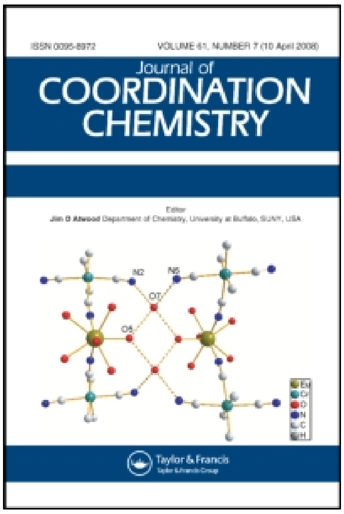

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Metal derivatives of thiosemicarbazones: crystal and molecular structures of mono- and di-nuclear copper(I) complexes with N^1-substituted thiosemicarbazones

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Metal derivatives of thiosemicarbazones: crystal and molecular structures of mono- and di-nuclear copper(I) complexes with N^1-substituted thiosemicarbazones

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The reactions of copper(II) chloride with a series of N^1-substituted thiosemicarbazones, $\{R^1(H)C^2{=}N^3{-}N^2(H){-}C^1({=}S){-}N^1HMe$, $R^1 = $ furan, Hftsc-*N*-Me; thiophene, Httsc-*N*-Me; phenyl, Hbtsc-*N*-Me$\}$ in 1 : 2 molar ratio yield copper(I) complexes : sulfur-bridged dinuclear complexes, $[Cu_2Cl_2(\mu\text{-S-Hftsc-}N\text{-Me})_2(\eta^1\text{-S-Hftsc-}N\text{-Me})_2]$ (**1**), $[Cu_2Cl_2(\mu\text{-S-Httsc-}N\text{-Me})_2(\eta^1\text{-S-Httsc-}N\text{-Me})_2]$ (**2**), and a mononuclear complex $[CuCl(\eta^1\text{-S–Hbtsc-}N\text{-Me})_2]$ (**3**). Complexes **1–3** have been characterized by elemental analysis (C, H, N), spectroscopy (IR, ^{1}H NMR) and X-ray crystallography. The $Cu(\mu\text{-}S)_2Cu$ cores in **1** and **2** form parallelograms with unequal bond distances {Cu–S, 2.2831(3), 2.5955(4) Å (**1**); 2.2641(9), 2.8006(10) Å (**2**)}. Bond angles at sulfur and copper are, Cu–S–Cu, S–Cu–S, 69.86(11), 110.12(17)° (**1**); 75.84(3), 104.16(3)° (2), respectively. The $Cu \cdots Cu$ separations are 2.806 Å (**1**) and 3.141 Å (**2**) with each copper center a distorted tetrahedron (96.67–119.28°). Bond parameters of **3**, Cu–S, 2.227(3), 2.224(3) Å, and 118.97–121.11° are different.

Keywords: Copper(I); Furan-2-carbaldehyde-*N*-methyl thiosemicarbazone; Thiophene-2-carbaldehyde-*N*-methyl thiosemicarbazone; Benzaldehyde-*N*-methyl thiosemicarbazone

1. Introduction

The coordination chemistry of aliphatic and aromatic thiosemicarbazones and their substituted derivatives have interest because of their pharmacological properties (antibacterial, antiviral, antifungal, antimicrobial, and anticancer), structural diversity, and ion sensing ability [1–10]. The structural chemistry of thiosemicarbazones with copper(I) is limited to triphenylphosphine coligand [11–15]. The ligands exhibit η^1-S (A) [13], μ_2-S (B) [14], N^3, S-chelation (C) [15], and N^3, S-chelation with S-bridging (D) [15a, c] in neutral form (scheme 1), and in the anionic form only N^2, S-chelation with S-bridging (E) has been observed [12a].

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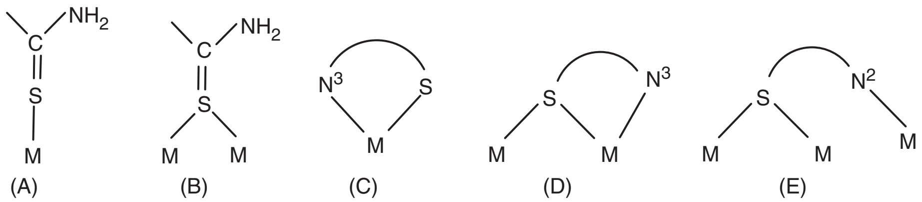


Scheme 1. Bonding modes.

There are only a few copper(I) halide complexes with thiosemicarbazones without triphenylphosphine coligand [16, 17]. This is attributed to the low solubility of copper(I)-thiosemicarbazone complexes and the tendency of copper(I) to slowly oxidize to copper(II) in the absence of coligands. Thus, tertiary phosphines are useful in enhancing solubility and stabilizing copper(I) [11–15, 19]. In this article, we report the synthesis, spectroscopy (^{1}H NMR and IR) and X-ray crystallography of copper(I) complexes with N^1-substituted thiosemicarbazones using $CuCl_2 \cdot 2H_2O$ instead of CuCl (scheme 2).

