a negligible amount of contribution, with less than 1 % in the rest of the series. The structures are further presented by a smaller insignificant proportion of H···S and H···N interactions, contributes a very small percentage of the molecular surfaces, that is less than 1.4 %. Thus, their contacts are almost insignificant throughout the whole series. Figure 10 illustrated the selected percentage of contributions of the Hirshfeld surface area. They represented the summarization of the quantitative information of intermolecular interactions contained in the molecular crystals (**CT1-CT7**). They all show almost similar pattern except for **CT5** show a larger percentage of other contacts, this is majorly contributed by the H···Cl contacts.





#### Acknowledgements

This work was funded by the University of Malaya, under grant BKP086-2016. The authors also thanked Research Centre for Crystalline Materials, Sunway University for permitting the usage of the single crystal X-ray diffractometer.

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Compound	Chemical Formula	P	Molecular Weight (g/mol)	Vield (%)	Melting Point (	C	(%)	H	(%)	N	(%)	
Compound	Chemical I ormula	K	wolcediar weight (g/mor)	1 Ieiu (70)	Weiting Folit (	Calc	Found	Calc	Found	Calc	Found	
CT1	$C_{50}H_{42}CuIN_2OP_2S$	Н	971.36	81	154-156	61.82	61.53	4.36	4.37	2.88	2.87	
CT2	$C_{51}H_{44}CuIN_2OP_2S$	3-Me	985.38	79	155-158	62.16	61.96	4.50	4.37	2.84	2.66	
CT3	$C_{51}H_{44}CuIN_2O_2P_2S$	3-OMe	1000.09	82	152-154	61.25	61.38	4.43	4.29	2.8	2.71	
CT4	$C_{50}H_{42}CuIN_2O_2P_2S$	3-ОН	987.08	85	156-158	60.84	60.93	4.29	4.02	2.84	2.73	
CT5	C <sub>50</sub> H <sub>41</sub> ClCuIN <sub>2</sub> OP <sub>2</sub> S	3-C1	1005.80	89	166-168	59.71	59.91	4.11	4.01	2.79	2.79	
CT6	$C_{51}H_{44}CuIN_2OP_2S$	2-Me	985.38	75	172-174	62.16	62.30	4.50	4.48	2.84	2.65	
CT7	$C_{51}H_{44}CuIN_2O_2P_2S$	2-OMe	1000.09	80	171-173	61.25	61.11	4.43	4.37	2.80	2.69	

 Table 1: Physical data of the phosphanecopper(I) complexes (CT1-CT7).

## Table 2: IR spectral assignments for the acylthiourea (T1-T7) and their phosphanecopper(I)

			Wavenumbe	$r, v (cm^{-1})$		
Compound	ΝН	C-0		Thioamic	le bands	
	11-11	C=0	Ι	II	III	IV
T1	3257.25 (m)	1671.54 (m)	1526.39 (s)	1357.40 (s)	1141.92 (s)	793.27 (m)
CT1	3049.03 (w)	1669.47 (m)	1517.77 (s)	-	1143.89 (s)	741.63 (s)
T2	3323.81 (m)	1667.59 (m)	1519.09 (s)	1353.65 (s)	1137.99 (s)	792.57 (m)
CT2	3048.65 (w)	1667.60 (m)	1514.77 (s)	-	1139.24 (s)	741.79 (s)
T3	3270.57 (m)	1671.77 (m)	1522.07 (s)	1357.38 (s)	1140.08 (s)	784.87 (m)
CT3	3206.26 (w)	1668.63 (m)	1518.13 (s)	- (	1142.55 (s)	742.00 (s)
T4	3320.67 (m)	1670.54 (m)	1518.50 (s)	1327.19 (s)	1140.23 (s)	735.15 (m)
CT4	3051.29 (w)	1670.69 (m)	1514.88 (s)		1138.95 (s)	741.94 (s)
T5	3287.13 (m)	1668.87 (m)	1516.94 (s)	1344.28 (s)	1140.86 (s)	792.00 (m)
CT5	3051.11 (w)	1667.26 (m)	1508.62 (s)		1146.98 (s)	742.84 (s)
T6	3258.02 (m)	1668.63 (m)	1517.80 (s)	1337.59 (s)	1151.07 (s)	742.56 (s)
CT6	3053.36 (w)	1667.53 (m)	1510.84 (s)	-	1148.00 (s)	740.11 (s)
T7	3267.41 (m)	1674.35 (m)	1538.75 (s)	1353.68 (s)	1151.26 (s)	750.70 (s)
CT7	3047.42 (w)	1673.41 (m)	1503.31 (s)	-	1148.48 (s)	742.12 (s)

