

Synthesis, molecular structures and ESI-mass studies of copper(I) complexes with ligands incorporating N, S and P donor atoms

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Abstract. Equimolar reaction of copper(I) bromide with 2-thiouracil (tucH₂) in acetonitrile-methanol formed a light yellow solid which on subsequent treatment with a mole of triphenyl phosphine (PPh₃) in chloroform has yielded a sulfur-bridged dinuclear complex, [Cu₂Br₂(μ-S-tucH₂)₂(PPh₃)₂].2CHCl₃ **1**. A reaction of copper(I) bromide with two moles of 2,4-dithiouracil (dtucH₂) in acetonitrile-methanol followed by addition of two moles of PPh₃, designed to form [Cu(μ-S,S-dtuc)₂(PPh₃)₄Cu] **2a**, instead resulted in the formation of previously reported polymer, {CuBr(μ-S,S-dtuc)(PPh₃)_n} **2**. Reaction of copper(I) iodide with 2-thiouracil (tucH₂) and PPh₃ in 1:1:2 molar ratio (Cu:H₂tuc:PPh₃) as well as that of copper(I) thiocyanate with pyridine-2-thione (pySH) or pyrimidine-2-thione (pymSH) and PPh₃ in similar ratio, yielded an iodo-bridged unsymmetrical dimer, [(PPh₃)₂(μ-I)₂Cu(PPh₃)] **3** and thiocyanate bridged symmetrical dimer, [(PPh₃)₂Cu(μ-N,S-SCN)₂Cu(PPh₃)₂] **4**, respectively. In both the latter reactions, thio-ligands which initially bind to Cu metal center, are de-ligated by PPh₃ ligand. Crystal data: **1**, P2₁/c: 173(2) K, monoclinic, a, 13.4900(6); b, 17.1639(5); c, 12.1860(5) Å; β, 111.807(5)°; R, 5.10%; **2**, Pbc_a: 296(2) K, orthorhombic, a, 10.859(3); b, 17.718(4); c, 23.713(6) Å; α = β = γ, 90°; R, 4.60%; **3**, P2₁: 173(2) K, monoclinic, a, 10.4208(7); b, 20.6402(12); c, 11.7260(7) Å; β, 105.601(7)°; R, 3.97%; **4**, P-1: 173(2) K, triclinic, a, 10.2035(4); b, 13.0192(5); c, 13.3586(6) Å; α, 114.856(4); β, 92.872(4)°; γ, 100.720(4)°; R, 3.71%. ESI-mass studies reveal different fragments of complexes.

Keywords. 2-Thiouracil; 2,4-dithiouracil; pyridine-2-thione; pyrimidine-2-thione; copper(I) bromide; copper(I) thiocyanate.

1. Introduction

The coordination chemistry of heterocyclic thioamide ligands, namely, pyridine-2-thiones, 2-thiouracils, 2,4-dithiouracils, imidazolidine-2-thiones and thiazolidine-2-thiones with transition/main-group metals has been the focus of many investigators describing synthesis and structures of compounds as well as their biochemical applications.^{1–42} Among applications, copper complexes have shown antitumor, anti-inflammatory and antimicrobial activities.^{2,14–16} Chart 1 shows the ligands under study. It is known that 2-thiouracil (tucH₂) with copper(I) has formed only mono-nuclear trigonal planar, [CuCl(κ¹-S-tucH₂)₂],¹⁷ and tetrahedral, [CuCl(κ¹-S-tucH₂)₂(PPh₃)₂]¹⁸ complexes. Further, 2-thiouracils have yielded mononuclear complexes with several other metals, namely, ruthenium(II),¹⁹ cobalt(III),^{20–22} gold(I),^{23–27} zinc(II),^{28,29} mercury(II)³⁰ and thallium(III).³¹ As regards dithiouracil (dtucH₂), with copper(I) halides

it has yielded mononuclear [CuBr(κ²-P,P-dppbz)(κ¹-S-dtucH₂)]{dppbz = 1,2-bis(diphenylphosphanyl)benzene},³² dinuclear [Cu₂(μ-X)(κ¹-S,κ¹-S-dtucH)(PPh₃)₄] (X = Cl, Br),³³ and polynuclear complexes [Cu(μ-S,S-dtucH₂)(PPh₃)X]_n (X = Cl, Br, I),³⁴ and with other metals, namely, silver(I), cobalt(III), titanium(III) and ruthenium(II),^{19,35–37} it has formed only mononuclear complexes.

Further, the coordination chemistry of copper(I) halides is well documented,^{1–3,10–13,17,18} however, there are only a few mononuclear complexes of heterocyclic thioamides with copper(I) thiocyanate or mercury(II) thiocyanate, namely, [Cu(NCS)L₂] (L = 1,3-imidazolidine-2-thione),^{38,39} [Cu(NCS)L(PPh₃)₂] (L = 4,6-dimethyl-pyrimidine-2-thione),⁴⁰ Hg(SCN)₂L₂] (L = tetrahydropyrimidine-2-thione),⁴¹ and one polymer, {Cu₂(μ-S-L)₂(μ-SCN)₂}_n (L = 1,3-imidazolidine-2-thione).⁴² In the present investigation, some reactions of 2-thiouracil, 2,4-dithiouracil, pyridine-2-thione and pyrimidine-2-thione with copper(I) halides/pseudo halides in presence of triphenylphosphine have been

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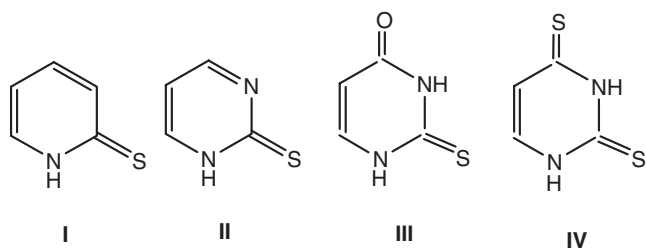


Chart 1. Molecular structures of thioligands under study.

carried out and the results of the study are reported in this paper.

2. Experimental

2.1 Materials

Copper(I) bromide/iodide/thiocyanate were prepared by reducing an aqueous solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ using SO_2 in the presence of NaX ($\text{X} = \text{Br}, \text{I}, \text{SCN}$) in water. The thio-ligands pyridine-2-thione, pyrimidine-2-thione, 2-thiouracil and 2,4-dithiouracil were procured from Sigma–Aldrich Ltd. Solvents were of Analytical Research grade and used as such. The IR spectrum was recorded using KBr pellets on Varian 660 FT IR in the $4000\text{--}200\text{ cm}^{-1}$ range. The ESI-mass spectra were recorded in DMSO using Bruker Daltonik LS-MS high resolution microTOF-Q II 10356.

