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Synthesis and crystal structure of [chlorobis(triphenylphospino) (p-chlorobenzaldehyde thiosemicarbazone)] copper(I) complex

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Abstract. Reactions of copper(I) halides with p-chlorobenzaldehyde thiosemicarbazone (H^1L) and triphenylphosphine in 1 : 1 : 2 molar ratio yielded complexes of stoichiometry, $[CuX(\eta^1\text{-S- }H^1L)(Ph_3P)_2]$ (X = I, **1**: Br, **2**; Cl, **3**). All the three complexes were characterized using analytical (CHNS) and spectroscopic (IR, ^{1}H NMR) techniques. The structure of complex **3** was confirmed by X-ray crystallography. It has been found to crystallize in the triclinic system with space group P-1 and unit cell parameters: a = 10.207(5) Å, b = 13.027(5) Å, c = 16.269(5) Å, α = 100.054(5)°, β = 99.228(5)° and γ = 97.234(5)°. This complex has distorted tetrahedral geometry with two phosphorus atoms from two triphenylphosphine ligands, thione sulfur of thiosemicarbazone ligand and chloride ion occupying the four corners of the tetrahedron. The structure of complex **3** was in contrast to sulfur-bridged dinuclear complex of copper(I) chloride with benzaldehydethiosemicarbazone, $[Cu_2Cl_2(\mu_2\text{-S-Hbtsc})_2(Ph_3P)_2]\cdot 2H_2O$. The intermolecular H-bonding, $Cl\cdots HC_{ph}$, 2.733 Å and π interactions, $\{CH_{ph}\cdots\pi$, 2.796; 2.776 Å$\}$ in this complex led to the formation of 1D chain. Two such 1D chains were cross-linked *via*, $Cl\cdots HC_{ph}$, 2.896 Å H-bonding to form a 2D network.

Keywords. p-chlorobenzaldehyde thiosemicarbazone; tetrahedral monomer; copper(I) halides; X-ray crystallography; hydrogen bonding; triphenylphosphine.

1. Introduction

Thiosemicarbazones ($R^1R^2C^2{=}N^3\text{-}N^2H\text{-}C^1(=S)N^1HR^3$) are important N, S-donor ligands as they exhibit variable bonding modes, structural diversity,[1–7] analytical applications[8–13] and biological activities (antibacterial, antifungal, antitumor, antiamoebic, antimalarial, antiviral, radioprotective, trypanocidal and anti-inflammatory activities).[14–18] Copper(I), being a soft acid, binds strongly with soft bases like sulfur, phosphorus and selenium.[19–24] Coordination chemistry of copper(I) halides with thiosemicarbazones had proved to be very interesting as the substituents on C^2 or N^1 atoms of thiosemicarbazones, halogen atoms and solvent system played important role in generating complexes of variable geometries, nuclearities and bonding modes (Chart 1).[24–32]

When C^2 carbon of thiosemicarbazone was substituted with pyridine, two phenyl rings or isatin ring at C^2 carbon, only tetrahedral monomers of type A were obtained,[19–25] whereas with thiophene, furan and pyrrole ring at C^2 carbon, it formed only dimers, either of type D or E depending upon the halogen atom attached.[19,28,29] Phenyl ring at N^1 atom of thiosemicarbazone resulted into formation of either three coordinated monomer (B) or sulfur bridged dimer (F), where no triphenylphosphine molecule coordinated.[28,29] Acetylthiophene-2-carbaldehyde thiosemicarbazone formed monomer with coordination number three of type C with copper(I) bromide and chloride.[30] A unique type of hetero-bridging (G) was observed in the complex of copper(I) iodide with acetophenone thiosemicarbazone.[31] It was observed in literature that solvent also played an important role in altering the bonding modes. For example, benzaldehyde thiosemicarbazone formed tetrahedral monomer in acetonitrile, whereas a halogen-bridged dimer was obtained from similar reaction in acetonitrile-chloroform mixture.[32] Similar reaction with copper(I) bromide in acetonitrile formed bromo-bridged dimer, while the use of acetonitrile-chloroform mixture as solvent changed the bridging mode from halogen-bridging to sulfur bridging.[32]