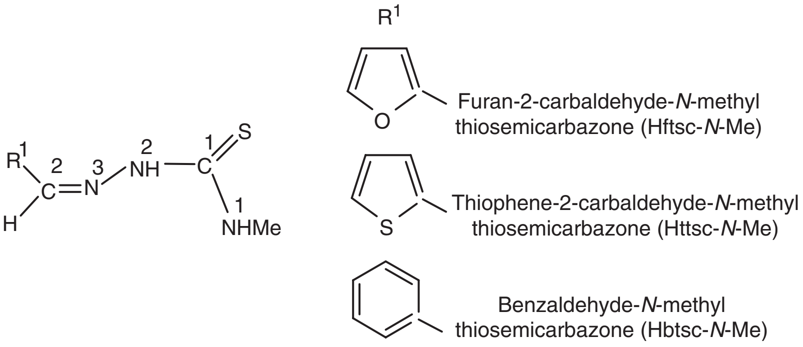
2. Experimental

Benzaldehyde, thiophene-2-carbaldehyde, furan-2-carbaldehyde, *N*-methyl thiosemicarbazide, and $CuCl_2 \cdot 2H_2O$ were procured from Sigma Aldrich Chemicals Ltd. C, H, and N analyses were obtained with a Thermo electron FLASHEA1112 CHNS analyzer. Infrared spectra were recorded as KBr pellets in the range 4000−200 cm^{-1} on a Pye–Unicam SP-3-300 spectrophotometer. Melting points were determined with a Gallenkamp electrically heated apparatus. ^{1}H NMR spectra were recorded on a JEOL AL-300 FT spectrometer operating at 300 MHz using $CDCl_3$ as solvent with TMS as internal reference.

2.1. *Synthesis of [Cu_2Cl_2(μ-S-Hftsc-N-Me)$_2$(η^1-S-Hftsc-N-Me)$_2$], 1*

To a light yellow solution of Hftsc-*N*-Me (0.022 g, 0.294 mmol) in methanol (10 mL) was added copper(II) chloride (0.025 g, 0.147 mmol) followed by stirring for 1 h. During stirring, green precipitate was formed. Upon refluxing for 1 h, yellow crystalline compound was separated and was recrystallized from a mixture of dichloromethane and acetonitrile at room temperature.

Yield: 32%; m.p. 230–232°C. Found: C, 36.09; H, 3.87; N, 18.05. $C_{28}H_{36}N_{12}Cu_2O_4S_4Cl_2$, Calcd: 36.18; H, 4.39; N, 18.06. Main IR peaks (KBr, cm^{-1}), ν(N–H), 3354 s, 3253s, (N^{1}H), 3121 s, (N^{2}H); ν(C–H), 3013 m, 2989 br, 2947 br; ν(C=N) + ν(C–C), 1588m, 1522m; ν(C–N), 1092s, 1028s, 939m; ν(C–S), 875s. ^{1}H NMR ($CDCl_3$, δ ppm): δ 11.8 (s, N^{2}H), 8.1s (C^{2}H), 7.5s (C^{4}H), 7.4s (C^{6}H + $CHCl_3$), 6.8s (C^{5}H), 6.5db (N^{1}H), 3.2d (CH_3).



Scheme 2. Ligands used.

2.2. *Synthesis of [Cu_2Cl_2(μ-S-Httsc-N-Me)$_2$(η^1-S-Httsc-N-Me)$_2$], 2*

To a light yellow solution of Httsc-*N*-Me (0.058 g, 0.293 mmol) in methanol (10 mL) was added copper(II) chloride (0.025 g, 0.147 mmol) and the contents were stirred for 1 h. During stirring, dark green compound separated and was recrystallized from a mixture of acetonitrile and methanol at room temperature.

Yield: 38%; m.p. 218–20°C. Found: C, 33.76; H, 3.62; N, 16.88. $C_{28}H_{36}N_{12}Cu_2S_8Cl_2$, Calcd: C, 33.70; H, 3.41; N, 16.85. Main IR peaks (KBr, cm^{-1}), ν(N–H), 3367s, 3269s, (N^1H), 3113s, (N^2H); ν(C–H), 3047m, 2997m, 2943br; ν(C=N) + ν(C–C), 1556s, 1529m; ν(C–N), 1090s, 1028s, 932s; ν(C–S), 850s. ^1H NMR data ($CDCl_3$, δppm,): δ 11.8s (N^2H), 8.4s (C^2H), 7.4s (C^4H), 7.3s (C^6H), 7.3s ($C^5H + CHCl_3$), 7.1s (N^1H), 3.3sb (CH_3).

2.3. *Synthesis of [CuCl(Hbtsc-N-Me)$_2$], 3*

To a solution of Hbtsc-*N*-Me (0.054 g, 0.293 mmol) in methanol (10 mL) was added copper(II) chloride (0.025 g, 0.147 mmol) and stirred for 2 h at room temperature. During stirring, white compound which separated was crystallized from a mixture of acetonitrile and methanol at room temperature.