2.2 Synthesis of $[\text{Cu}_2\text{Br}_2(\mu\text{-S-tucH}_2)_2(\text{PPh}_3)_2] \cdot 2\text{CHCl}_3$ (1)

To a colorless solution of copper(I) bromide (0.025 g, 0.17 mmol) in acetonitrile (5 mL) was added a solution of 2-thiouracil (0.022 g, 0.17 mmol) in methanol (5 mL) and the resulting solution was stirred for about 24 h at room temperature. The mother liquor was removed and the light yellow solid left was placed in chloroform. To it was added triphenylphosphine (0.045 g, 0.17 mmol) and stirred for 30 min and it formed a clear solution. Slow evaporation of this solution yielded light yellow crystals, which were characterized using X-ray crystallography. Yield: 0.059 g; 64%; M.p. $178\text{--}180^\circ\text{C}$. Main IR peaks (KBr, cm^{-1}): ν (O-H), 3435w; ν (N-H), 3150m; ν (C-H), 3075m, 3015w, 2965w; ν (C-N) + δ (C-H) 1580m, 1475s; 1430s, 1319m, ν (C-S) 1150m; ν (P-C), 1090(s); 1025m, 989m, 920w, 848m, 740m, 690s, 518m. ESI-mass data: (A) m/z 403.03(obsvd.), 403.94 (calcd.), formula, $\text{C}_{18}\text{H}_{15}\text{BrCuP}$, species, $[\text{CuBr}(\text{PPh}_3)]^+$; (B) m/z 587.11(obsvd.), 587.11 (calcd.), formula, $\text{C}_{36}\text{H}_{30}\text{CuP}_2$, species, $[\text{Cu}(\text{PPh}_3)_2]^+$; (C) m/z 728.95(obsvd.), 728.96 (calcd.), formula, $\text{C}_{36}\text{H}_{30}\text{BrCu}_2\text{P}_2$, species, $[\text{Cu}_2\text{Br}$

$(\text{PPh}_3)_2]^+$; (D) m/z 991.04(obsvd.), 991.72 (calcd.), formula, $\text{C}_{30}\text{H}_{27}\text{Br}_2\text{Cu}_3\text{N}_6\text{O}_3\text{PS}_3$, species, $[\text{Cu}_3\text{Br}_2(\text{H}_2\text{uc})_3(\text{PPh}_3)_2]^+$.

2.3 Synthesis of $\{\text{CuBr}(\mu\text{-S,S-dtucH}_2)(\text{PPh}_3)\}_n$ (2)

To a colorless solution of copper(I) bromide (0.025 g, 0.17 mmol) in acetonitrile (5 mL) was added a solution of 2, 4-dithiouracil (0.050 g, 0.35 mmol) in methanol (5 mL) and the resulting solution was stirred for about 24 h at room temperature. To the green precipitate formed was added solid PPh_3 (0.091 g, 0.35 mmol) and the contents stirred until a clear solution was obtained. The slow evaporation of the solution at room temperature formed red crystals which were characterized using X-ray crystallography. The formation of the product $[\text{Cu}(\mu\text{-S,S-dtuc})_2(\text{PPh}_3)_4\text{Cu}]$ was expected, however, X-ray crystallography supported the formation of $\{\text{CuBr}(\mu\text{-S,S-dtucH}_2)(\text{PPh}_3)\}_n$ 2. Yield: 0.068 g; 72%; M.p. $288\text{--}290^\circ\text{C}$. Lack of solubility prevented recording of ESI-mass spectrum.

2.4 Synthesis of $[(\text{PPh}_3)_2\text{Cu}(\mu\text{-I})_2\text{Cu}(\text{PPh}_3)]$ (3)

To a colorless solution of copper(I) iodide (0.015 g, 0.08 mmol) in acetonitrile (5 mL) was added a solution of 2-thiouracil (0.011 g, 0.08 mmol) in methanol (5 mL) and the resulting solution was stirred for about 24 h at room temperature. To it was added triphenylphosphine (0.041 g, 0.16 mmol), stirred for 30 min and it formed a clear solution. Slow evaporation of this solution yielded colorless crystals which were characterized using X-ray crystallography. The formation of product, $[\text{CuI}(\kappa^1\text{-S-tucH}_2)(\text{PPh}_3)_2]$ was expected, however, X-ray crystallography supported the formation of unsymmetrical dinuclear complex, $[(\text{PPh}_3)_2(\mu\text{-I})_2\text{Cu}(\text{PPh}_3)]$ 3. Yield: 0.062 g; 67%; M.p. $184\text{--}185^\circ\text{C}$. ESI-mass data: (A) m/z 587.07(obsvd.), 587.11 (calcd.), formula, $\text{C}_{36}\text{H}_{30}\text{CuP}_2$, species, $[\text{Cu}(\text{PPh}_3)_2]^+$; (B) m/z 603.06(obsvd.), 603.10 (calcd.), formula, $\text{C}_{36}\text{H}_{30}\text{CuP}_2\text{O}$, species, $[\text{Cu}(\text{OPPh}_3)(\text{PPh}_3)]^+$; (C) m/z 849.13(obsvd.), 849.20(calcd.), formula, $\text{C}_{54}\text{H}_{45}\text{CuP}_3$, species, $[\text{Cu}(\text{PPh}_3)_3]^+$; (D) m/z 992.97(obsvd.), 993.11 (calcd.), formula, $\text{C}_{54}\text{H}_{45}\text{CuIOP}_3$, species, $[\text{CuI}(\text{PPh}_3)_2(\text{OPPh}_3)]^+$.

2.5 Synthesis of $[(\text{PPh}_3)_2\text{Cu}(\mu\text{-N,S-SCN})_2\text{Cu}(\text{PPh}_3)_2]$ (4)

To a colorless solution of copper(I) thiocyanate (0.015 g, 0.12 mmol) in acetonitrile (10 mL) was added solid pyridine-2-thione (0.014 g, 0.12 mmol) and the resulting solution was stirred for about 24 h at room temperature. It led to the formation of red precipitate

and addition of triphenylphosphine (0.065 g, 0.24 mmol) in chloroform (5 mL) formed a clear solution. Slow evaporation of this solution yielded yellow crystals which were characterized using x-ray crystallography. It was designed to obtain $[\text{Cu}(\text{SCN})(\kappa^1\text{-S-pySH})(\text{PPh}_3)_2]$, however, X-ray crystallography supported the formation of $[(\text{PPh}_3)_2\text{Cu}(\mu\text{-N,S-SCN})_2\text{Cu}(\text{PPh}_3)_2]$ **4**. Similarly, with pyrimidine-2-thione, the expected product $[\text{Cu}(\text{SCN})(\kappa^1\text{-S-pymSH})(\text{PPh}_3)_2]$ could not be obtained, rather

the identical product **4** was formed. Yield: 0.125 g; 78%; M.p. 182–184°C. ESI-mass data: (A) m/z 587.17 (obsvd.), 587.11 (calcd.), formula, $\text{C}_{36}\text{H}_{30}\text{CuP}_2$, species, $[\text{Cu}(\text{PPh}_3)_2]^+$; (B) m/z 603.16 (obsvd.), 603.11 (calcd.), formula, $\text{C}_{36}\text{H}_{30}\text{CuP}_2\text{O}$, species, $[\text{Cu}(\text{OPPh}_3)(\text{PPh}_3)]^+$; (C) m/z 849.28 (obsvd.), 849.20 (calcd.), formula, $\text{C}_{54}\text{H}_{45}\text{CuP}_3$, species, $[\text{Cu}(\text{PPh}_3)_3]^+$; (D) m/z 970.19 (obsvd.), 970.10 (calcd.), formula, $\text{C}_{55}\text{H}_{45}\text{Cu}_2\text{NP}_3\text{S}$, species, $[(\text{PPh}_3)\text{Cu}(\text{SCN})\text{Cu}(\text{PPh}_3)_2]^+$.