In continuation to this work, in this paper, reaction of p-cholorobenzaldehye thiosemicarbazone (H^1L, I) with copper(I) halides in the presence of triphenylphosphine as co-ligand has been investigated. The synthesized

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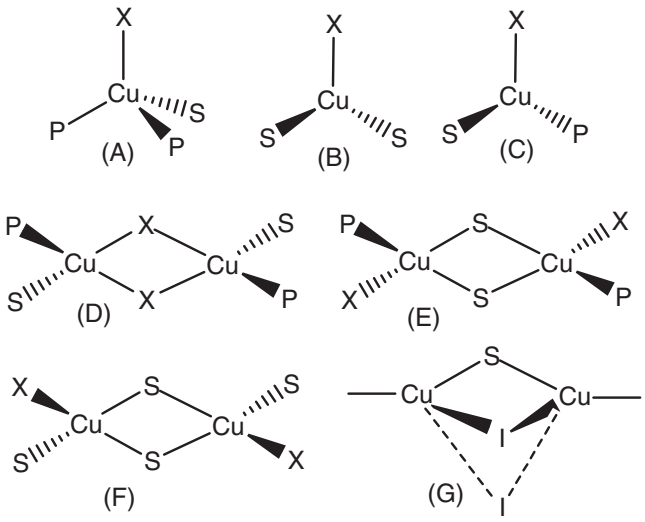
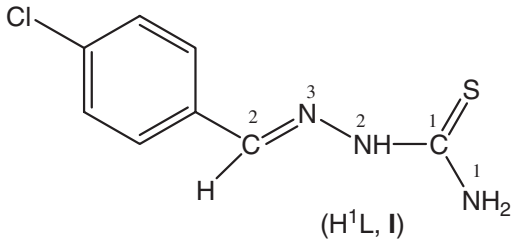


Chart 1. Types of bonding modes and nuclearity obtained for copper(I) halide complexes of thiosemicarbazones.

complexes were characterized using elemental analysis, IR, ^{1}H NMR and single crystal X-ray crystallography (complex **3**).



2. Experimental

2.1 *Synthesis*

2.1a *[CuI($\eta^1 - S - H^1L$)(Ph_3P_2)]* ***1***: To a solution of CuI (0.050 g, 0.26 mmol) in 15 mL of acetonitrile was added solid H^1L (0.056 g, 0.26 mmol) and the reaction mixture was stirred for 3-4 h. To this was added solid Ph_3P (0.137 g, 0.52mmol) and stirred for 10-20 min. The yellow coloured clear solution thus obtained was filtered and kept for crystallization at room temperature. Yield: 80%; M.p. 190-192°C. Elemental analysis for $C_{44}H_{38}N_3P_2SClCuI$, Found (%): C, 56.87; H, 4.06; N, 4.51; S, 3.46. Calcd. (%): C, 56.89; H, 4.09; N, 4.52; S, 3.45. Main IR peaks (KBr, cm^{-1}), υ(N–H), 3474s,3358m,3229; υ(–NH–), 3129m; υ(C–H_{Ph}), 3050s; $\delta(NH_2) + \upsilon$(C=N) $+\upsilon$(C–C), 1632s, 1539s; υ(C=S) 829m (thioamide moiety), υ(P–C_{Ph}),1094s. ^{1}H NMR ($CDCl_3$, δ ppm,): 10.23s (1H, N^2H), 8.20s (1H, C^2H), 7.67-6.93m (34H, $C^{4,5,7,8}$H+Ph_3P).

Complexes **2** and **3** were prepared by similar method.