Yield: 48%; m.p. 225–27°C. Found: C, 44.49; H, 4.53; N, 17.30. $C_{18}H_{22}N_6CuS_2Cl$, Calcd: C, 44.71; H, 4.41; N, 17.39. Main IR peaks (KBr, cm^{-1}), ν(N–H), 3367s, 3294m, (N^1H), 3115m, (N^2H); ν(C–H), 3008m, 2958br, 2935m, 2799m; ν(C=N) + ν(C–C), 1554m, 1524m; ν(C–N), 1097m, 1028m, 961m; ν(C–S), 861m. ^1H NMR data ($CDCl_3$, δ ppm): δ 11.9s (N^2H), 8.3s (C^2H), 7.7sb ($C^{4,8}H$), 7.4sb ($C^{5-7}H$), 7.3s ($N^1H + CHCl_3$), 3.2d (CH_3).

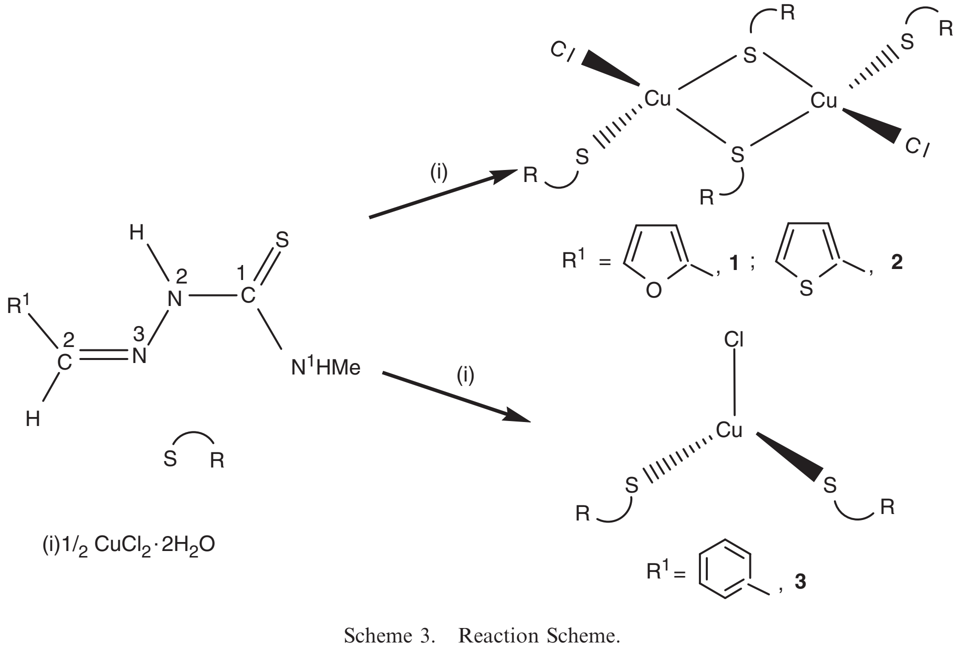
2.4. *Crystallography*

Prismatic crystals of **1** and **3** were mounted on a Bruker X8 Kappa APEXII diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The unit cell dimensions and intensity data were measured at 100(1) K for **1** and at 103 K for **3**. The data were processed with APEX2 [18a] and corrected for absorption using SADABS (transmissions factors: 1.000–0.819) [18b]. The structure was solved by direct methods using SHELXS-97 [18c] and refined by full-matrix least-squares techniques against F^2 using SHELXL-97 [18d]. Positional and anisotropic atomic displacement parameters were refined for all nonhydrogen atoms. Hydrogens were located in difference maps and included 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.

Prismatic crystals of **2** were mounted on an automatic Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator and Mo-Kα radiation ($\lambda = 0.71073$ Å). The unit cell dimensions and intensity data were measured at 296 K. The structure was solved by direct methods and refined by full-matrix least-squares based on F^2 with anisotropic thermal parameters for nonhydrogen atoms using XCAD-49 (data reduction) and SHELXL (absorption correction, structure solution refinement, and molecular graphics) (scheme 3).

3. Results and discussion

The reactions of $CuCl_2 \cdot 2H_2O$ with N^1-substituted thiosemicarbazone ligands, namely Hftsc-*N*-Me, Httsc-*N*-Me and Hbtsc-*N*-Me, yield copper(I) complexes, $[Cu_2Cl_2(\text{Hftsc-}N\text{-Me})_4]$ (**1**), $[Cu_2Cl_2(\text{Httsc-}N\text{-Me})_4]$ (**2**), and $[CuCl(\text{Hbtsc-}N\text{-Me})_2]$ (**3**) instead of copper(II) complexes, $[CuL_2]$. Direct reaction of copper(I) chloride with the ligands under similar conditions did not yield crystalline compounds and slowly oxidized to copper(II). However, following the route described in this article, a new type of dimeric



Scheme 3. Reaction Scheme.

complex has been isolated. Compounds **1**–**3** have low solubility in chloroform, dichloromethane, and acetonitrile, and are stable to air and moisture.

