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The influence of substituents (R) at N^1 atom of thiophene-2-carbaldehyde thiosemicarbazones $\{(C_4H_3S)HC^2{=}N^3{-}N(H){-}C^1(=S)N^1HR\}$ on bonding, nuclearity and H-bonded networks of copper(I) complexes

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ABSTRACT

The nuclearity, bonding and H-bonded networks of copper(I) halide complexes with thiophene-2-carbaldehyde thiosemicarbazones $\{(C_4H_3S)HC^2{=}N^3{-}N(H){-}C^1(=S)N^1HR\}$ are influenced by R substituents at N^1 atom. Thiophene-2-carbaldehyde-N^1-methyl thiosemicarbazone (HttscMe) or thiophene-2-carbaldehyde-N^1-ethyl thiosemicarbazone (HttscEt) have yielded halogen-bridged dinuclear complexes, $[Cu_2(\mu\text{-}X)_2(\eta^1\text{-}S\text{-}Htsc)_2(Ph_3P)_2]$ (Htsc, X: HttscMe, I, **1**; Br, **2**; Cl, **3**; HttscEt, I, **4**; Br, **5**; Cl, **6**), while thiophene-2-carbaldehyde-N^1-phenyl thiosemicarbazone (HttscPh) has yielded mononuclear complexes, $[CuX(\eta^1\text{-}S\text{-}HttscPh)_2]$ (X, I, **7a**; Br **8**; Cl, **9**) and a sulfur bridged dinuclear complex, $[Cu_2(\mu\text{-}S\text{-}HttscPh)_2(\eta^1\text{-}S\text{-}HttscPh)_2I_2]$ **7b** co-existing with **7a** in the same unit cell. These results are in contrast to S-bridged dimers $[Cu_2(\mu\text{-}S\text{-}Httsc)_2(\eta^1\text{-}Br)_2(Ph_3P)_2]\cdot 2H_2O$ and $[Cu_2(\mu\text{-}S\text{-}Httsc)_2(\eta^1\text{-}Cl)_2(Ph_3P)_2]\cdot 2CH_3CN$ obtained for R = H and X = Cl, Br (Httsc = thiophene-2-carbaldehyde thiosemicarbazone) as reported earlier. The intermolecular $CH_{Ph}\cdots\pi$ interaction in **1**–**3** (2.797 Å, **1**; 3.264 Å, **2**; 3.257 Å, **3**) have formed linear polymers, whereas the $CH_{Ph}\cdots X$ and $N^3\cdots HCH$ interactions in **4**–**6** (2.791, 2.69 Å, **5**; 2.776, 2.745 Å, **6**, respectively) have led to the formation of H-bonded 2D polymer. The $PhN^1H\cdots\pi$, interactions (2.547 Å, **8**, 2.599 Å, **9**) have formed H-bonded dimers only. The Cu···Cu separations are 3.221–3.404 Å (**1**–**6**).

1. Introduction

Thiosemicarbazones possessing several donor atoms are versatile ligands, and have formed mononuclear, dinuclear and polynuclear complexes with transition metals [1–6]. These ligands have also displayed ion-sensing ability [7–10], metal extraction properties [11,12] and pharmacological properties [13–17]. Thiosemicarbazones have displayed interesting H-bonded 1D and 2D networks encapsulated organic molecules in the voids [6]. The coordination compounds of several metals with thiophene-2-carbaldehyde thiosemicarbazone (R = H, Httsc, I) exist as mononuclear and dinuclear complexes [6,18–24,32,33]. Chart 1 shows various bonding modes of Httsc (neutral or anionic), namely: (i) η^1-S (mode A) [22], (ii) μ-S (mode B) [23], (iii) N^3, S-chelation (mode C) [20], (iv) N^2, S-chelation (mode D) [19] and (v) N^3, S-chelation-cum-S-bridging (mode E) [24] in these complexes.

Heterocyclic thiosemicarbazones in literature have generally formed dinuclear complexes, e.g. thiophene-2-carbaldehyde thiosemicarbazone formed an iodo-bridged dimer $[Cu_2(\mu\text{-}I)_2(\eta^1\text{-}S\text{-}Httsc)_2(Ph_3P)_2]$ with copper(I) iodide and S-bridged dimers $[Cu_2(\mu\text{-}S\text{-}Httsc)_2(\eta^1\text{-}Br)_2(Ph_3P)_2]\cdot 2H_2O$ and $[Cu_2(\mu\text{-}S\text{-}Httsc)_2(\eta^1\text{-}Cl)_2(Ph_3P)_2]\cdot 2CH_3CN$ with copper(I) bromide or chloride, respectively [22,23]. Dinuclear copper complexes are very important due to their role in many copper proteins [25] electrolytic reduction of carbon dioxide [26] and other catalytic activities [27–29]. Further close Cu···Cu contacts in dimers are anticipated to promote photoluminescent properties [30,31]. In this paper, a series of substituted thiophene-2-carbaldehyde thiosemicarbazones as shown in Chart 2 have been used for their interaction with copper(I) halides and the results are presented herewith. The influence of substituents (R) at N^1 on bonding nuclearity and H-bonded networks is investigated.

2. Experimental

2.1. Chemical reagents

Copper(I) halides were prepared by the reduction of $CuSO_4\cdot 5H_2O$ using SO_2 in the presence of NaX (X = Cl, Br, I) in distilled water [34]. N^1-methyl thiosemicarbazide, N^1-ethyl

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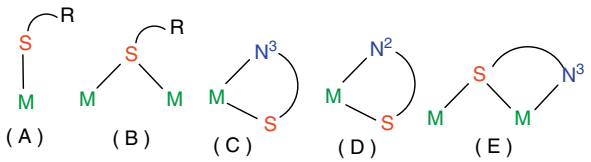
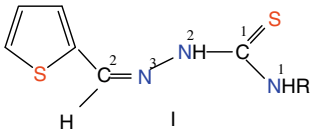


Chart 1.



I

R

Me HttscMe = thiophene-2-carbaldehyde-N^1-methyl thiosemicarbazone

Et HttscEt = thiophene-2-carbaldehyde-N^1-ethyl thiosemicarbazone

Ph HttscPh = thiophene-2-carbaldehyde-N^1-phenyl thiosemicarbazone

Chart 2.

thiosemicarbazide, N^1-phenyl thiosemicarbazide, thiophene-2-carbaldehyde and Ph_3P were procured from Aldrich Sigma Ltd. Thiosemicarbazone ligands were prepared by condensation of thiophene-2-carbaldehyde with respective thiosemicarbazides.