2.1b *[CuBr($\eta^1 - S - H^1L$)(Ph_3P_2)]* ***2***: Yield: 75%; M.p. 178-180°C. Elemental analysis for $C_{44}H_{38}N_3P_2SClCuBr$, Found (%): C, 59.91; H, 4.29; N, 4.74; S, 3.62. Calcd. (%): C, 59.93; H, 4.31; N, 4.76; S, 3.63.Main IR peaks (KBr, cm^{-1}), υ(N–H), 3476s,3362s,3285m; υ(–NH–), 3134m; υ(C–H_{Ph}), 3051s; $\delta(NH_2) + \upsilon$(C=N) $+\upsilon$(C–C), 1582s, 1541s; υ(C=S) 820m (thioamide moiety),υ(P–C_{Ph}),1094s. ^{1}H NMR ($CDCl_3$, δ ppm,): 10.41s (1H, N^2H), 8.14s (1H, C^2H), 7.68-6.97m (34H, $C^{4,5,7,8}$H+Ph_3P).

2.1c *[CuCl($\eta^1 - S - H^1L$)(Ph_3P_2)]* ***3***: Yield: 78%; M.p. 181-183°C. Elemental analysis for $C_{44}H_{38}N_3P_2SCl_2Cu$, Found (%): C, 63.07; H, 4.52; N, 5.00; S, 3.84. Calcd. (%): C, 63.04; H, 4.54; N, 5.01; S, 3.82.Main IR peaks (KBr, cm^{-1}), υ(N–H), 3449s,3362s,3285m; υ(–NH–), 3160m; υ(C–H_{Ph}), 3050s; $\delta(NH_2) + \upsilon$(C=N) $+\upsilon$(C–C), 1591s, 1545s; υ(C=S) 818s (thioamide moiety),υ(P–C_{Ph}),1092s. ^{1}H NMR ($CDCl_3$, δ ppm,): 10.35s (1H, N^2H), 8.16s (1H, C^2H), 7.65-6.98m (34H, $C^{4,5,7,8}$H+Ph_3P).

2.2 *Chemicals and physical measurements*

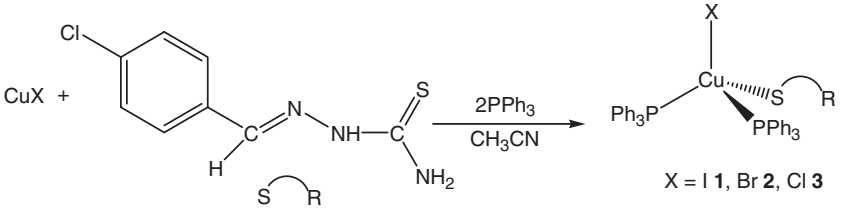
Potassium chloride, potassium bromide, potassium iodide, triphenylphosphine, p-chloro-benzaldehyde, thiosemicarbazide and triphenylphosphine were procured from Loba Pvt. Ltd, Copper(I) iodide, bromide and chloride were prepared by the reduction of $CuSO_4 \cdot 5H_2O$ using SO_2 in the presence of KI, KBr or KCl in water.[33] p-chlorobenzaldehydethiosemicarbazone was prepared by refluxing p-chlorobenzaldehyde and thiosemicarbazides in methanol for 4-5 h. C, H and N analyses were obtained with a Thermoelectron FLASHEA1112 CHNS analyzer. Infrared spectra were recorded from KBr pellets in the range 4000-200 cm^{-1} on a SHIMADZU FTIR 8400S spectrophotometer. Melting points were determined with an electrically heated Gallenkamp apparatus. ^{1}H NMR were recorded on an AV500 FT spectrometer operating at a frequency of 500 MHz using $CDCl_3$as solvent with TMS as the internal standard. X-ray Diffraction(XRD) patterns of the powder were recorded on PANalytical X-ray powder diffractrometer (Model X'pert^3 powder) with CuKα radiation (λ =1.5406 Å) with scan speed 0.066 degree per second in the 2θ range 5-40 for **1**, 5-80 degrees for **2** and 5-50 degrees for **3**.

2.3 *X-ray data collection, structure solution and refinement*

X-ray intensity data of 29686 reflections (of which 6397 unique) were collected on *X'calibur* CCD equipped

Table 1. Crystallographic data of complex **3**.