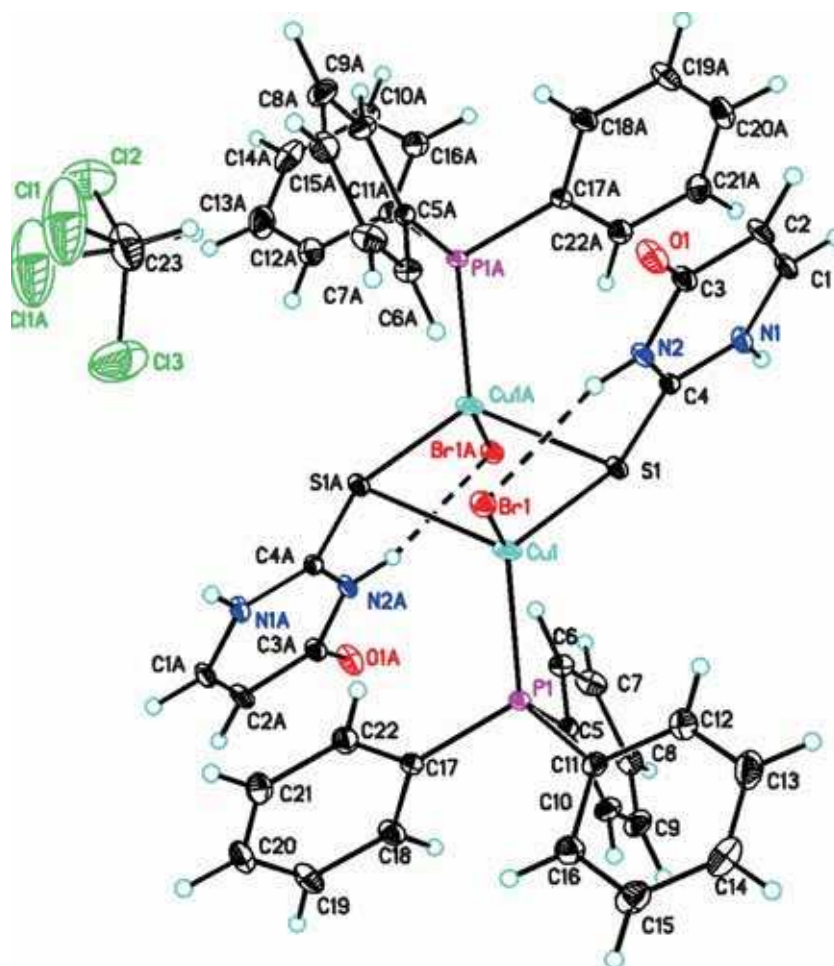


Figure 1. Molecular structure of $[\text{Cu}_2\text{Br}_2(\mu\text{-S-tucH}_2)_2(\text{PPh}_3)_2] \cdot 2\text{CHCl}_3$ **1**.

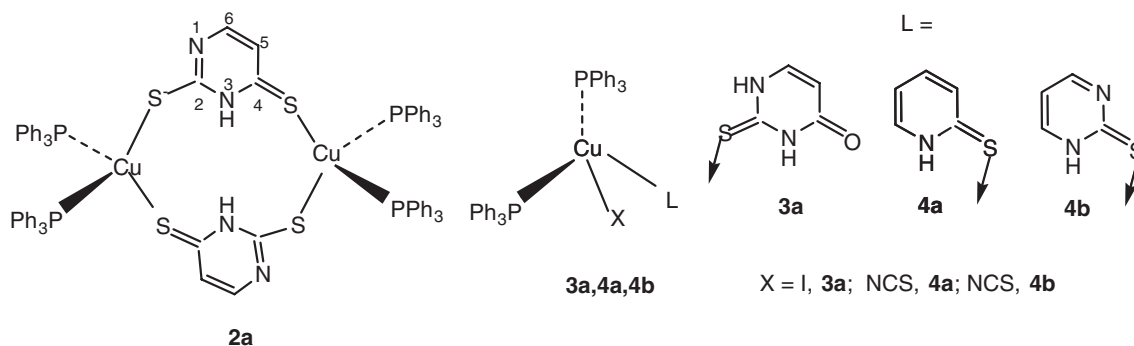


Chart 2. A view of bonding pattern of expected complexes from the reactions 2 to 4.

2.6 X-ray crystallography

A single crystal was mounted on a glass fiber and used for data collection with a Xcalibur, Eos, Gemini (**1**, **3-4**, 173(2) K) or with a Bruker Kapa – Apex (II) CCD diffractometer (**2**; 296(2) K) both equipped with graphite monochromated Mo- $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$). The data recorded at low temperature was processed with CrysAlisPro CCD (data collection), CrysAlisPro RED (cell refinement, data reduction).⁴³ The structure was solved by direct methods using the program SHEXS-97, refined by full-matrix least-squares techniques against F^2 using SHELX-97 and molecular graphics from SHELXL.⁴⁴ The data collected at room temperature was also processed with Bruker Kapa – Apex(II) CCD and corrected for absorption using SADABS.¹⁰ The structures were solved by direct methods using SIR-92 software⁴⁵ and refined by full-matrix least-squares method based on F^2 using the program using SHELX-97.⁴⁴ Atomic scattering factors were taken from “International Tables for Crystallography”.⁴⁶