2.2. Measurements

Elemental analysis for C, H and N were carried out using a thermoelectron FLASHEA1112 analyser. The melting points were determined with a Gallenkamp electrically heated apparatus. The IR spectra of the ligands and the complexes were recorded in the range, 4000–200 cm^{-1} (using KBr pellets) on the FTIR-SHIMADZU 8400 Fourier Transform Spectrophotometer and on Pye–Unicam SP-3-300 spectrophotometer. ^1H NMR spectra were recorded on a JEOL AL300 FT spectrometer at 300 MHz in $CDCl_3$ with TMS as the internal reference. ^{13}C NMR spectra of complexes were recorded at a frequency of 75.45 MHz using $CDCl_3$ as solvent, and TMS as internal reference. ^{31}P NMR spectra were recorded at 121.5 MHz with o-phosphoric acid as the external reference taken as zero position.

2.3. Synthesis of compounds

2.3.1. $[Cu_2(\mu\text{-}I)_2(\eta^1\text{-}S\text{-}HttscMe)_2(Ph_3P)_2]$ **1**

To a solution of copper(I) iodide (0.025 g, 0.131 mmol) in 15 ml acetonitrile, the ligand HttscMe (0.026 g, 0.131 mmol) was added, and contents stirred for 3–4 h. It formed yellow precipitates and addition of Ph_3P (0.034 g, 0.131 mmol) followed by stirring for 5–10 min formed a yellow colored solution, which on slow evaporation at room temperature yielded yellow crystals. Yield, 0.0616 g, 72%, m.p. 200–202 °C. *Anal. Calc.* for $C_{50}H_{48}Cu_2I_2N_6S_4P_2$(%): C, 46.05; H, 3.68; N, 6.45. Found: C, 46.58; H, 3.76; N, 6.47%. IR data (KBr, cm^{-1}): 3369(s) ν(N–H); 3145(m) ν(–NH–); 2991(m) $\nu(C-H)_{Ph}$; 2767(w) $\nu(C-H)_{Me}$; ν(C=N) + ν(C=C) 1668(m), 1586(m), 1560(m); $\nu(P-C_{Ph})$ 1092(s); ν(C–N) 1027(s); ν(C=S) 852(s). ^1H NMR ($CDCl_3$, δ ppm): 11.55s (–N^2H), 8.54s (C^2H), 7.32–7.56 m ($C^{4,6}H$ + PPh_3 + N^1H), 7.06dd (C^5H), 3.15d (–CH_3). ^{13}C NMR data (δ (ppm); J (Hz), $CDCl_3$): 176.8 (C^1), 138.2 (C^2), 137.2 (C^3), 130.7 (C^6), 128.3 (C^4), 127.7 (C^5), 134.0 (o-C, J_{P-C}, 14.33, PhP), 128.6 (m-C, J_{P-C}, 9.05, PhP), 129.9 (p-C, PhP), 30.8 (CH_3). ^{31}P NMR ($CDCl_3$, δ ppm): –30.5 ppm, $\Delta\delta$ (δ complex – δ ligand) 35.11 ppm.

Complexes **2–9** are prepared by similar method

2.3.2. $[Cu_2(\mu\text{-}Br)_2(\eta^1\text{-}S\text{-}HttscMe)_2(Ph_3P)_2]$ 2

Yield, 0.0716 g, 68%, m.p. 220–222 °C. Anal. Calc. for $C_{50}H_{48}Cu_2Br_2N_6S_4P_2$(%): C, 49.62; H, 3.97; N, 6.94. Found: C, 49.69; H, 4.18; N, 6.05%. IR data (KBr, cm^{-1}): 3371(w) ν(N–H); 3144(m) ν(–NH–); 2985(m) $\nu(C-H)_{Ph}$; 2785(w) $\nu(C-H)_{Me}$; ν(C=N) + ν(C=C) 1674(m), 1591(m); $\nu(P-C_{Ph})$ 1099(s); ν(C–N) 1029(s); ν(C=S) 850(s). ^1H NMR ($CDCl_3$, δ ppm): 12.16s (–N^2H), 8.52s (C^2H), 7.31–7.52 m ($C^{4,6}H$ + PPh_3 + N^1H_2), 7.05dd (C^5H), 3.19d (–CH_3). ^{13}C NMR data (δ (ppm); J (Hz), $CDCl_3$): 173.9 (C^1), 140.7 (C^2), 137.9 (C^3), 131.8 (C^6), 127.9 (C^5), 133.9 (o-C, J_{P-C}, 15.01, PhP), 128.7 (m-C, J_{P-C}, 9.85, PhP), 130.0 (p-C, PhP), 30.6 (CH_3). ^{31}P NMR ($CDCl_3$, δ ppm): –2.71 ppm, $\Delta\delta$ (δ complex – δ ligand) 1.99 ppm.

2.3.3. $[Cu_2(\mu\text{-}Cl)_2(\eta^1\text{-}S\text{-}HttscMe)_2(Ph_3P)_2]$ **3**

Yield, 0.102 g, 72%, m.p. 222–225 °C. Anal. Calc. for $C_{50}H_{48}Cu_2Cl_2N_6S_4P_2$(%): C, 53.19; H, 4.25; N, 7.44. Found: C, 53.51; H, 3.82; N, 6.56%. IR data (KBr, cm^{-1}): 3375(s) ν(N–H); 3109(m) ν(–NH–); 2947(m) $\nu(C-H)_{Ph}$; 2788(w) $\nu(C-H)_{Me}$; ν(C=N) + ν(C=C) 1645(m), 1581(m); $\nu(P-C_{Ph})$ 1091(s); ν(C–N) 1027(s); ν(C=S) 850(s). ^1H NMR ($CDCl_3$, δ ppm): 12.54s (–N^2H), 8.46s (C^2H), 7.30–7.53 m ($C^{4,6}H$ + PPh_3 + N^1H_2), 7.06dd (C^5H), 3.20d (–CH_3). ^{13}C NMR data (δ (ppm); J (Hz), $CDCl_3$): 174.4 (C^1), 141.1 (C^2), 138.0 (C^3), 131.7 (C^6), 127.9 (C^5), 133.9 (o-C, J_{P-C}, 15.09, PhP), 128.7 (m-C, J_{P-C}, 9.81, PhP), 130.0 (p-C, PhP), 30.6 (CH_3). ^{31}P NMR ($CDCl_3$, δ ppm): –1.58 ppm, –30.3 $\Delta\delta$ (δ complex – δ ligand) 3.12, 34.96 ppm.