## complexes (CT1-CT7) (cm<sup>-1</sup>).

w = weak, m = medium, s = strong

	Chemical shifts, δ (ppm)										
Compound		$^{1}\mathrm{H}$				<sup>13</sup> C{ <sup>1</sup> H}			<sup>31</sup> P		
Compound	N(1)H	Aromatic	Others	C=S	C=O	Aromatic due to acylthiourea	Aromatic due to PPh3	Others	PPh3		
CT1	9.86 (s, 1H)	8.04-7.19 (m, 40H)	-	178.24	168.01	137.36, 133.88, 133.32, 133.06, 131.31, 127.12, 124.67	134.18, 129.69, 128.94, 128.47	-	-5.38		
CT2	9.92 (s, 1H)	8.04-7.18 (m, 39H)	2.34 (s, 3H) -Me	178.09	168.09	138.92, 137.22, 133.85, 133.36, 133.09, 131.30, 128.99, 127.93, 125.20, 121.77	134.18, 129.68, 128.74, 128.56	21.49 - Me	-5.41		
CT3	9.81 (s, 1H)	8.03-6.80 (m, 39H)	3.76 (s, 3H) -OMe	177.92	168.96	159.93, 138.43, 133.90, 133.25, 132.99, 131.31, 129.64, 116.60, 113.18, 109.74	134.17, 129.72, 129.05, 128.58	55.51 - OMe	-5.3		
CT4	9.61 (s, 1H)	7.98-6.74 (m, 39H)	5.14 (s, 1H) -OH	177.91	167.73	155.95, 138.51, 133.16, 132.89, 131.35, 130.01, 128.25, 116.52, 114.14, 111.37	134.16, 129.78, 129.13, 128.63	-	-5.09		
CT5	9.93 (s, 1H)	8.05-7.19 (m, 39H)	-	178.33	168.15	138.44, 134. 43, 133.29, 133.03, 131.09, 129.89, 128.61, 127.14, 124.64, 122.71	134.16, 129.71, 129.06, 128.57	-	-5.38		
CT6	9.95 (s, 1H)	8.05-7.19 (m, 39H)	2.28 (s, 3H) -Me	179.15	168.10	136.00, 133.91, 133.63, 133.08, 132.79, 131.19, 130.86, 127.91, 126.61, 126.48	134.22, 129.76, 128.94, 128.57	18.09 - Me	-5.33		
CT7	9.61 (s, 1H)	8.52-7.21 (m, 39H)	3.92 (s, 3H) -OMe	176.58	167.63	151.16, 134.05, 133.12, 132.85, 131.58, 128.21, 127.14, 126.88, 123.73, 120.20	134.19, 129.76, 128.99, 128.58	56.07 - OMe	-5.41		
*s= single, d= doublet, t= triplet, m=multiplet											