The IR spectra of **1**–**3** reveal the presence of the ν(N–H) bands in the range 3367–3254 cm^{-1} due to N^{1}H and 3121–3113 cm^{-1} due to N^{2}H. The presence of ν(N–H) bands due to N^{2}H suggests that the ligands coordinate to copper in the neutral form [14, 17]. Diagnostic ν(C=S) bands in the region 850–875 cm^{-1} are lower energy than the free ligands, 860–880 cm^{-1}, attributed to weakening of C=S due to coordination of thione sulfur. The ν(C–H), ν(C=N) + ν(C–C) and ν(C–H) bands also show low- and high-energy shifts vis-à-vis the free ligands. Single crystal X-ray crystallography has been used to establish the molecular structures.

3.1. *Crystal structures*

Atomic numbering schemes of **1**–**3** are shown in figures 1–3, respectively. Complexes **1** and **2** crystallize in the monoclinic system with $P2(1)/c$ and $P1(21)/a$ space groups, respectively, while **3** crystallized in the orthorhombic system with *Pbca* space group (table 1). In **1**, the copper is bonded to one Cl, two S atoms from Hftsc-*N*-Me forming a three-coordinated unit, {CuCl(Hftsc-*N*-Me)$_2$}, and two such units dimerize via sulfur to form a sulfur-bridged dimer [Cu$_2$Cl$_2$(μ-S-Hftsc-*N*-Me)$_2$(η^1-S-Hftsc-*N*-Me)$_2$] **1** (figure 1). Terminal chlorides occupy *trans* positions across the central Cu(μ-S)$_2$Cu core. The sulfur bridging is similar to dinuclear complexes of copper(I) with heterocyclic thioamides, [Cu$_2$Cl$_2$(μ-S-mimzSH)$_4$] (**4**), [Cu$_2$Br$_2$(μ-S-mimzSH)$_4$] (**5**), and

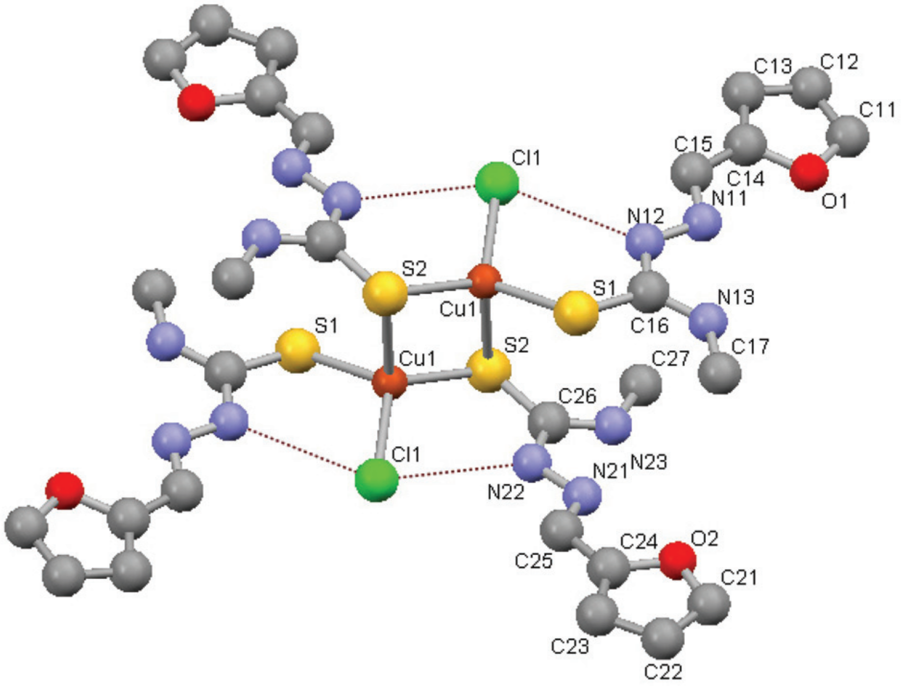


Figure 1. Structure of **1** with numbering scheme.