2.3.4. $[Cu_2(\mu\text{-}I)_2(\eta^1\text{-}S\text{-}HttscEt)_2(Ph_3P)_2]$ **4**

Yield, 0.0620 g, 71%, m.p. 230–235 °C. Anal. Calc. for $C_{52}H_{52}Cu_2I_2N_6S_4P_2$(%): C, 46.88; H, 3.91; N, 6.31. Found: C, 46.91; H, 4.10; N, 6.71%. IR data (KBr, cm^{-1}): 3371(s) ν(N–H); 3149(m) ν(–NH–); 3047(m) $\nu(C-H)_{Ph}$; 2933(m) $\nu(C-H)_{-CH_2-}$; 2856(w) $\nu(C-H)_{Me}$; ν(C=N) + ν(C=C) 1594(m), 1556(s); $\nu(P-C_{Ph})$ 1099(s); ν(C–N) 1041(s); ν(C=S) 850(s). ^1H NMR ($CDCl_3$, δ ppm): 11.51s (–N^2H), 8.54s (C^2H), 7.30–7.54 m ($C^{4,6}H$ + PPh_3 + N^1H_2), 7.06dd (C^5H), 3.64 m (–CH_3), 1.28t (–CH_2–).^{13}C NMR data (δ (ppm); J (Hz), $CDCl_3$): 172.8 (C^1), 139.5 (C^2), 137.9 (C^3), 131.6 (C^6), 128.7 (C^4), 127.8 (C^5), 134.0 (o-C, J_{P-C}, 15.08, PhP), 128.6 (m-C, J_{P-C}, 9.35, PhP), 129.8 (p-C, PhP), 38.8 (–CH_2–), 14.5 (–CH_3). ^{31}P NMR ($CDCl_3$, δ ppm): –5.07 ppm, $\Delta\delta$ (δ complex – δ ligand) –0.37 ppm.

2.3.5. $[Cu_2(\mu\text{-}Br)_2(\eta^1\text{-}S\text{-}HttscEt)_2(Ph_3P)_2]$ **5**

Yield, 0.0808 g, 75%, m.p. 210–212 °C. Anal. Calc. for $C_{52}H_{52}Cu_2Br_2N_6S_4P_2$(%): C, 50.44; H, 4.20; N, 6.79. Found: C, 50.37; H, 4.77; N, 6.83%. IR data (KBr, cm^{-1}): 3371(s) ν(N–H); 3134(m) ν(–NH–); 3045(m) $\nu(C-H)_{Ph}$; 2983(m) $\nu(C-H)_{-CH_2-}$; 2935(w) $\nu(C-H)_{Me}$; ν(C=N) + ν(C=C) 1620(m), 1594(m), 1556(s); ν(C–N) 1042(s); $\nu(P-C_{Ph})$ 1099(s); ν(C=S) 850(s). ^1H NMR ($CDCl_3$, δ ppm): 12.11s (–N^2H), 8.54s (C^2H), 7.37–7.50 m ($C^{4,6}H$ + PPh_3 + N^1H_2), 7.05dd (C^5H), 3.67 m (–CH_3), 1.28t (–CH_2–). ^{31}P NMR ($CDCl_3$, δ ppm): –2.95 ppm, $\Delta\delta$ (δ complex – δ ligand) 1.75 ppm.

2.3.6. $[Cu_2(\mu\text{-}Cl)_2(\eta^1\text{-}S\text{-}HttscEt)_2(Ph_3P)_2]$ **6**

Yield, 0.100 g, 69%, m.p. 210–212 °C. Anal. Calc. for $C_{52}H_{52}Cu_2Cl_2N_6S_4P_2$(%): C, 54.35; H, 4.53; N, 7.32. Found: C, 54.20; H, 5.12; N, 7.33%. IR data (KBr, cm^{-1}): 3362(s), 3292(s) ν(N–H); 3141(m) ν(–NH–); 3045(m) $\nu(C-H)_{Ph}$; 2975(m) $\nu(C-H)_{-CH_2-}$; 2931(w) $\nu(C-H)_{Me}$; ν(C=N) + ν(C=C) 1595(m), 1561(s); $\nu(P-C_{Ph})$ 1094(s); ν(C–N) 1047(s); ν(C=S) 850(s). ^1H NMR ($CDCl_3$, δ ppm): 12.48s (–N^2H), 8.47s (C^2H), 7.30–7.52 m ($C^{4,6}H$ + PPh_3 + N^1H_2), 7.05dd (C^5H), 3.67 m (–CH_3), 1.30t (–CH_2–). ^{31}P NMR ($CDCl_3$, δ ppm): –1.77 ppm, $\Delta\delta$ (δ complex – δ ligand) 2.93 ppm.

Though complexes **7–9** were prepared by the method similar to that for **1**, direct reactions of copper(I) halides with two mole of

thiosemicarbazome ligand (HttscPh) in 1:2 molar ratio in acetonitrile yielded identical products.

*2.3.7. [CuI(η^1-S-HttscPh)$_2$] **7***

Two types of crystals (i) *Brown crystals:* Yield, 0.05 g, 54%, m.p. 190–195 °C. *Anal. Calc.* for $C_{24}H_{22}CuIN_6S_4$(%): C, 40.42; H, 3.09; N, 11.79. Found: C, 40.25; H, 3.28; N, 11.10%. IR data (KBr, cm^{-1}): 3304(s) ν(N–H); 3118(m) ν(–NH–); 3006(m) ν(C–H)$_{Ph}$; 2937(m); ν(C=N) + ν(C=C) 1620(m), 1596(m), 1560(s); ν(C–N) 1045(s); ν(C=S) 826(s). ^{1}H NMR ($CDCl_3$, δ ppm): 11.44s (–N^{2}H), 8.87s (C^{2}H), 8.59s (C^{6}H), 7.29d (C^{4}H), 7.36–7.51 m (Ph), 7.1dd (C^{5}H) and (ii) *Colorless crystals*: 0.02 g, 36% yield, m.p. 210–215 °C. Anal. Calc. for $C_{18}H_{15}PCuI$(%): C, 47.73; H, 3.31; Found: C, 48.02; H, 3.42%.

*2.3.8. [CuBr(η^1-S-HttscPh)$_2$] **8***

Two types of crystals (i) *Brown crystals:* Yield, 0.0649 g, 56%, m.p. 212–215 °C. Anal. Calc. for $C_{24}H_{22}CuBrN_6S_4$(%): C, 43.27; H, 3.31; N, 12.62. Found: C, 43.09; H, 3.60; N, 12.91%. IR data (KBr, cm^{-1}): 3321(s) ν(N–H); 3132(m) ν(–NH–); 3028(m) ν(C–H)$_{Ph}$; 2983(m); ν(C=N) + ν(C=C) 1620(m), 1591(m), 1544(s); ν(C–N) 1043(s); ν(C=S) 828(s). ^{1}H NMR ($CDCl_3$, δ ppm): 11.80s (–N^{2}H), 8.87s (C^{2}H), 8.55s (C^{6}H), 7.29d (C^{4}H), 7.36–7.51 m (Ph), 7.1dd (C^{5}H) and (ii) *Colorless crystal*: Yield 0.03 g, 40%, m.p. 190–195 °C.