3. Results and Discussion

3.1 Synthesis and general comments

The addition of solution of tucH_2 in methanol to copper(I) bromide solution in acetonitrile followed by stirring gave light yellow precipitate. The precipitate was

suspended in chloroform and addition of triphenylphosphine (equimolar reaction, $\text{Cu:tucH}_2:\text{PPh}_3:: 1:1:1$) formed a clear solution which on slow evaporation gave crystals whose single crystal X-ray crystallographic study supported the formation of dinuclear complex $[\text{Cu}_2\text{Br}_2(\mu\text{-S-tucH}_2)_2(\text{PPh}_3)_2]\cdot 2\text{CHCl}_3$ **1** (figure 1). The reaction of copper(I) iodide with tucH_2 and PPh_3 in 1:1:1 molar ratio in $\text{CH}_3\text{CN-MeOH}$ mixture (1:1 v/v) did not give a crystalline product similar to **1** and thus reaction in presence of two moles of PPh_3 was carried out in same $\text{CH}_3\text{CN-MeOH}$ mixture. From this reaction, it was expected to obtain the product, $[\text{CuI}(\kappa^1\text{-S-tucH}_2)(\text{PPh}_3)_2]$ **3a** (chart 2). However, X-ray crystallography supported the formation of a dinuclear complex, $[(\text{PPh}_3)_2(\mu\text{-I})_2\text{Cu}(\text{PPh}_3)]$ **3** (figure 3). Here in this reaction, the thio-ligand initially clearly binds to the metal center (yellow precipitate), but the addition of PPh_3 replaced tucH_2 yielding the colorless dimer **3**. Reaction of copper(I) thiocyanate with pySH (or pymSH) and PPh_3 (1:1:2 molar ratio) in acetonitrile-chloroform was designed to obtain mononuclear complexes, $[\text{Cu}(\text{SCN})(\kappa^1\text{-S-L})(\text{PPh}_3)_2]$ (chart 2, L = pySH , **4a**; pymSH , **4b**), however, X-ray crystallography supported the formation of dinuclear complex $[(\text{PPh}_3)_2\text{Cu}(\mu\text{-N,S-SCN})_2\text{Cu}(\text{PPh}_3)_2]$ **4** in each case (figure 4). Here, in these reactions also, the thio-ligands pySH (or pymSH) gave red precipitate with copper(I) thiocyanate suggesting binding to metal center, but the addition of PPh_3 deligated the thio-ligands yielding dinuclear complex **4**

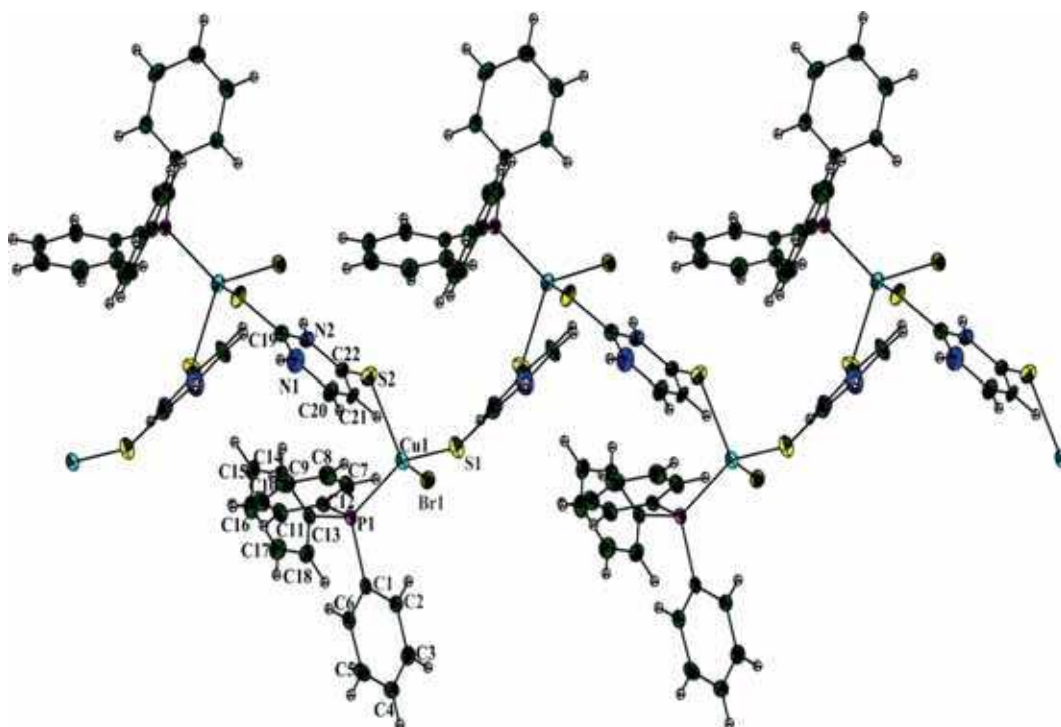


Figure 2. Structure of polymer $\{\text{CuBr}(\mu\text{-S,S-dtucH}_2)(\text{PPh}_3)\}_n$ **2**.

in each case. Finally, reaction of copper(I) bromide with 2, 4-dithiouracil and PPh₃ in acetonitrile-methanol in 1:2:2 molar ratio was designed to obtain [Cu(μ-S,S-dtuc)₂(PPh₃)₄Cu] **2a** (chart 2), however, X-ray crystallography supported the formation of polymer, {CuBr(μ-S,S-dtucH₂)(PPh₃)_n} **2** (figure 2).

3.2 IR spectra and molecular structure of [Cu₂Br₂(μ-S-tucH₂)₂(PPh₃)₂].2CHCl₃ **1**

The IR spectral data support the presence of both thio-ligand triphenylphosphine in complex **1**. The ν(N-H) and ν(O-H) bands appeared at 3150(m) and 3435(w) cm⁻¹, respectively, suggesting that thio-ligand tucH₂ is coordinating to the metal center as neutral ligand. Similarly, the diagnostic ν(C-S) band occurred at 1150(m) cm⁻¹ which is at low energy relative to the free ligand. The ν(P-C_{ph}) band at 1090(s) cm⁻¹ showed the presence of PPh₃ in complex **1**.

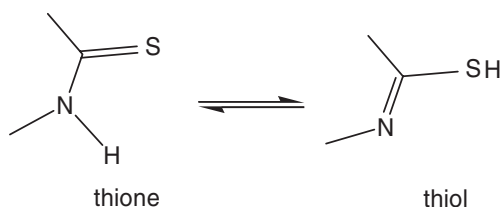
The molecular structure of dinuclear complex [Cu₂Br₂(μ-S-tucH₂)₂(PPh₃)₂].2CHCl₃ **1** is shown in figure 1. Compound **1** crystallized in monoclinic crystal system in P2₁/c space group (table 1). Each Cu metal atom is bonded to two bridging sulfur atoms at Cu-S bond distances of 2.3004(8), 2.5969(9) Å, to one P donor atom at Cu-P bond distance of 2.2325(8) Å and to one halogen atom at Cu-Br bond distance of 2.4137(5) Å (table 2). The central core Cu₂S₂ of the dinuclear complex comprises a parallelogram with unequal Cu-S bond distances as noted above. The Cu-S-Cu and S-Cu-S bond angles of 77.79(3) and 102.21(3)°, respectively are typical of Cu₂S₂ cores in different dinuclear complexes.⁴⁷ The angles around each Cu metal center vary in the range, 99 to 117° suggesting distorted tetrahedral geometry. The C-S bond distance of 1.696(3) Å is in between the C=S double-bond length of 1.62 Å and the C-S single-bond length of 1.81 Å.^{48,49} This shows weakening of C-S bond on coordination but there is considerable double-bond character in it.

Table 1. Crystal data for compounds **1-4**.