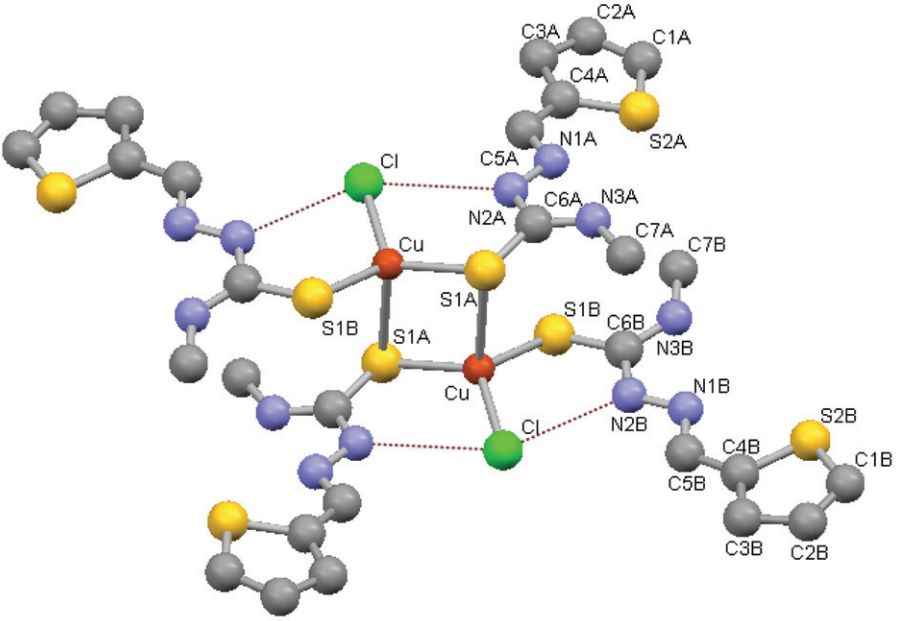


Figure 2. Structure of **2** with numbering scheme.

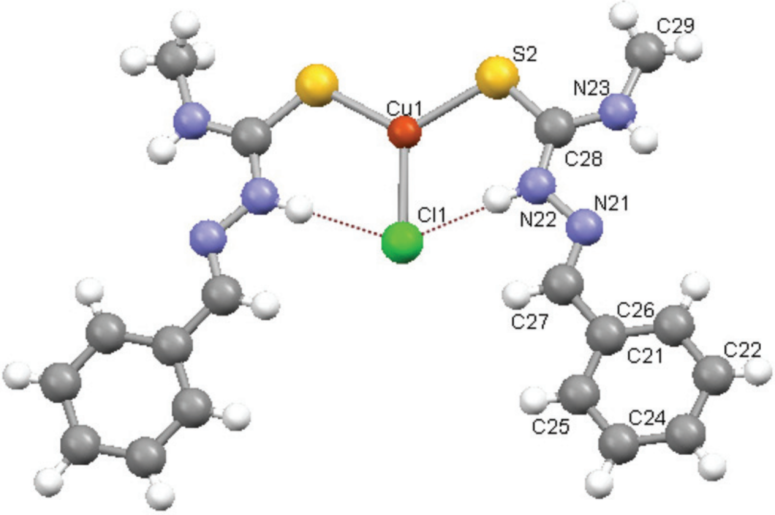


Figure 3. Structure of **3** with numbering scheme.

$[Cu_2I_2(\mu\text{-S-mimzSH})_4]$ (**6**) (mimzSH = 1-methyl-1,3-imidazoline-2-thione) [19]. The central $Cu(\mu\text{-S})_2Cu$ core in **1** forms a parallelogram with unequal Cu–S bond distances {2.283(3), 2.596(4) Å}, which are close to {2.308(4), 2.522(4) Å **4**; 2.312(6), 2.510(6) Å **5**; 2.324(2), 2.454(3) Å **6**} [19] and are also close to the sulfur bridged dinuclear thiosemicarbazone complexes, $[Cu_2Cl_2(\mu_2\text{-S-Hbsc})_2(Ph_3P)_2] \cdot 2CH_3CN$ and

Table 1. Crystallograhic data for **1**–**3**.

	1	**2**	**3**
Empirical formula	$C_{28}H_{36}Cl_2Cu_2N_{12}O_4S_4$	$C_{28}H_{36}Cl_2Cu_2N_{12}S_8$	$C_{18}H_{22}ClCuN_6S_2$
M	930.91	995.15	485.53
T(K)	100(2)	296(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2(1)/c$	$P1(21)/a$	$Pbca$
Units of dimensions (Å, °)			
a	10.7816(2)	9.9400(3)	17.0207(12)
b	18.4660(3)	18.4678(6)	11.9507(8)
c	9.7760(2)	11.3536(4)	21.8371(12)
α	90.00	90.00	90.00
β	102.8380(10)	101.652(3)	90.00
γ	90.00	90.00	90.00
V (Å^3)	1897.68(6)	2041.23(12)	4441.9(5)
Z	2	2	8
D_{Calcd} (Mg m^{-3})	1.629	1.619	1.452
μ(Mo-Kα) (mm^{-1})	1.534	1.622	1.308
Reflections collected	60,075	17,159	99,037
Independent reflections, R_{int}	4707, 0.0286	6768, 0.0346	10,794, 0.0306
Final R indices			
R_1	0.0219	0.0451	0.0338
wR_2	0.0542	0.1182	0.0753