*2.3.9. [CuCl(η^1-S-HttscPh)$_2$] **9***

Two types of crystals (i) *Brown crystals:* Yield, 0.0753 g, 48%, m.p. 212–215 °C. Anal. Calc. for $C_{24}H_{22}CuClN_6S_4$(%): C, 46.38; H, 3.45; N, 13.53. Found: C, 46.21; H, 3.87; N, 13.00%. IR data (KBr, cm^{-1}): 3326(s) ν(N–H); 3138(m) ν(–NH–); 3041(m) ν(C–H)$_{Ph}$; 2978(m); ν(C=N) + ν(C=C) 1620(m), 1585(m), 1541(s); ν(C–N) 1040(s); ν(C=S) 830(s). ^{1}H NMR ($CDCl_3$, δ ppm): 11.99s (–N^{2}H), 8.89s (C^{2}H), 8.47s (C^{6}H), 7.29d (C^{4}H), 7.37–7.52 m (Ph), 7.1dd (C^{5}H) and (ii) *Colorless crystals*: Yield, 0.04 g, 48%, m.p. 185–189 °C.

2.4. X-ray crystallography

The data for **2–4**, and **9** were collected at 293 K, on a Siemens P4 diffractometer using XSCANS [35]. The θ–2θ technique was used to measure the intensities, up to a maximum of 2θ = 50°, with graphite monochromatised Mo Kα radiator (λ = 0.71073 Å). The data were corrected for Lorentz and polarization factors. An empirical psi absorption correction was applied. The structures were solved by direct methods and refined by full-matrix least-squares methods based on F^2. Hydrogen atoms were fixed geometrically and were not refined. Scattering factors from the International Tables for X-ray crystallography were used [36]. Data reduction, structure solution, refinement and molecular graphics were performed using SHELXTL-PC [37] and WINGX [38].

The data for **7** and **8** were measured on Bruker AXS SMART APEX CCD diffractometer. Data were reduced and corrected for absorption using SMART and SAINT [39]. The structures were solved by direct methods and refined by full-matrix least-squares based on F^2 with anisotropic thermal parameters for non-hydrogen atoms using SHELXTL (structure solution, refinement and some molecular graphics). All non-hydrogen atoms atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and were refined with an isotropic displacement parameter 1.5 (methyl) or 1.2 times (all others) that of the adjacent carbon or oxygen atom.

Crystals of **1** and **5** were mounted on a Bruker SMART CCD 1000 diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The unit cell dimensions and intensity data were measured at 100 K. The data were processed with SAINT [40] and corrected for absorption using SADABS (transmissions factors: 0.724–0.515) [38]. The structure was solved by direct methods using the program SHELXS-97 and refined by full-matrix least-squares techniques against F^2 using SHELXL-97 [41]. Positional and anisotropic atomic displacement parameters were refined for all non-hydrogen atoms. Hydrogen atoms bonded to carbon were placed geometrically and the N–H hydrogen atoms were initially positioned at sites determined from difference maps, but the positional parameters of all H atoms were included as fixed contributions riding on attached atoms with isotropic thermal parameters 1.2 times those of their carrier atoms. Criteria of a satisfactory complete analysis were the ratios of rms shift to standard deviation less than 0.001 and no significant features in final difference maps.

A prismatic crystal of complex **6** was mounted on an automatic Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator, and Mo Kα radiation (λ = 0.71073 Å). The unit cell dimensions and intensity data were measured at 296 K. The structures were solved by the direct methods and refined by full-matrix least-square based on F^2 with anisotropic thermal parameters for non-hydrogen atoms using XCAD-49 (data reduction), and SHELXL (absorption correction, structure solution refinement and molecular graphics) [42].

3. Results and discussion

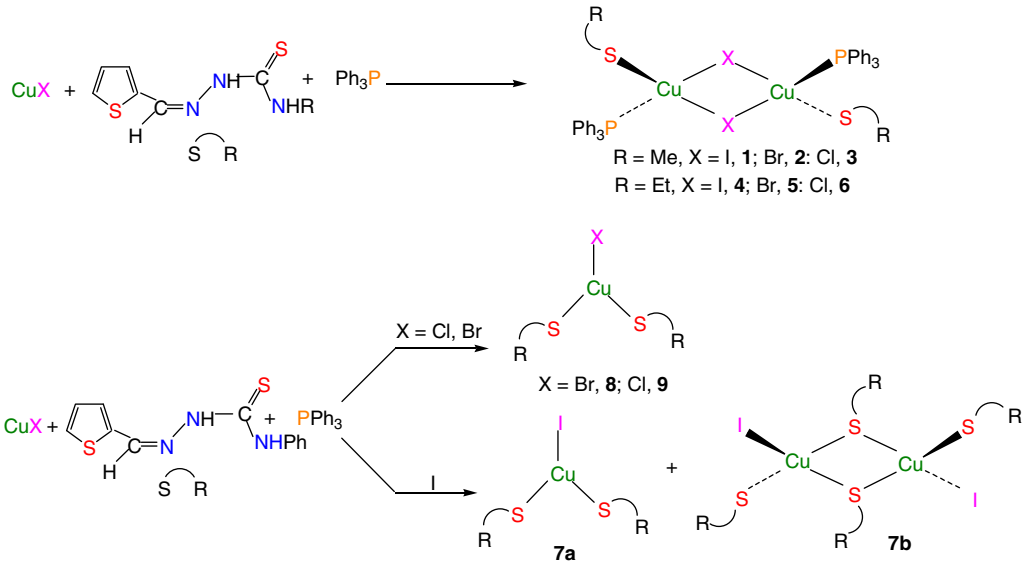
3.1. Synthetic and general properties

Thiophene-2-carbaldehyde thiosemicarbazones were reacted with copper(I) halides in the presence of triphenylphosphine and have yielded compounds of variable nuclearities. Scheme 1 depicts compounds formed with thiophene-2-carbaldehyde thiosemicarbazones (HttscMe, HttscEt, HttscPh). Direct reactions of copper(I) halides with thiosemicarbazones generally yield insoluble products, which could not be crystallized and triphenylphosphine was necessary for obtaining crystalline products.