Empirical Formula	$C_{44}H_{38}Cl_2CuN_3P_2S$
Formula Weight	837.21
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Crystal size (mm)	0.3 x 0.2 x 0.2
Space group	P-1
Z, calculated	2
Density (g cm^{-3})	1.339
Absorption coefficient (mm^{-1})	0.817
a (Å)	10.207(5)
b (Å)	13.027(5)
c (Å)	16.269(5)
α (°)	100.054(5)
β (°)	99.228(5)
γ (°)	97.234(5)
V(A^3)	2075.9(14)
F(000)	864
Theta range for data collection (°)	3.48-26.00
Limiting indices	$-12 \geq h \geq 12$, $-16 \geq k \geq 16$, $-20 \geq l \geq 20$
Reflections	29686
Collected/unique	8127
Completeness to theta	3.48-26.00
Data/restraints	8127/0/423
Goodness-of- fit on F^2	1.031
Final R indices	R1 = 0.0378 wR2 = 0.0866
[I> 2σ(I)]	6397
R indices (all data)	R1 = 0.0543 wR2 = 0.0969
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.326, −0.343



Scheme 1. Reaction scheme for synthesis of complexes **1**-**3**.

Table 2. Selected bond length (Å) and bond angles (°) for complex **3**.

Bond Lengths			
Cu(1) – S(1)	2.4534(9)	S(1) – C(12)	1.697(3)
Cu(1) – Cl(1)	2.3350(13)	C(12) – N(7)	1.320(3)
Cu(1) – P(1)	2.3024(10)	C(12) – N(8)	1.327(3)
Cu(1) – P(2)	2.2832(8)		
Bond Angles			
P(1) - Cu(1) - P(1)	123.54(3)	Cl(1) – Cu(1) – S(1)	106.84(3)
P(2) – Cu(1) – Cl(1)	110.93(3)	N(7) – C(12) – N(8)	117.5(2)
P(1) – Cu(1) – Cl(1)	102.32(3)	S(1) – C(12) – N(7)	123.8(2)
P(2) – Cu(1) – S(1)	102.50(3)	Cu(1) – S(1) – C(12)	114.23(9)
P(1) – Cu(1) – S(1)	109.90(3)		

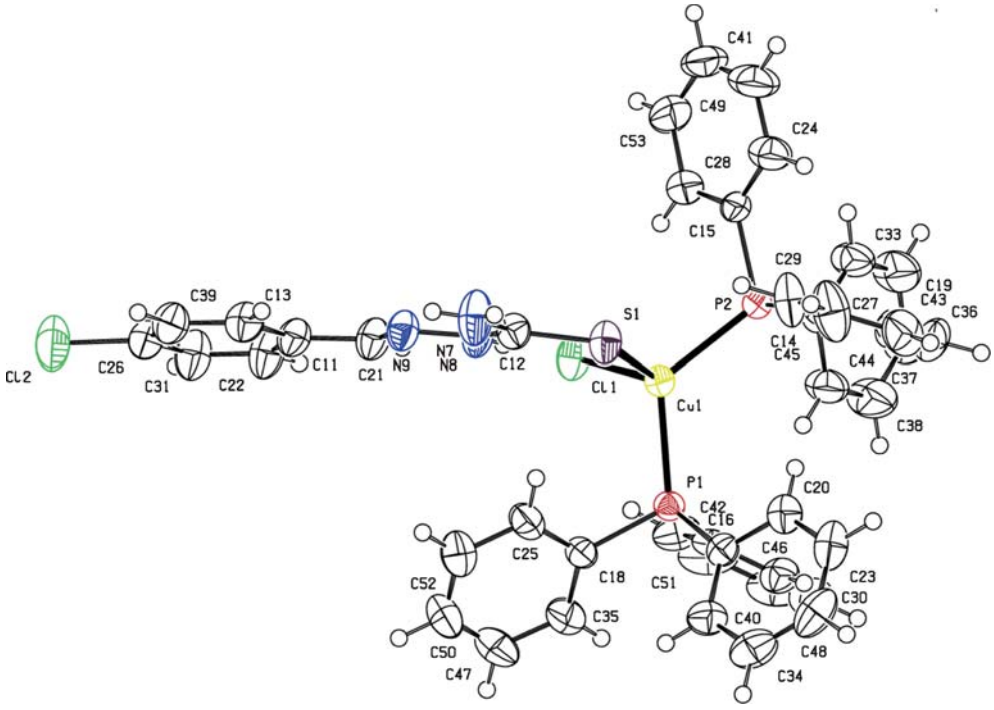


Figure 1. Molecular structure of complex **3**.