	1	2	3	4
Empirical formula	C ₄₄ H ₃₈ Br ₂ Cu ₂ N ₄ -2P ₂ S ₂ ·2(CHCl ₃)	C ₂₂ H ₁₉ BrCuN ₂ PS ₂	C ₅₄ H ₄₅ Cu ₂ I ₂ P ₃	C ₇₄ H ₆₀ Cu ₂ N ₂ P ₄ S ₂
T(K)	173(2)	296(2)	173(2)	173(2)
M	1306.48	549.95	1167.69	1292.32
λ (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Triclinic
Space group	P2 ₁ /c	Pbca	P2 ₁	P-1
		Unit cell dimensions		
a(Å)	13.4900(6)	10.859(3)	10.4208(7)	10.2035(4)
b(Å)	17.1639(5)	17.718(4)	20.6402(12)	13.0192(5)
c(Å)	12.1860(5)	23.713(6)	11.7260(7)	13.3586(6)
α(°)	90	90	90	114.856(4)
β(°)	111.807(5)	90	105.601(7)	92.872(4)
γ(°)	90	90	90	100.720(4)
V(Å ³)	2619.64(19)	4562(2)	2429.2(3)	1565.63(13)
Z	2	8	2	1
D _{calcd} (g cm ⁻³)	1.656	1.601	1.596	1.371
μ(mm ⁻¹)	2.826	2.974	2.281	0.894
F(000)	1304	2208	1156	668
Flack parameter	—	—	-0.037(14)	—
Reflections collected	19801	23140	18423	19647
Unique reflections	8706,	5652,	12271,	10396,
	R _{int} = 0.0446	R _{int} = 0.0741	R _{int} = 0.0385	R _{int} = 0.0293
Data/restraints/ parameters	8706/ 12/303	5652 / 2 / 268	12271/ 1/551	10396/0/379
Goodness- of- fit	1.033	1.001	1.027	1.041
Reflns.with [I > 2σ(I)]	6392	3432	10749	8428
R Indices				
R ₁	0.0510	0.0460	0.0397	0.0371
wR ₂	0.1115	0.1036	0.0794	0.0827
R indices(all data)				
R ₁	0.0805	0.0950	0.0497	0.0518
wR ₂	0.1288	0.1240	0.0856	0.0912
Largest diff.	1.649 e.Å ⁻³ ,	0.630 e.Å ⁻³ ,	1.209 e.Å ⁻³ ,	0.445 e.Å ⁻³ ,
Peak and hole	-1.260 e.Å ⁻³	-0.456 e.Å ⁻³	-0.717 e.Å ⁻³	-0.383 e.Å ⁻³

Table 2. Bond lengths (Å) and angles (°) of compounds **1-4**.

1		2	
Cu1- S1	2.3004(8)	Cu1-S1	2.2887(12)
Cu1 - S1	2.5969(9)	Cu1-S2	2.4052(13)
Cu1- P1	2.2325(8)	Cu1- P1	2.2418(12)
Cu1- Br1	2.4137(5)	Cu1 - Br1	2.5010(7)
S1 - C4	1.696(3)	S1-C19, S2-C22	1.659(4), 1.674(4)
S1- Cu1- Br1	114.33(2)	P1-Cu1- S1	119.65(5)
Br1- Cu1- S1	99.47(2)	P1-Cu1- S1	119.65(5)
S1- Cu1- S1	102.21(3)	P1- Cu1- S2	105.79(5)
P1- Cu1- Br1	116.39(3)	S1- Cu1- S2	102.18(5)
P1- Cu1- S1	110.87(3)	P1- Cu1- Br1	109.06(4)
P1 -Cu1- S1	111.82(3)	S1- Cu1-Br1	112.34(4)
Cu1- S1- Cu1	77.79(3)	S2- Cu1- Br1	106.61(4)
3		4	
Cu1-I1, Cu2-I1	2.5078(7), 2.8019(7)	Cu1- S1	2.3951(4)
Cu1-I2, Cu2-I2	2.5660(7), 2.7079(7)	Cu1- P1	2.2813(5)
Cu1- P1	2.2199(16)	Cu1- P2	2.3094(4)
Cu2- P2	2.2673(13)	Cu1- N1	2.0328(13)
Cu2- P3	2.2592(15)	S1- C37	1.6522(16)
Cu1- Cu2	3.0249(9)		
Cu1-I1-Cu2,	69.20(2),	P1 -Cu1- S1	111.158(17)
Cu1-I2- Cu2	69.94(2)		
I1- Cu1- I2,	116.39(3),	P1- Cu1- P2	121.716(16)
I2-Cu2- I1	102.99(2)		
P1- Cu1- I1	131.15(5),	P2- Cu1- S1	104.877(17)
P1- Cu1- I2	112.43(5)		
P2- Cu2- I1,	100.08(4),	N1- Cu1- S1	98.24(4)
P2- Cu2- I2	107.63(4)		
P3- Cu2- I1,	110.69(4),	N1- Cu1- P1	112.85(4)
P3-Cu2- I2	108.81(4)		
P3 -Cu2- P2	124.44(6)	N1- Cu1- P2	105.19(4)

**Chart 3.** Thione-thiol tautomerism.

It may be noted that 2-thiouracil has three types of donor atoms: N, S and O. However, it has bonded to Cu^I only through sulfur in a bridging mode (HSAB principle) and the ligand remains neutral. This coordination property is similar to that of pyridine-2-thione (pySH), pyrimidine-2-thione (pymSH) which display sulfur bridging in dinuclear complexes, [Cu₂(μ-S-pySH)₂(PPh₃)₂Br₂],⁵⁰ [Cu₂(μ-S-pySH)₂(m-tolyl₃P)₂Br₂],⁵¹ [Cu₂(μ-S-pySH)₂(p-tolyl₃P)₂Br₂],⁴⁷ [Cu₂(μ-S-pySH)₂(p-tolyl₃P)₂I₂],⁵² and [Cu₂(μ-S-pymSH)₂(p-tolyl₃P)₂Cl₂],⁵³ (m-tolyl₃P/p-tolyl₃P are tri-m-tolylphosphine/tri-p-tolylphosphine, respectively).