For X = Cl, Br, I, thiophene-2-carbaldehyde thiosemicarbazones (HttscMe, HttscEt) have formed halogen-bridged dimers, [Cu$_2$(μ-X)$_2$(η^1-S-HL)$_2$(Ph$_3$P)$_2$] (HL = HttscMe, X = I, **1**; Br, **2**; Cl, **3**; HttscEt, X = I, **4**; Br, **5**; Cl, **6**) (Scheme 1). A theoretical study on copper(I) halides interaction with model thiosemicarbazone, H$_2$C=N–NH–C(=S)–NH$_2$ and PH$_3$ has shown only halogen bridging as favoured mode of bonding in dimeric copper(I) halide complexes [22]. The theoretical; studies with two water molecules H-bonded to halogens showed stabilization of sulfur-bridging for X = Cl, Br. This type of behavior has been established in [Cu$_2$(η^1-Br)$_2$(μ-S-Httsc)$_2$(Ph$_3$P)$_2$] · 2H$_2$O and [Cu$_2$(η^1-Cl)$_2$(μ-S-Httsc)$_2$(Ph$_3$P)$_2$] · 2CH$_3$CN were obtained [22]. The chlorine–water and bromine–water H-bonding being stronger than iodine–water, appear to have made sulfur bridging possible in above complexes, while for X = I, halogen bridging occurs ([Cu$_2$(μ-I)$_2$(η^1-S-Httsc)$_2$(Ph$_3$P)$_2$]) as predicted. Interestingly For X = Cl, Br, the introduction of methyl and ethyl substituents (R) at N^1 has led to the change in bridge bonding from sulfur-bridging (for Httsc) to halogen-bridging (for HttscMe and HttscEt ligands) in **2**, **3**, **5** and **6**.

The introduction of phenyl substituent at N^1(R), prevents coordination by PPh$_3$ causing copper(I) halides to bind to rather two thio-ligands resulting in three coordinated complexes [CuX(η^1-S-HttscPh)$_2$] (X = I, **7**; Br, **8**; Cl, **9**). It is possible that Ph$_3$P and thio-ligand with phenyl at N^1 nitrogen pose greater steric limiting coordination of copper(I) halides to thio-ligands only. However, the iodide complex exists as a three coordinated species (**7a**) along with its sulfur-bridged dimeric form, [Cu$_2$I$_2$(μ-S-HttscPh)$_2$(η^1-S-HttscPh)$_2$] **7b**, in the same unit cell.

The presence of both, ν(N–H) bands in the range 3304–3375 cm^{-1} (due to –N^{1}HR) and ν(N–H) bands in the range, 3109–3161 cm^{-1}, in complexes **1**–**9** support the coordination of neutral ligand. The (N–H) band of –N^{1}HR group showed high-energy shift in complexes vis-à-vis that in lies free ligands (see Supplementary material). The most characteristic thioamide band due to ν(C=S)



Scheme 1.

lies in the range 826–852 cm^{-1} in complexes **1–9** undergoes low energy shifts vis-à-vis the free ligands (856–860 cm^{-1}). This indicates the coordination of sulfur to the copper center. The $-N^1HR$ groups (R = methyl, ethyl, phenyl) in complexes appeared in the range, 2935–2767 cm^{-1}. The $\nu(P-C_{Ph})$ bands in complexes **1–6** appeared in the range, 1091−1099 cm^{-1}, and supported the presence of coordinated triphenylphosphine in all these complexes.

3.2. Crystal structure

Complexes **1–6** crystallized in triclinic system with space group $P\bar{1}$, whereas complexes **7–9** crystallized in monoclinic system with space group $P2(1)/c$. The unit cell of complex **7** contains both three coordinated (**7a**), and its dimeric unit (**7b**) (Table 1).

3.2.1. Dinuclear complexes

X-ray crystallography has shown that the thio-ligands, namely, HttscMe and HttscEt coordinate to copper(I) centers in η^1-S mode in halogen-bridged dimers $[Cu_2(\mu\text{-}X)_2(\eta^1\text{-}S\text{-}HL)_2(Ph_3P)_2]$ **1–6**. In these dimers, two bridging halogen, one P and one S atoms formed tetra-coordination around each copper atom. The central cores $Cu(\mu\text{-}X)_2Cu$ form parallelograms and Ph_3P/Htsc ligands occupy trans positions across these cores. The representative structures of these halogen-bridged dimers are shown in Figs. 1–3. It is noted that the substitution at N^1 shortens the Cu−S bond {Httsc, 2.3503(**9**) [21], HttscMe, 2.331−2.316, HttscEt, 2.306−2.298 Å} (Table 2). The Ph_3P ligands are terminally bonded and with a given substituent, the Cu–P bond distances decreases with the increase in electronegativity of the halogen atoms {HttscMe, 2.257(**1**), 2.238(**2**), 2.231(**3**); HttscEt, 2.260(**4**), 2.231(**5**), 2.227(**6**) Å}. The substituents also influence copper−halogen distance marginally as shown in Table 2. The Cu···Cu contacts lie in the range, 3.22−3.40 Å, which are greater than the sum of van der Waal's radius of copper atoms, 2.80 Å [43]. In the $Cu(\mu\text{-}X)_2Cu$ core, the angles at copper and bridging halogen atoms vary in the complementary fashion. For copper(I) iodide complexes with Httsc, HttscMe and HttscEt, the angles at iodide increase with the increase in bulk of the substituent at N^1: Httsc, 72.65°, HttscMe, 72.934°, HttscEt, 76.97°. The angles at bromine (**2**, **5**) or chlorine (**3**, **6**) are nearly unaffected with the change of the substituents at N^1. The angles around each copper atom revealed a distorted tetrahedral geometry (72.93−118.14°).

3.2.2. Three coordinated monomers

The ligand, HttscPh (R = Ph) has not formed dinuclear complexes similar to **1–6**, rather three coordinated complexes, namely, $[CuX(\eta^1\text{-}S\text{-}HttscPh)_2]$ (X = I, **7**; Br, **8** (Fig. 4); Cl, **9**) with no PPh_3 ligand bonded, were obtained. Each copper is bonded to two sulfur atoms, and one halogen atom adopting distorted trigonal planar geometry {angles, 112.63−122.45°}. However, the iodide complex has both three coordinated $[CuI(\eta^1\text{-}S\text{-}HttscPh)_2]$ **7a**, and its dimer $[Cu_2(\mu\text{-}S\text{-}HttscPh)_2(\eta^1\text{-}S\text{-}HttscPh)_2I_2]$ **7b**, moieties in the same unit cell (Fig. 5). As expected, the Cu−S/Cu−X bond distances are shorter than those in dinuclear complexes discussed above (Table 3). The three coordinated trigonal planar complexes in coinage metal thiosemicarbazone chemistry are rare [44,45].