with graphite monochromated MoKα radiation (λ = 0.71073 Å). The crystal used for data collection was of dimensions 0.3 x 0.2 x 0.2 mm. The cell dimensions were determined by least-squares fit of angular settings of 10580 reflections in the θ range 3.48 to 29.08°. The intensities were measured by ω scan mode for θ ranges 3.48 to 24.99°. 1798 reflections were treated as observed ($I > 2\sigma(I)$). Data were corrected for Lorentz, polarization and absorption factors. The structure was solved by direct methods using SHELXS97.[34] All non-hydrogen atoms of the molecule were located in the best E-map. Full-matrix least-squares refinement was carried out using SHELXL97.[35] The final refinement cycles converged to an R = 0.0320 and wR (F^2) = 0.0835 for the observed data. Residual electron densities ranged from −0.167 to 0.175 eÅ^{-3}. The crystallographic data are summarized in table 1.

3. Results and Discussion

Reaction of p-chlorobenzaldehydethiosemicarbazone (H^1L) with copper(I) halides (I, Br, Cl) and triphenylphosphine in 1 : 1 : 1 (L : M : PPh_3) molar ratio formed insoluble compounds of stoichiometry, {$CuX(H^1L)(Ph_3P)$}. An effort was made to solubilize it, but no crystalline product was obtained. To solubilize these compounds, one extra mole of triphenylphosphine was added, which yielded complexes of stoichiometry, [$CuX(\eta^1$-S-$H^1L)(Ph_3P)_2$] (X = I (**1**), Br (**2**), Cl (**3**) (scheme 1). Geometry around copper center was found to be distorted tetrahedral in complex **3**. This monomer was in contrast to the previous results with benzaldehydethiosemicarbazone, where sulfur bridged dimer [$Cu_2(\mu_2$-S-$Hbtsc)_2(Ph_3P)_2Cl_2]\cdot 2H_2O$ was formed with copper(I) chloride.[19] It was already proved by theoretical studies that tetrahedral monomer and halogen-bridged dimers were thermodynamically more stable than S-bridged dimers. The S-bridged dimers could be stabilized by H-bonding between hydrogen atom of solvent molecule and halogen atom.[19] Since there is no solvent molecule entrapped in the lattice of complex **3**, formation of tetrahedral molecule is thermodynamically more favored. The CHN analysis of complexes **1**-**3** indicates that the molecular formula for all the three complexes are similar. The PXRD pattern. The peaks in PXRD pattern of

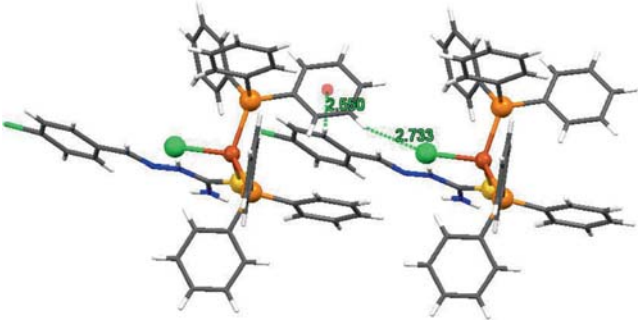


Figure 2. Interaction between two molecules of complex **3**.