Heterocyclic thioamide ligands are believed to display thione-thiol tautomerism in liquid state (chart 3). In their complexes, they coordinate as neutral or anionic

ligands (after loss of –NH proton). As neutral ligands the coordination to metal center occurs through thione sulfur either in monocoordination or in μ-S bridging as for example observed in complex **1**, which is concluded from X-ray crystallography. As anionic ligand thiol form loses –NH proton and the anion coordinates to the metal center through S or N,S-donor atoms through a variety of coordination possibilities.^{1-3,11}

3.3 Molecular structures of complexes **2-4**

Compound **2** crystallized in orthorhombic crystal system in Pbc_a space group (table 1). The thio-ligand 2,4-dithiouracil acts as a bridging ligand with each sulfur atom bonding to different metal centers. Each Cu metal center is binding to one S donor atom of 2,4-dtucH₂, one Br atom and one PPh₃ atom generating three coordinate moiety, CuBr(μ-S,S-dtucH₂)(PPh₃). This moiety combines with another similar moiety leading to the formation of the polymer, {CuBr(μ-S,S-dtucH₂)(PPh₃)_n **2** (figure 2). The geometry around each metal center is distorted tetrahedron. It is noted here that the crystal data and bond parameters of this complex are similar to the previously reported polymeric structure

reported from the same laboratory by direct reaction of copper(I) bromide with 2,4-dtucH₂ and PPh₃.³³ Compound [(PPh₃)₂(μ-I)₂Cu(PPh₃)] **3** has the structure shown

in figure 3. Both iodides bridge two Cu metal centers. One copper atom is bonded to two P donor atoms and two bridging iodides with distorted tetrahedral

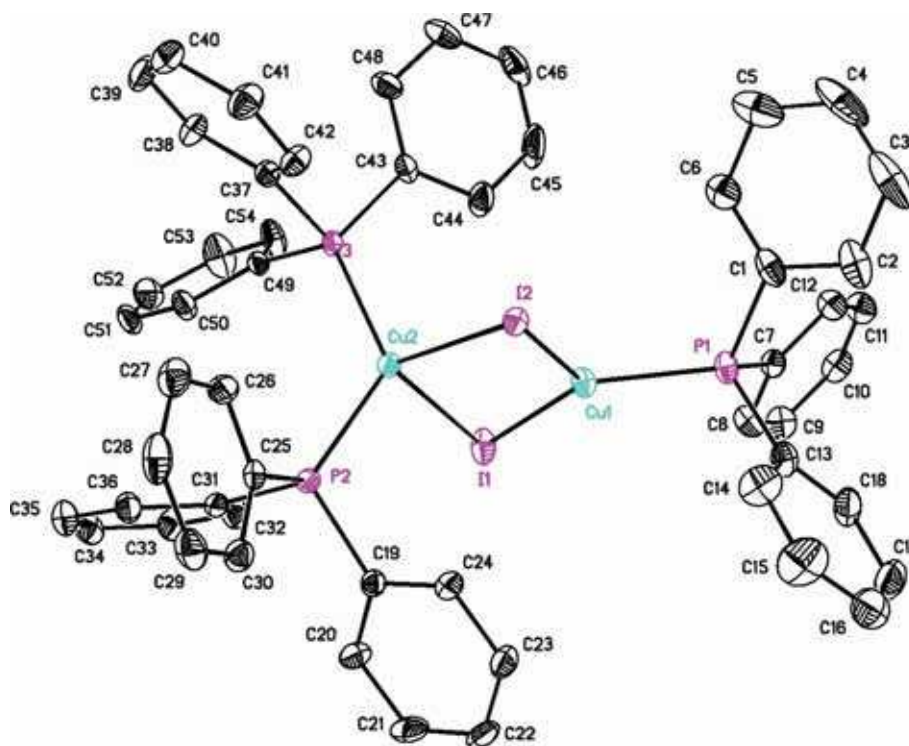


Figure 3. Molecular structure of [(PPh₃)₂(μ-I)₂Cu(PPh₃)] **3**.

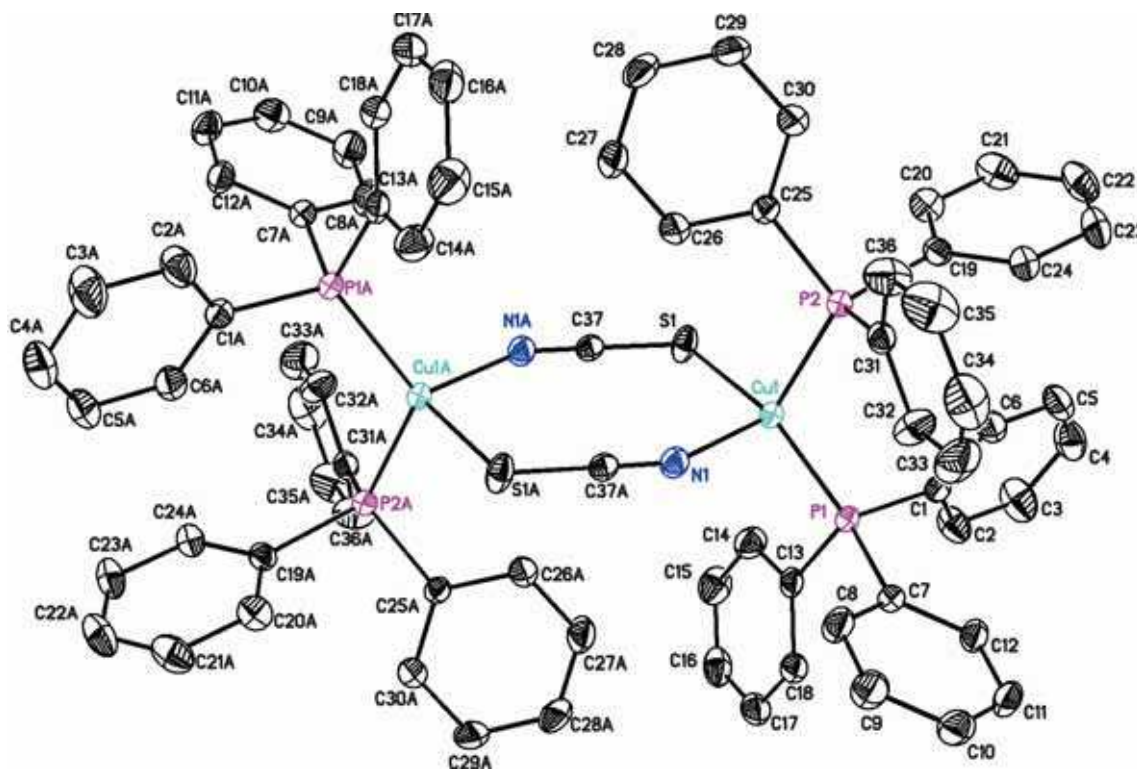


Figure 4. Molecular structure of [(PPh₃)₂Cu(μ-N,S-SCN)₂Cu(PPh₃)₂] **4**.

geometry, while second copper atom is bonded to two bridging iodides and one P donor atom with distorted trigonal planar geometry. The crystal data/bond parameters are similar to previously reported structure.⁵⁴ Finally, compound $[(\text{PPh}_3)_2\text{Cu}(\mu\text{-N,S-SCN})_2\text{Cu}(\text{PPh}_3)_2]$ **4** has the structure shown in figure 4. The SCN moiety acts as a bridge connecting two metal centers. Each copper metal atom is bonded to two P donor atoms, one N and one S donor atoms from NCS group forming distorted tetrahedral geometry around each metal center. As commented in section 3.1, in both reactions leading to the formation of **3** and **4**, the thio-ligands were de-ligated suggesting strong tendency to generate unsymmetrical dinuclear complex **3** and

NCS bridged dimer **4**. The bond parameters are similar to previously reported parameters in literature.⁵⁵ It is added here that complex **3** has been reported in literature from direct reaction of copper(I) iodide with triphenylphosphine.⁵⁴ Likewise, the reaction of $\text{CuCl}(\text{PPh}_3)_3$ with $(\text{SCN})_2$ is also reported to yield complex **4**.⁵⁵