3.3. Packing networks

In complexes **1–9**, there is intra-molecular imino hydrogen-halogen hydrogen bonding ($N^2H\cdots X$) (Chart 3). The substituted amino group (HN^1R, R = Me, Et) is engaged in strong H-bonding with azomethine (N^3) nitrogen ($N^3\cdots HN^1R$) in **1–9**. Dinuclear complexes **1–3** are interconnected via $-C-H\cdots\pi$ interactions involving phenyl rings of Ph_3P leading to the formation of 1D networks (Fig. 6). The inter-molecular H-bonding is different in complexes **4–6**. Here azomethine nitrogen is engaged in interaction with $-CH_2$ group of ethyl substituent at N^1 ($N^3\cdots HCH$, Et), resulting in a linear chain along a-axis. Two such linear chains are interconnected via phenyl–halogen interactions ($-C-H\cdots X$) yielding 2D networks (Fig. 7).

Three coordinated monomers **8** and **9** are interconnected via $-N^1HPh$ groups involving intermolecular $N^1H\cdots\pi(Ph)$ interactions forming dimers (Fig. 8). There is no intermolecular interaction in **7a** and **7b**.

3.4. Solution phase studies

In ^1H NMR spectra, the most characteristic N^2H signal in the free ligands (HttscMe, δ 9.15 ppm; HttscEt, δ 10.16 ppm; HttscPh, 11.33 ppm) showed downfield shifts in complexes **1–9**, which indicate the coordination of ligands to a metal center. Appearence of N^2H signal ensures that no deprotonation occurred during complexation. Further the C^2H signals of free ligands (HttscMe, δ 7.93 ppm; HttscEt, δ 8.15 ppm; HttscPh, δ 9.16 ppm) undergo downfield shifts in complexes **1–6** {δ 8.46–8.89 ppm} and upfield

Table 1
Crystallographic data for complexes **1**–**9**.

	Compound **1**	Compound **2**	Compound **3**	Compound **4**	Compound **5**	Compound **6**	Compound **7**	Compound **8**	Compound **9**
Formula	$C_{50}H_{48}Cu_2I_2N_6P_2S_4$	$C_{50}H_{48}Br_2Cu_2N_6P_2S_4$	$C_{50}H_{48}Cl_2Cu_2N_6P_2S_4$	$C_{52}H_{52}Cu_2I_2N_6P_2S_4$	$C_{52}H_{52}Br_2Cu_2N_6P_2S_4$	$C_{52}H_{52}Cl_2Cu_2N_6P_2S_4$	$C_{96}H_{88}Cu_4I_4N_{24}S_{16}$	$C_{24}H_{22}BrCuN_6S_4$	$C_{24}H_{22}ClCuN_6S_4$
Molecular weight (amu)	1304.00	1210.02	1121.10	1332.06	1238.08	1149.16	2852.83	666.17	621.71
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$ (no. 2)	$P\bar{1}$	$P2(1)/c$	$P2(1)/c$	$P2(1)/c$
a (Å)	10.7328(2)	11.1860(10)	11.0530(10)	11.242(5)	10.5727(3)	10.8063(13)	25.6035(10)	12.0011(6)	12.193(5)
b (Å)	10.8736(2)	11.302(2)	11.1610(10)	11.911(5)	11.2893(3)	11.3069(9)	12.2375(5)	11.7383(5)	11.722(5)
c (Å)	11.8583(2)	12.0360(10)	12.1320(10)	11.932(5)	13.0352(3)	12.7986(19)	18.4646(7)	19.7185(9)	19.676(5)
α (°)	107.1810(10)	91.580(10)	107.540(10)	92.395(5)	114.7500(10)	111.902(10)	90.00	90.00	90.000
β (°)	103.3190(10)	107.050(10)	91.470(10)	106.676(5)	93.0050(10)	92.163(11)	102.5190(10)	106.8350(10)	105.051(5)
γ (°)	94.1030(10)	113.460(10)	113.100(10)	112.062(5)	106.5950(10)	109.364(9)	90.00	90.00	90.000
V (Å^3)	1272.01(4)	1316.3(3)	1294.8(2)	1398.2(10)	1327.39(6)	1345.4(3)	5647.8(4)	2658.7(2)	2715.7(17)
Z	1	1	1	2	1	1	2	4	4
T (K)	100(2)	295(2)	295(2)	293(2)	100(2)	296(2)	298(2)	100(2)	295(2)
Calculated density (g/cm^{-3})	1.702	1.526	1.438	1.582	1.549	1.418	1.677	1.664	1.521
μ (mm^{-1})	2.318	2.585	1.188	2.111	2.566	1.146	2.188	2.665	1.236
Number of observatory reflections	7822	4898	4715	5187	5455	8559	14 031	6462	5057
Number of parameters	298	298	298	307	307	308	665	341	325
R (%)	1.72	4.96	4.12	0.0321	0.0308	4.58	4.07	4.04	7.13
wR (%)	4.00	12.50	10.56	0.0797	0.0567	8.39	9.75	9.39	16.00

Fig. 1. Structure of $[Cu_2(\mu\text{-}I)_2(\eta^1\text{-}S\text{-}HttscMe)_2(Ph_3P)_2]$ **1** with numbering scheme.

Fig. 2. Structure of $[Cu_2(\mu\text{-}Br)_2(\eta^1\text{-}S\text{-}HttscMe)_2(Ph_3P)_2]$ **2** with numbering scheme.

Fig. 3. Structure of $[Cu_2(\mu\text{-}Cl)_2(\eta^1\text{-}S\text{-}HttscMe)_2(Ph_3P)_2]$ **3** with numbering scheme (complex **4**–**6** have similar structures).

shift in **7**–**9** (δ 8.87–8.89 ppm). The ring protons of Ph_3P, which appeared in the range, δ 7.29–7.53 ppm, have obscured N^1HR^2 proton signals in these complexes. The methyl protons of $-N^1HCH_3$ appear as a doublet in the range, δ 3.15–3.19 ppm in **1**–**3**. The ethyl protons

Table 2
Important bond lengths (Å) and bond angles (°) of halogen-bridged dimers (**1**–**6**).