## Table 3: <sup>1</sup>H NMR assignments of phosphanecopper(I) complexes (CT1-CT7) (ppm).

Parameter	CT1	CT2	CT3	CT4	CT5	CT6	CT7
CCDC No	1865948	1865949	1875061	1874984	1865944	1865945	1865946
Empirical formula	$C_{50}H_{42}CuIN_2OP_2S$	$C_{51}H_{44}CuIN_2OP_2S$	$C_{51}H_{44}CuIN_2O_2P_2S$	$C_{50}H_{42}CuIN_2O_2P_2S$	C <sub>50</sub> H <sub>41</sub> Cl <sub>1</sub> CuIN <sub>2</sub> OP <sub>2</sub> S	$C_{51}H_{44}CuIN_2OP_2S$	C <sub>51</sub> H <sub>44</sub> CuIN <sub>2</sub> O <sub>2</sub> P <sub>2</sub> S
Formula weight	971.30	985.32	1005.75	987.30	1976.03	985.33	1001.32
Temperature/ K	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Wayalangth	CuK <sub>α</sub>	CuK <sub>α</sub>	CuK <sub>a</sub>	CuK <sub>a</sub>	CuK <sub>α</sub>	CuK <sub>α</sub>	CuK <sub>α</sub>
wavelength	$(\lambda = 1.54178)$	$(\lambda = 1.54178)$	$(\lambda = 1.54178)$	$(\lambda = 1.54178)$	$(\lambda = 1.54178)$	$(\lambda = 1.54178)$	$(\lambda = 1.54178)$
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_{1}/c$	$P2_{1}/c$	$P2_{1}/c$	$P2_{1}/c$	<i>P</i> -1	<i>P</i> -1	$P2_{1}/c$
a/ Å	10.4262(3)	10.7295(5)	10.2510	10.3834(10)	11.7876(10)	11.6335(6)	10.4317(5)
b/ Å	22.6541(6)	22.7196(10)	22.8713(10)	22.3572(10)	12.7342(12)	12.5117(6)	22.8237(12)
c/ Å	18.8774(6)	18.6290(8)	19.0029(10)	18.7591(10)	17.6274(15)	18.0259(8)	19.1489(10)
α/ °	90.000	90.000	90.000	90.000	79.475(7)	88.279(4)	90.000
β/°	90.491(3)	91.489(4)	91.230	91.400	74.273(7)	71.833(4)	90.266(5)
γ/ °	90.000	90.000	90.000	90.00	65.999(9)	67.611(5)	90.000
Volume/ Å <sup>3</sup>	4458.60(2)	4539.70(4)	4454.44(3)	4353.51(5)	2318.8(4)	2293.3(2)	4559.1(4)
Z	4	4	4	4	2	2	4
$\rho_{calc}, g/cm^3$	1.536	1.536	1.495	1.506	1.412	1.395	1.459
μ/ mm <sup>-1</sup>	7.583	7.583	7.585	7.753	7.790	7.324	7.411
F (000)	2088	2088	2036	2000	995	980	2032
$2\Theta$ range for		Y					
data	7.80 to 148.02	7.78 to 148.34	6.04 to 153.08	6.16 to 153.2	7.62 to 147.78	7.68 to 148.044	7.74 to 147.66
collection/°							

## Table 4: Crystal data and refinement details for phosphanecopper(I) complexes (CT1-CT7).

Reflections collected	19369	19651	57755	56828	16134	15880	11884		
Independent reflections	7863	8943	9308	9073	9097	8904	7312		
	[Rint = 0.0385,	[Rint = 0.0525,	[Rint = 0.0287,	[Rint =0.0320,	[Rint = 0.0918,	[Rint = 0.0859,	[Rint = 0.0292,		
	Rsigma = 0.0365]	Rsigma = 0.0558]	Rsigma = 0.0179]	Rsigma = 0.0194]	Rsigma =0.0827]	Rsigma = 0.0789]	Rsigma =0.0417]		
Data/ restraints/ parameters	7863/0/524	8943/0/534	9308/0/542	9073/0/529	9097/0/533	8904/0/534	7312/0/543		
Goodness-of-fit on F2	1.023	1.021	1.046	0.990	1.033	1.136	1.028		
Final R indices	R1 = 0.0557,	R1 = 0.0588,	R1 = 0.0207,	R1 = 0.0274,	R1 = 0.0745,	R1 = 0.0782,	R1 = 0.0457, wR2 =		
[I>=2σ (I)]	wR2 = 0.1480	wR2 = 0.1529	wR2 = 0.0517	wR2 = 0.0738	wR2 = 0.1848	wR2 = 0.2036	0.1249		
Final R indices	R1 = 0.0592,	R1 = 0.0649,	R1 = 0.0212,	R1 = 0.0283,	R1 = 0.0819,	R1 = 0.0858,	R1 = 0.0504, wR2 =		
(all data)	wR2 = 0.1535	wR2 = 0.1622	wR2 = 0.0520	wR2 = 0.0747	wR2 = 0.1982	wR2 = 0.2221	0.1319		
Largest diff. peak/ hole/ e.Å-3	1.20/-1.94	1.31/-1.98	0.28/-0.89	1.44/-1.23	2.45/-1.91	2.12/-2.80	1.10/-1.18		

Table 5: Selected bond lengths (Å) for phosphanecopper(I) complexes (CT1- CT7).