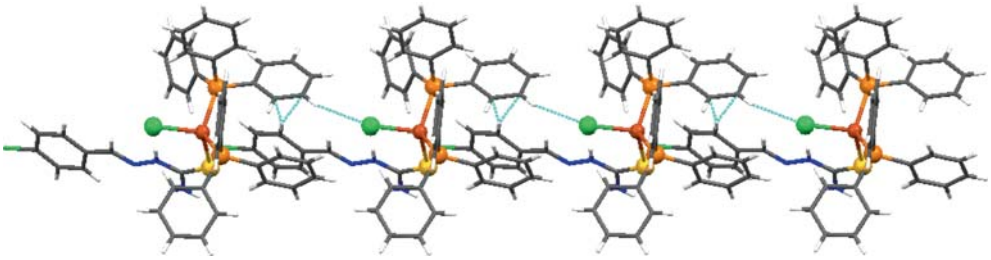


Figure 3. Intermolecular iteractions leading to the formation of 1D chain in **3**.

these complexes appeared at different angles implying that the lattice structure of these complexes may be different due to the presence of different anions or solvent molecules (See Supplementary Information).

The ν(N-H) band due to (-NH_2) and (-NH-) groups appeared in ranges, 3476-3285 cm^{-1} and 3160-3129 cm^{-1}, respectively. Presence of these bands suggested that thiosemicarbazone coordinated as neutral ligand in these complexes. Low energy shift of ν(C=S) in complexes **1**-**3** (829 (**1**), 820 (**2**), 818(**3**) cm^{-1}) *vis-à-vis* free ligand (854 cm^{-1}) supported binding of ligand *via* thione sulfur. The appearance of characteristic ν(P-C_{Ph}) in range 1092-1094 cm^{-1} in complexes **1**-**3** indicated coordination of Ph_3P to metal center.

3.1 *Structure of complex 3*

The crystallographic data and important bond parameters (bond lengths and bond angles) of complex **3** are given in tables 1 and 2, respectively. The molecular structure along with numbering scheme is given in figure 1. Complex **3** crystallized in triclinic crystal system with space group P-1.

In complex **3**, thione sulfur of p-chlorobenzaldehydethiosemicarbazone, chloride ion and two phosphorus atoms from two triphenylphosphine ligands occupied tetrahedral sites around the copper center. The Cu−S bond length in complex **3**, 2.4534(9) Å is close to the other copper(I) halide-thiosemicarbazone complexes reported in literature.[19,20,25–27] The Cu−Cl bond length, 2.3350(13) Å is less than the sum of ionic radii of Cu and Cl (Cu^+, Cl^-, 2.58 Å).[36] The Cu-P bond lengths, {2.3024(10), 2.2832(8) Å **3**} are close to literature value.[19,20,25–27] The C-S bond length, 1.697(3) Å in **3** is close to free ligand (1.687(3) Å),[37] but much shorter than that, {1.772(4)Å} in [PyPhHg(btsc)] (btsc = anionic form of benzaldehyde thiosemicarbazone),[38] which indicates that ligand is coordinated to copper center in thione form. Two S−Cu−P bond angles are different, {S−Cu−P(1), 109.90(3)°; S−Cu−P(2), 102.50(3)°}. The S−Cu−Cl and P−Cu−P bond angles are 106.84(3)° and 123.54(3)° respectively. The variation in these angles in **3** from 109.5° reveals distortion from regular tetrahedral geometry. Coordination of two bulky triphenylphosphine molecules to copper, creates maximum distortion in P−Cu−P bond angle, 123.54°. The Cu-S-C bond angle, 114.23(9)° is much larger than that in [2-PyPhHg(btsc)], {99.09(12)°}, where thiosemicarbazone ligand forms a chelate ring.[38]