Complex (ligand), X	Cu–S	Cu–X	Cu–P	Cu–X–CU	X–Cu–X	Cu···Cu
1 (I)[a]	2.3306(4)	2.6917(2) 2.7278(2)	2.2570(4)	72.934(6)	107.06(2)	3.2213
2 (Br)[a]	2.3129(14)	2.5506(7) 2.5675(8)	2.2381(12)	83.39(2)	96.61(2)	3.404
3 (Cl)[a]	2.3163(13)	2.4185(11) 2.4492(11)	2.2312(11)	85.84(4)	94.16(2)	3.315
4 (I)[b]	2.3214(14)	2.7268(10) 2.7002(12)	2.2605(12)	76.971(18)	103.029(18)	3.377
5 (Br)[b]	2.2977(7)	2.4981(3) 2.5544(4)	2.2308(7)	83.635(12)	96.365(12)	3.3690
6 (Cl)[b]	2.3062(8)	2.3798(8) 2.4640(8)	2.2273(9)	85.19(3)	94.81(3)	3.279
(I)[c]	2.3505(9)	2.6466(4) 2.8171(5)	2.2613(9)	75.586(14)	104.414(14)	3.351 [21]

[a] HttscMe.
[b] HttscEt.
[c] Httsc.

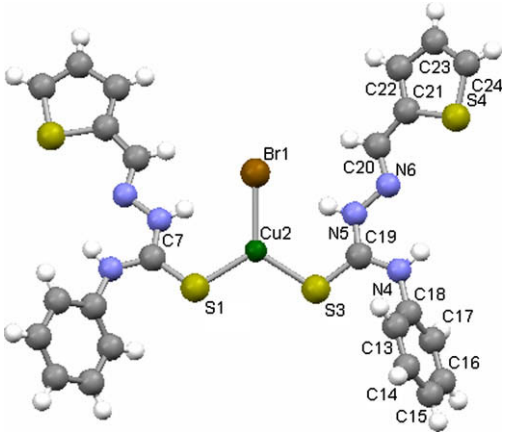


Fig. 4. Structure of [CuBr(η^1-S-HttscPh)$_2$] **8** with numbering scheme (complex **9** has similar structure).

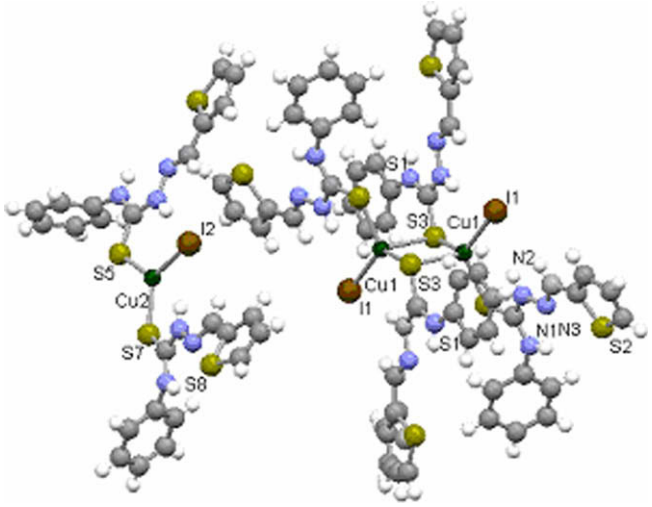
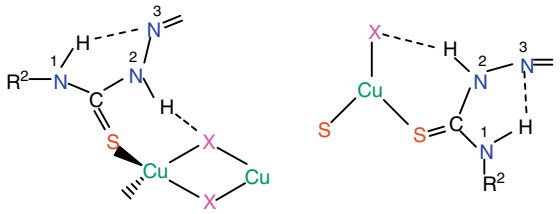


Fig. 5. Structure of complex **7** {[CuI(η^1-S-HttscPh)$_2$] [Cu_2I_2(μ-S-HttscPh)$_2$(η^1-S-HttscPh)$_2$]} with numbering scheme.

Table 3
Important bond lengths (Å) and bond angles (°) of three coordinated monomers.

Ligand complex no. (X)	Cu–X	Cu–P	Cu–S	S–CuS	X–CuS
7[a,d]	2.5876(5) (I)	–	2.2526(9); 2.2613(9)	112.63(4)	123.53(3)
8[d]	2.4207(4) (Br)	–	2.2201(8); 2.2387(7)	116.13(3)	122.45(2)
9[d]	2.295(3) (Cl)	–	2.214(3); 2.234(3)	116.21(10)	121.73(9)

[d] HttscPh.



[a]R = Me or Et, X = I, Br,Cl **1-6** [b]R = Ph; X = I, Br, Cl **7-9**

Chart 3.

of $-N^1HC_2H_5$ group appear as two sets, one multiplet (δ 3.64–3.67 ppm, CH_2); and one triplet (δ 1.27–1.30 ppm, CH_3) in complexes **4**–**6**. The coordination of ligand to copper results in a stable complex with a defined orientation of the N^1H proton. The N^1 atom becomes a stable chiral center resulting in the coupling of the N^1H proton with protons of alkyl groups (doublet of N–Me group) and a diasterotopical splitting of CH_2 of ethyl group (multiplet). The phenyl protons of $-N^1HC_6H_5$ appear in the range, δ *7.36–7.52* ppm in **7**–**9**. The C^5H protons of thiophene ring appeared as a doublet of doublet in the range, δ *7.06–7.1* ppm in these complexes, while other ring protons are obscured by protons of triphenyl phosphine.

^{13}C NMR spectra of representative complexes, namely, **1–4** showed signals for ^1C carbons at δ 176.8, 173.9, 174.3, 172.8 ppm, respectively, which are upfield vis-à-vis free ligand (HttscMe, δ 177.8 ppm **1**–**3**; HttscEt, 176.9 ppm **4**). The ^2C carbon

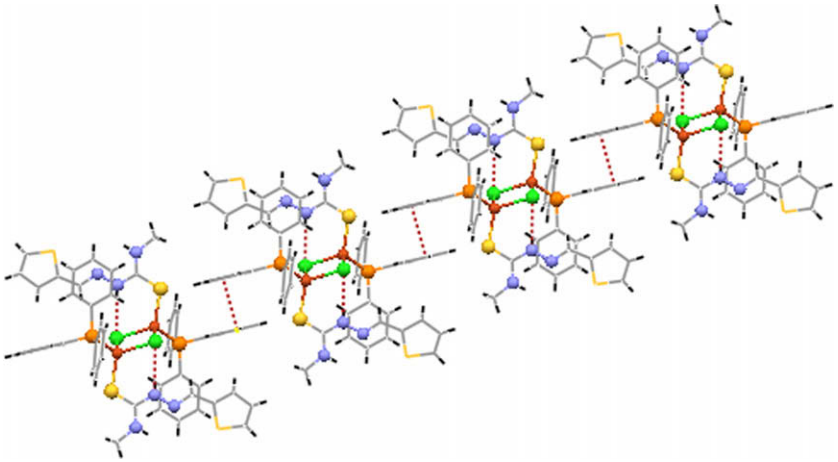


Fig. 6. Packing diagram of $[Cu_2(\mu\text{-}Cl)_2(\eta^1\text{-}S\text{-}HttscMe)_2(Ph_3P)_2]$ **3** (complexes **1** and **2** have similar packing).