Atom	Atom	Length/Å
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		CT1	CT2	CT3	CT4	CT5	CT6	CT7
Cu1	S1	2.3745(9)	2.3588(9)	2.3266(4)	2.3426(5)	2.4089(14)	2.4095(16)	2.3550(10)
Cu1	I1	2.6350(6)	2.6369(6)	2.6106(2)	2.6520(3)	2.6462(8)	2.6349(8)	2.6330(6)
Cu1	P1	2.2883(9)	2.2886(10)	2.2912(4)	2.2786(5)	2.2836(13)	2.2870(15)	2.3061(10)
Cu1	P2	2.2840(9)	2.2833(9)	2.2801(4)	2.2730(5)	2.2989(13)	2.2915(16)	2.2966(10)

 Table 6: Selected bond angles (\*) for phosphanecopper(I) complexes (CT1- CT7).

Atom	Atom	Atom	Angle/°							
			CT1	CT2	CT3	CT4	CT5	CT6	CT7	
P1	Cu1	S1	99.71(3)	101.52(3)	99.93(15)	99.77(2)	108.50(5)	106.69(6)	99.62(4)	
P1	Cu1	I1	104.93(3)	105.92(3)	105.03(13)	103.73(17)	104.02(4)	101.49(4)	106.16(3)	
P1	Cu1	P2	123.46(4)	123.37(4)	124.24(16)	124.12(2)	123.42(6)	122.53(6)	123.52(4)	
P2	Cu1	S1	104.14(4)	103.73(4)	106.88(16)	104.75(2)	102.19(6)	103.75(6)	106.87(4)	
P2	Cu1	I1	109.07(3)	108.63(3)	107.83(12)	108.85(16)	110.62(4)	115.58(5)	107.50(3)	
S1	Cu1	I1	115.84(3)	113.75(3)	112.88(12)	116.06(16)	107.26(4)	115.58(5)	113.18(3)	



R=H, 3-Me, 3-OMe, 3-OH, 3-Cl, 2-Me, 2-OMe

Figure 1: N-benzoyl-N'-(3-substituted phenyl)thiourea. (T1-T7).



R= H, 3-Me, 3-OMe, 3-OH, 3-Cl, 2-Me, 2-OMe

Scheme 1: Preparation of phosphanecopper(I) complexes (CT1-CT7).



Figure 2: Three-dimensional structure of CT1 complex.



Figure 3: Three-dimensional structure of CT5 complex.



Figure 4: Relevant complementary patches and the neighbouring molecule on the shape index

surface of CT5



Figure 5: Curvedness mapping of CT6



Figure 6: Electrostatic potential mapping and the polymeric neighboring molecules of CT4



Figure 7: Neighbouring molecules associated with intermolecular hydrogen bonding on a d<sub>norm</sub>

of CT3.



Figure 8: 2D fingerprint plots of CT1 (Full), CT3 (H···H contacts) and CT2 (H···C contacts)



Figure 9: 2D fingerprint plots of CT7 (H···O contacts), CT4 (H···I contacts) and CT5 (C···C

contacts)



Figure 10: Percentage contributions of the Hirshfeld surface area for phosphanecopper(I) complexes (CT1-CT7).

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## Highlights

- Acylthiourea coordinated to Cu(I) metal as monodentate S-donor ligand.
- They were stabilized by the hydrogen bonding.
- The complexes were isostructural and displayed distorted tetrahedral geometry.
- They crystallized in the monoclinic  $P2_1/c$  or  $P\overline{1}$  space group.
- Intermolecular interactions of crystal system were analyzed using Hirshfeld surface.

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