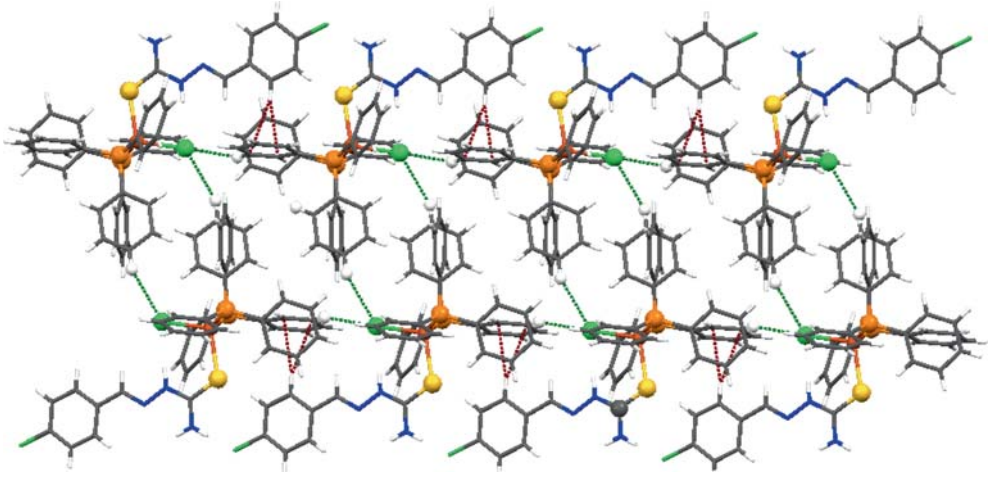


Figure 4. Inter molecular H-bonding within two 1D layer to form 2D layer isn complex **3**.

3.2 *Supramolecular Architecture of complex **3***

Intermolecular H-bonding and different π-interactions in complex **3** has resulted in the formation of 2D sheet. The stepwise formation of supramolecular architecture of this complex can be explained as: two molecules of complex **3** are interconnected via H-bonding between chloride ion and phenyl hydrogen of triphenylphosphine, $Cl\cdots HC_{ph}$, 2.733 Å. These molecules also show strong π interaction, $\{CH_{ph}\cdots\pi$, 2.796; 2.776 Å$\}$ to form dimeric unit. The distance between phenyl hydrogen of p-cholorobenzaldehyde ring and centroid of phenyl ring of triphenylphosphine is 2.550 Å (figure 2). The same interactions are repeated to form 1D layer (figure 3).

Two such 1D layers are cross-linked by inter molecular H-bonding between metal bonded chloride ion of one layer and hydrogen phenyl ring of triphenylphosphine molecule of second ring, $Cl\cdots HC_{ph}$, 2.896 Å and vice-versa to form a 2D sheet (figure 4).

3.3 *Solution phase behavior*

A broad singlet appeared in ^{1}H NMR spectra of complexes **1-3** in range δ10.23-10.41 ppm due to N^2H proton. This signal shifted to low field *vis-à-vis* free ligand (δ 9.32 ppm). The presence of N^2H signal in complexes **1**-**3** ensured the coordination of thiosemicarbazones as neutral ligands. The C^2H proton of thiosemicarbazone appeared at δ 8.20 (**1**), 8.14 (**2**) and 8.16 ppm (**3**). Other ring protons got obscured by the signals due to triphenylphosphine ring protons (δ 7.65-6.93 ppm).

4. Conclusions

Reactions of copper(I) halides with p-chlorobenzaldehyde thiosemicarbazone and triphenylphosphine formed compounds of formula, $[CuX(\eta^1\text{-S-H}^1L)(Ph_3P)_2]$ (X = I, **1**; Br, **2**; Cl, **3**). X-ray structure of complex **3** revealed a distorted tetrahedral geometry, in contrast to sulfur-bridged dimer with benzaldehydethiosemicarbazone.[19] Reason for change in nuclearity could be the absence of solvent in the lattice. The intermolecular H-bonding, $Cl\cdots HC_{ph}$, 2.733 Å and π interactions, $\{CH_{ph}\cdots\pi$, 2.796; 2.776 Å$\}$ led to the formation of 1D chain. Two such 1D chains were cross-linked via H-bonding, $Cl\cdots HC_{ph}$, 2.896 Å to form 2D network.

Supplementary Information (SI)

All details have been deposited with the Cambridge Crystallographic Data Centre, CCDC for **3** is 1042089. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: 44-1223-336-033; email: deposit@ccdc.cam.ac.uk; or http://www.ccdc.cam.ac.uk). Cif file of complex **3** and PXRD patterns of complexes **1**-**3** are given in Supplementary Information, available at www.ias.ac.in/chemsci.

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