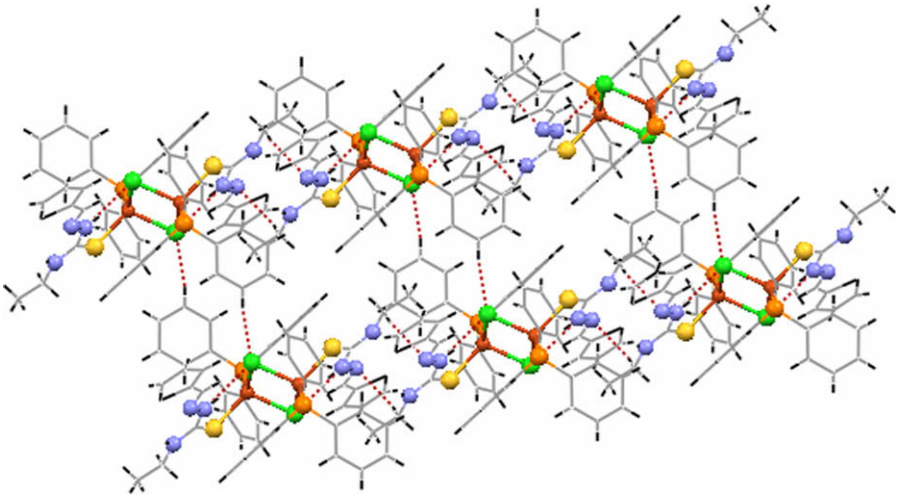


Fig. 7. Packing diagram of $[Cu_2(\mu\text{-}Cl)_2(\eta^1\text{-}S\text{-}HttscEt)_2(Ph_3P)_2]$ **6** (complexes **4** and **5** have similar packing).

signals at 139.8(**1**), 140.7(**2**), 141.1(**3**) and 139.9(**4**) ppm are low field relative to the free ligand (138.16 ppm **1**–**3**; 137.8 ppm **4**). The behavior of these complexes is similar to the literature trend [22,23]. The methyl carbon at N^1 gives signal in the range, 30.6–30.8 ppm in complexes **1**–**3**. Complex **4** showed $-CH_2-$ and CH_3- signals at 38.8 and 14.5 ppm, respectively. Further, the ring carbon signals do not show any significant shifts on complexation, but i-C, o-C, m-C and p-C signals of Ph_3P are clearly resolved in complexes.

^{31}P NMR of complexes **2**, **4**–**6** showed a single signal in the range, δ *−1.77* to δ *−5.07* ppm and are similar to those observed in case of halogen-bridged dimers in literature [22]. ^{31}P signal in complex **1** appeared at δ *−30.5* ppm with a coordination shift of $\Delta\delta$ (δ complex − δ ligand), 35.1 ppm. Such high coordination shift is a characteristic of S-bridged dimer in literature, which indicates isomerisation of iodo-bridged dimer into S-bridged dimer in complex **1** [22]. Complex **3** shows two bands at δ *−1.58* and δ *−30.3* ppm, which supports equilibrium between S-bridged dimer and halogen-bridged dimer in solution phase.

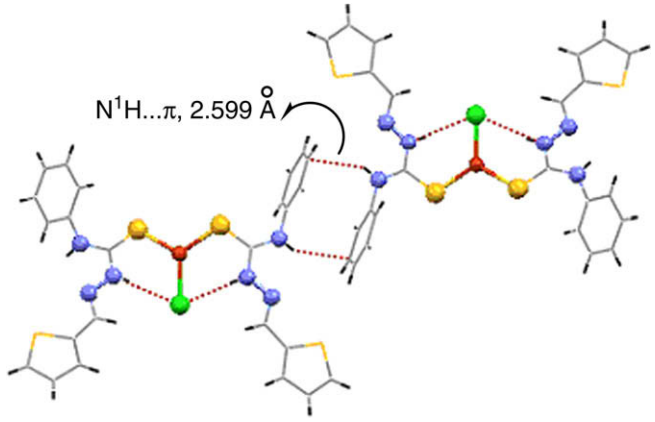


Fig. 8. Packing diagram of $[CuCl(\eta^1\text{-}S\text{-}HttscPh)_2]$ **9** (complex **8** has similar packing diagram).

4. Conclusion

The presence of methyl/ethyl (HttscMe/HttscEt) substituents at N^1 nitrogen of thio-phene-2-carbaldehyde thiosemicarbazones $\{(C_4H_3S)HC^2{=}N^3{-}N(H){-}C^1(=S)N^1HR\}$ has led to the formation of halogen-bridged dinuclear complexes **2**, **3**, **5**, **6** for X = Br, Cl, and this behavior is different from that of Httsc for these halides [22,23]. These observations strongly point to the role of sustituents at N^1 atoms in changing the nature of bridging. The effect could be steric or involving H-bond interaction, or a combination of these

factors. The presence of phenyl at N^1 has yielded three coordinated complexes **7–9**, when copper(I) halides were reacted in 1:1:1 (Cu:HttscPh:PPh_3) or 1:2 (Cu:2HttscPh) molar ratios. In each case, the product was identical, i.e. no PPh_3 was coordinating. The fact that copper(I) is preferring to bind to two thio-ligands shows that phenyl at N^1 is probably decreasing Lewis basicity of sulfur and copper is opting for two thio-ligands yielding three coordinated complexes and these complexes have strong intramolecular –$N^2H\cdots X$ interaction which probably is preventing coordination by PPh_3. Alternatively, in complexes **2**, **3**, **5**, **6** and **7–9**, it is the steric bulk at N^1 which is favouring halogen bridging or preferring a three coordinating geometry. Two monomeric units of **7a** combine via weak Cu···S bonds forming dimeric **7b** moieties.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.03.043.

CCDC 691915, 691916, 691917, 691918, 691919, 691920, 691921, 691922, 691923, 691924 and 691925 contain the supplementary crystallographic data for complexes **1**, **2**, **3**, **4**, **5**, **6**, **7**, **8**, **9**, **10** and **11**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/data_request/cif>.

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