$[Cu_2Br_2(\mu_2\text{-S-}H_2ptsc)_2(Ph_3P)_2] \cdot 2H_2O$ {2.366(6), 2.410(6) and 2.377(6), 2.404(6), respectively} (where Hbtsc = benzaldehyde thiosemicarbazone, H_2ptsc = pyrrole-2-carbaldehyde thiosemicarbazone) (table 2) [14a]. Further, the terminal Cu–S {2.271(3) Å} and Cu–Cl bond distances {2.371(3) Å} are similar to those in the literature [19]. The bond angles at each copper in **1** (96.67–118.47°) reveal that copper is in a distorted tetrahedral environment. The bond angles, Cu–S–Cu and S–Cu–S, within Cu(μ-S)Cu core at 69.86(11) and 110.12(17)° are similar to 72.42(13) and 107.57(1)° in **4** (table 3). The Cu ··· Cu distance {2.801 Å} is equal to twice the van der Waals radius of the Cu {2.80 Å} [17]. The N^2H hydrogens of both terminal and bridging ligands are engaged in intramolecular H-bonds {$N^2H_{(br.)} \cdots Cl$, $N^2H_{(ter)} \cdots Cl$} with the chlorides in **1** (table 4). The two dimeric units are interconnected via intermolecular interaction {$N^1H \cdots S^*(C{=}S)$} involving sulfur from terminal Hftsc-*N*-Me to form a 2D polymeric chain (figure 4).

The structure of **2** is similar to that of **1**. One bridging Cu–S bond distance is shorter {2.264(9) Å} and the second is longer {2.801(10) Å}, similar to those in **1**. The terminal bond distances, Cu–S {2.260(9) Å} and Cu–Cl {2.349(9) Å}, are close to those in **1**. The bond angles at each copper in **2** lie in the range 96.77–119.28° for a distorted tetrahedral environment. The bond angle Cu–S–Cu {75.84(3)°}, is larger while S–Cu–S {104.16(3)°} is less than in **1**. The Cu ··· Cu distance {3.141 Å} is longer than in **1**. H-bonding in **2** is similar to that in **1** (figure 5). The C–S bond distances of bridging {1.712(13), **1**; 1.705(3) Å, **2**} and terminal ligands {1.704(13), **1**; 1.698(3) Å, **2**} are shorter than a C–S single bond {1.81 Å} and longer than a C=S double bond {1.62 Å}, indicating partial double bond character of C=S in **1** and **2** [20].

Table 2. Selected bond lengths (Å) and angles (°) for **1–3**.

1			
Cu1–S1	2.2714(3)	S1–Cu1–S2	111.606(13)
Cu1–S2	2.28331(3)	S2–Cu1–S2$^{\#1}$	110.115(17)
Cu1–S2$^{\#1}$	2.5955(4)	S1–Cu1–S2$^{\#1}$	100.738(12)
S1–C16	1.7041(13)	S2–Cu1–Cl1	118.469(13)
Cu1–Cl1	2.3706(3)	S1–Cu1–Cl1	116.282(13)
Cu1–Cu1	2.8060(3)	Cl1–Cu1–S2$^{\#1}$	96.669(12)
S2–C26	1.7120(13)	Cu1–S2–Cu1$^{\#1}$	69.89(11)
2			
Cu–S1B	2.2600(9)	S1B–Cu–S1A	114.08(3)
Cu–S1A	2.2641(9)	S1B–Cu–S1A	96.77(3)
S1A–Cu$^{\#1}$	2.8006(10)	S1A–Cu–S1A	104.16(3)
Cu–Cl	2.3492(9)	S1B–Cu–Cl	117.66(3)
S1B–C6B	1.698(3)	S1A–Cu–Cl	119.28(3)
S1A–C6A	1.705(3)	Cl–Cu–S1A	99.19(3)
		Cu–S1A–Cu	75.84(3)
3			
Cu1–S2	2.223(3)	S2–Cu1–S1	121.106(12)
Cu1–S1	2.2269(3)	S1–Cu1–Cl1	118.968(12)
Cu1–Cl1	2.3055(3)	S2–Cu2–Cl1	119.586(12)
S2–C28	1.7122(11)		
S1–C18	1.7133(11)		

Table 3. Important bond lengths (Å) and angles (°) in Cu(μ–S)$_2$Cu cores.

Complex	Cu–S	C–S	M–S–M	S–M–S	Cu···Cu
[Cu$_2$Cl$_2$(Hftsc-*N*-Me)$_4$] (this work) **1**	2.283(3), 2.596(4)	1.712(13)	69.86(11)	110.12(17)	2.806(3)
[Cu$_2$Cl$_2$(Httsc-*N*-Me)$_4$] (this work) **2**	2.264(9), 2.801(10)	1.705(3)	75.84(3)	104.16(3)	3.141
[Cu$_2$Cl$_2$(mimzSH)$_4$] **4**	2.3075(4), 2.5218(4)	1.715(2)	72.42(13)	107.57(1)	2.858(4)
[Cu$_2$Br$_2$(mimzSH)$_4$] **5**	2.3118(6), 2.5098(6)	1.710(2)	70.49(8)	106.85(2)	2.877(6)
[Cu$_2$I$_2$(mimzSH)$_4$] **6**	2.324(2), 2.454(3)	1.722(9)	73.141(19)	109.51(8)	2.759(2)