3.4 ESI-mass data of complexes 1-4

The ESI-mass of **1** has shown four most significant species, namely, $[\text{CuBr}(\text{PPh}_3)]^+$, $[\text{Cu}(\text{PPh}_3)_2]^+$, $[\text{Cu}_2\text{Br}(\text{PPh}_3)_2]^+$ and $[\text{Cu}_3\text{Br}_2(\text{tucH}_2)_3(\text{PPh}_3)_2]^+$. The most intense signal and its isotopic pattern due to

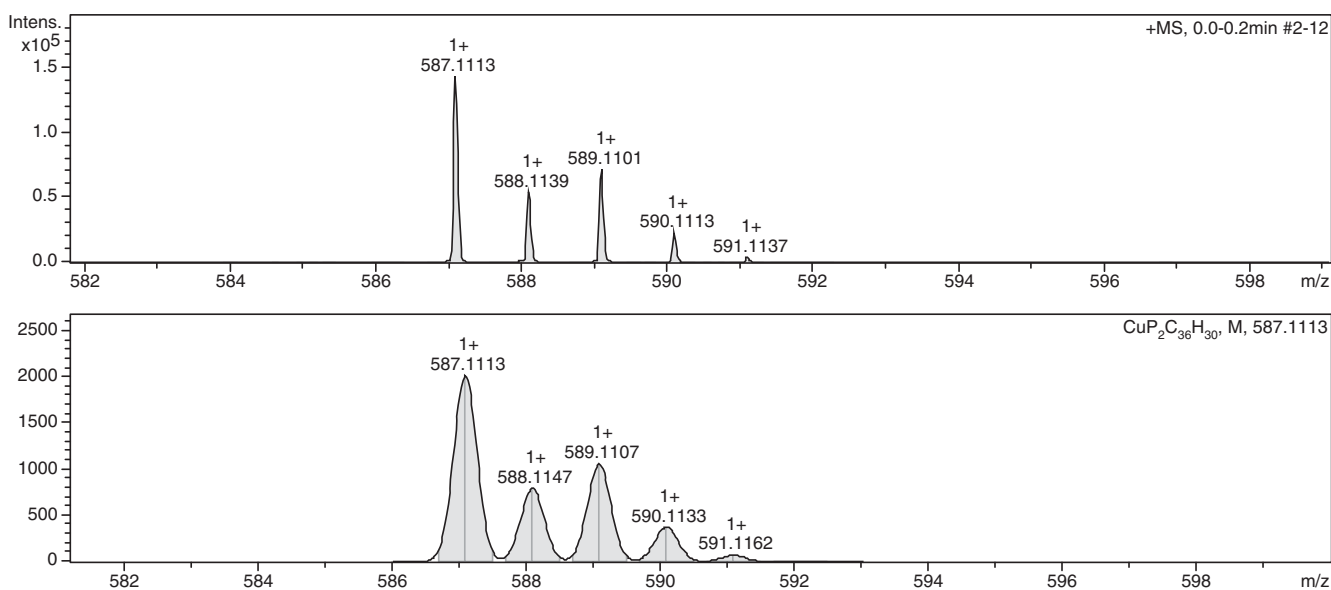


Figure 5. ESI-mass species $[\text{Cu}(\text{PPh}_3)_2]^+$ of complex **1**.

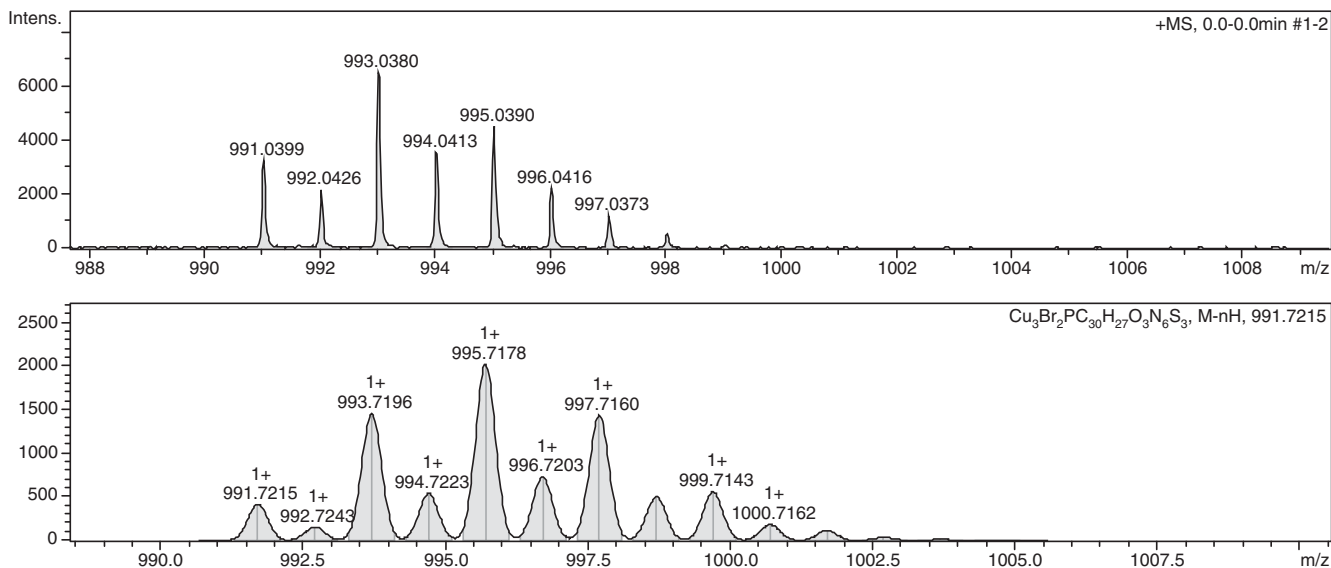


Figure 6. ESI-mass species $[\text{Cu}_3\text{Br}_2(\text{tucH}_2)_3(\text{PPh}_3)_2]^+$ of complex **1**.