Copper in mononuclear **3** is coordinated to one chloride and two sulfurs from terminally bonded Hbtsc-*N*-Me (η^1-S) ligands. The slightly different Cu–S bond distances {2.227(3), 2.224(3) Å} in **3** are shorter than bridging and terminal Cu–S bond distances in **1** and **2**, but similar to {2.2269(7), 2.2321(7) Å} in [CuI(η^1-S-Hbztsc)$_2$] (Hbztsc = benzophenone thiosemicarbazone) [17]. The Cu–Cl bond distance, 2.306(3) Å, and slightly unequal C–S bond distances, {1.713(11), 1.712(11) Å} in **3** are close to those in **1** and **2**. The bond angles around copper in monomeric complex **3** {118.97–121.11°} reveal a distorted trigonal planar geometry. The H-bonding pattern is different in **3**. Both N^{1}H and N^{2}H are engaged in intramolecular interactions {N^{2}H···Cl, N^{1}H···N^3} (figure 6). From the packing diagram, it is clear that phenyl groups have intermolecular interactions {(Ph)H···C(Ph)*}. Further chlorides are also engaged in intermolecular interactions {N^{1}H···Cl*, (Ph)H···Cl*} and generate a linear 2D chain.

Table 4. Hydrogen bonds (in Å) for **1–3**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
1				
N(12)–H(12A)···Cl(1)	0.86	2.35	3.2089(11)	171.8
N(13)–H(13A)···S(1)	0.84	2.52	3.2169(11)	141.54
N(22)–H(22A)···Cl(1)	0.82	2.36	3.1726(11)	172.0
2				
N(2A)–H(2AB)···Cl	0.86	2.35	3.207(3)	176.5
N(2B)–H(2BB)···Cl	0.86	2.38	3.216(3)	164.5
N(3B)–H(3BB)···S(1B)	0.86	2.65	3.321(3)	164.5
3				
N(12)–H(12A)···Cl(11)	0.88	2.26	3.1354(10)	176.6
N(13)–H(13A)···N(11)	0.87	2.28	2.6611(12)	106.4
N(13)–H(13A)···Cl(1)	0.87	2.65	3.4270(10)	149.3
N(22)–H(22A)···Cl(1)	0.88	2.31	3.1713(10)	166.6
N(23)–H(23A)···N(21)	0.86	2.25	2.6431(12)	107.7

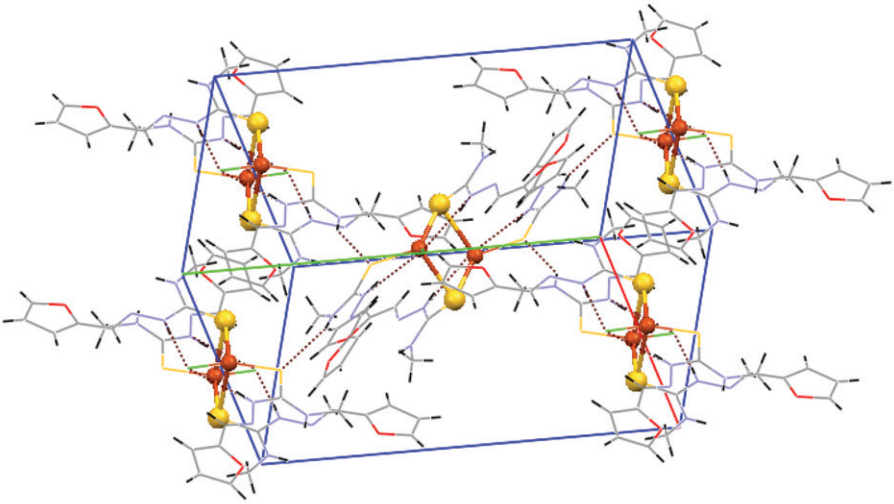


Figure 4. Packing diagram of [Cu_2Cl_2(μ-S-Hftsc-*N*-Me)$_2$(η^1-S-Hftsc-*N*-Me)$_2$].

3.2. *NMR spectroscopy*

In proton NMR spectra of compounds **1–3**, the imino hydrogen signals (N^2H) at δ 11.8, 11.8, 11.9 ppm showed downfield shifts vis-à-vis the free ligands (δ 10.8, 9.2, 9.4 ppm), respectively, confirming that the ligands coordinate to copper in the neutral form. The signals due to C^2H and N^1H protons {δ 8.1, 6.5, **1**; 8.4, 7.1, **2**; 8.3, 7.3 ppm, **3**, respectively} shift downfield vis-à-vis the free ligands (Supplementary Material). The N^1CH_3 protons are a doublet in **1** and **3** {δ 3.2 ppm, $J_{CH3} = 4.2$ Hz; 3.2 ppm, $J_{CH3} = 4.8$ Hz, respectively} and a broad singlet in **2** at δ 3.3 ppm. Aromatic protons in these complexes appear in the range δ 6.7–7.7 ppm.

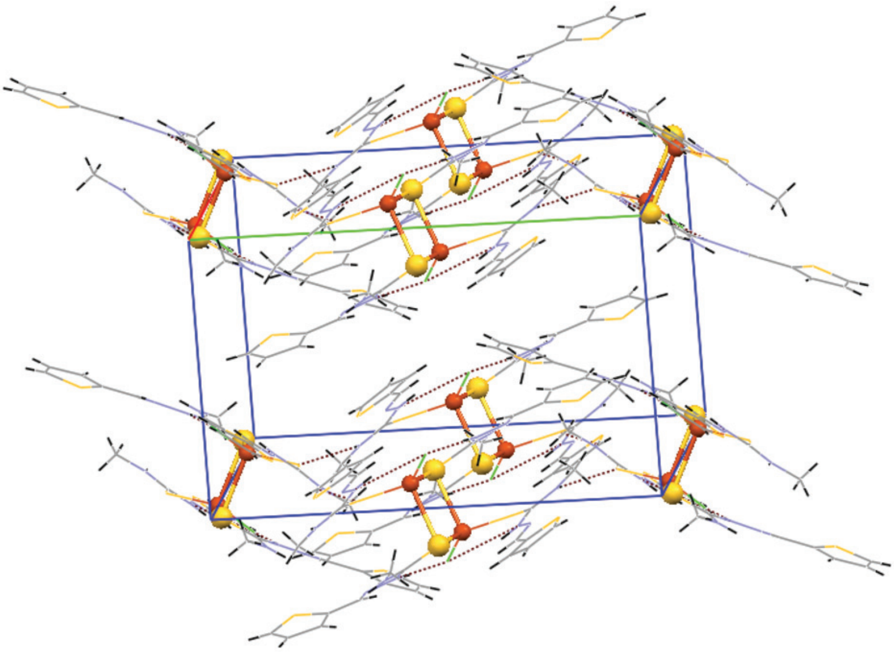


Figure 5. Packing diagram of [$Cu_2Cl_2(\mu$-S-Httsc-*N*-Me$)_2(\eta^1$-S-Httsc-*N*-Me$)_2$].

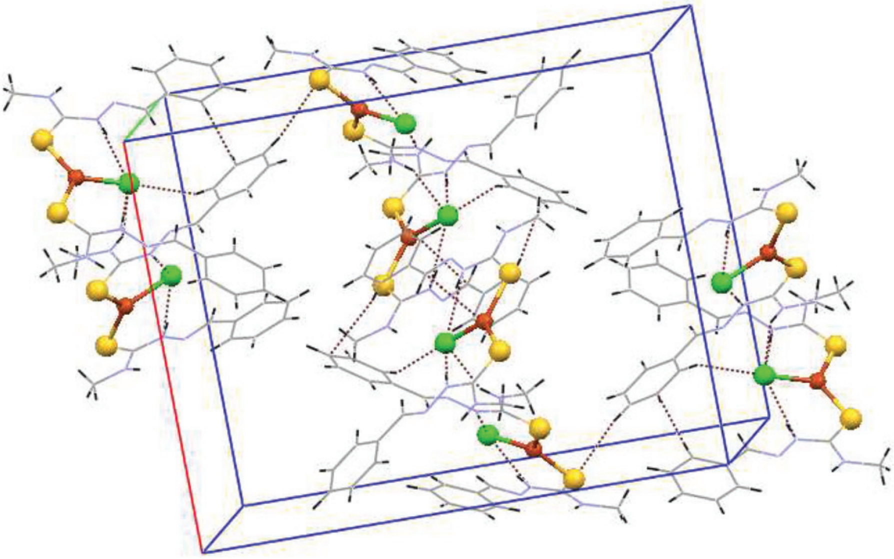


Figure 6. Packing diagram of [CuCl(η^1-S-Hbtsc-*N*-Me$)_2$].

4. Conclusion

New dinuclear complexes of copper(I) with N^1-substituted thiosemicarbazone ligands, namely [$Cu_2Cl_2(\mu$-S-Hftsc-*N*-Me$)_2(\eta^1$-S-Hftsc-*N*-Me$)_2$] and [$Cu_2Cl_2(\mu$-S-Httsc-*N*-Me$)_2(\eta^1$-S-Httsc-*N*-Me$)_2$], are reported. Similarly, a mononuclear complex

[CuCl(η^1-S-Hbtsc-*N*-Me)$_2$] **3**, represents a new example of three-coordinated copper(I) complex with a thiosemicarbazone [16, 17]. In these complexes 2D polymeric chains are formed by intermolecular interactions, {$N^1H \cdots S^*(C{=}S)$, **1**, **2**; {$(Ph)H \cdots C(Ph)^*$, $N^1H \cdots Cl^*$, $(Ph)H \cdots Cl^*$, **3**}.

Supplementary material

Full details have been deposited with the Cambridge Crystallographic Data Centre, CCDC: for **1**–**3** is 693855–693857. 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).

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