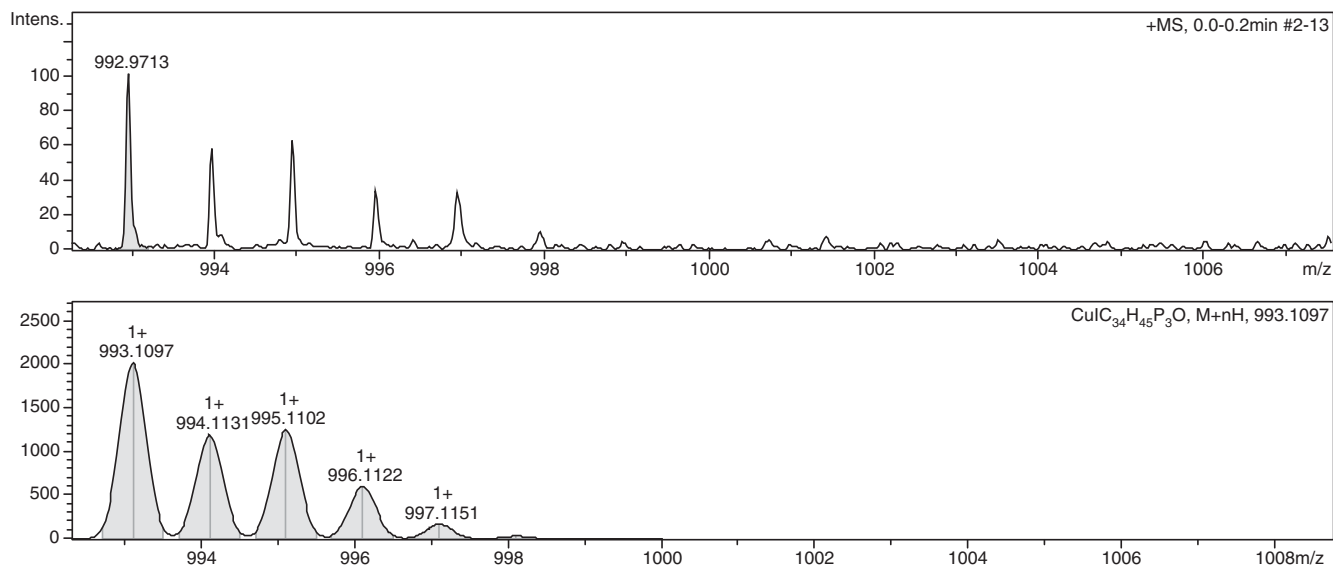


Figure 7. ESI-mass species $[\text{CuI}(\text{PPh}_3)_2(\text{OPPh}_3)]^+$ of complex 3.

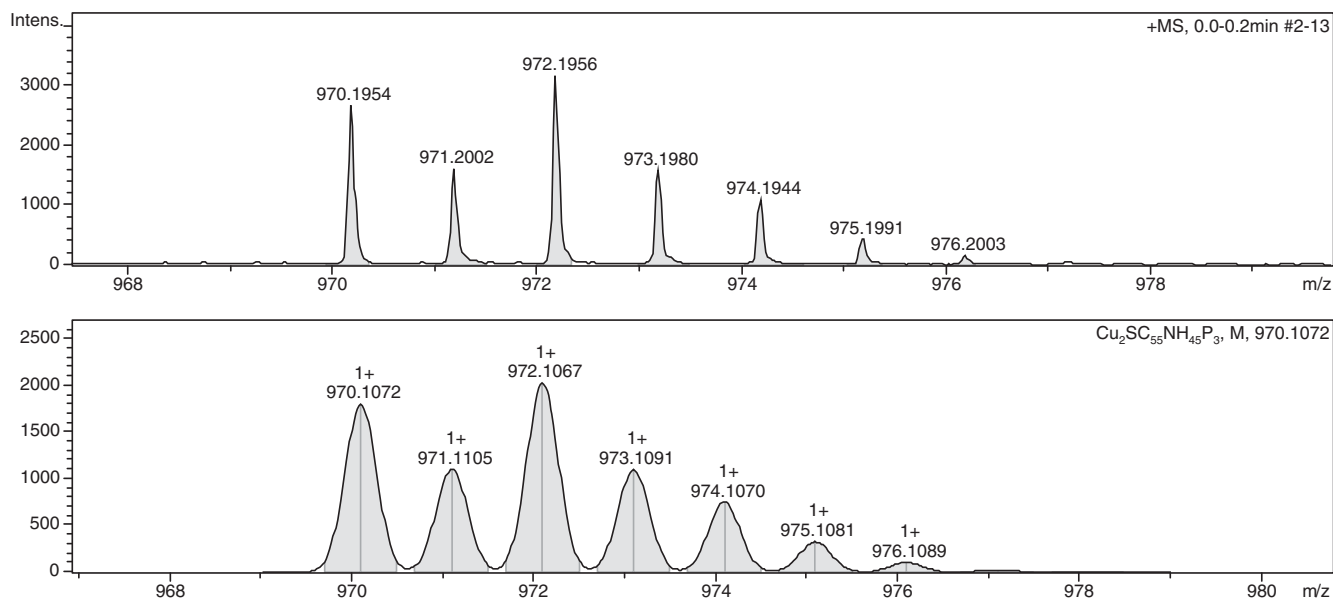


Figure 8. ESI-mass species $[(\text{PPh}_3)\text{Cu}(\text{SCN})\text{Cu}(\text{PPh}_3)_2]^+$ of complex 4.

$[\text{Cu}(\text{PPh}_3)_2]^+$ is shown in figure 5. Interestingly, the rearranged species $[\text{Cu}_3\text{Br}_2(\text{tucH}_2)_3(\text{PPh}_3)_2]^+$ reveals the presence of both the thio-ligand and PPh_3 ligands coordinated to copper(I) metal centre (figure 6). Complex 3 has shown 4 most significant species, $[\text{Cu}(\text{PPh}_3)_2]^+$, $[\text{Cu}(\text{OPPh}_3)(\text{PPh}_3)]^+$, $[\text{Cu}(\text{PPh}_3)_3]^+$ and $[\text{CuI}(\text{PPh}_3)_2(\text{OPPh}_3)]^+$. Interestingly, ESI-mass has shown the formation of OPPh_3 i.e., oxidation of PPh_3 . Figure 7 depicts the species $[\text{CuI}(\text{PPh}_3)_2(\text{OPPh}_3)]^+$ of complex 3 with its isotopic pattern. Finally, ESI-mass spectrum of complex 4 has shown mass species, namely, $[\text{Cu}(\text{PPh}_3)_2]^+$, $[\text{Cu}(\text{OPPh}_3)(\text{PPh}_3)]^+$, $[\text{Cu}(\text{PPh}_3)_3]^+$ and $[(\text{PPh}_3)\text{Cu}(\text{SCN})\text{Cu}(\text{PPh}_3)_2]^+$ (see figure 8).

4. Conclusions

Sulfur-bridged dimer $[\text{Cu}_2\text{Br}_2(\mu\text{-S-tucH}_2)_2(\text{PPh}_3)_2] \cdot 2\text{CHCl}_3$ **1** is the first example of a dinuclear complex of 2-thiouracil/ 2,4-dithiouracil class of ligands. With 2-thiouracil, only mononuclear complexes are reported as highlighted in Introduction. The 2,4-dithiouracil has strong tendency to form polynuclear complex **2** as noted with copper(I) bromide. Formation of **3** demonstrates strong tendency of 2-thiouracil to yield unsymmetrical iodide bridged dimer. Finally, due to ambidentate nature of NCS moiety, copper(I) thiocyanate complex with pyridine-2-thione/pyrimidine-2-thione underwent

de-ligation of thio-ligand in presence of PPh_3 ligand yielding NCS bridged dinuclear complex **4**. ESI-mass studies have shown the formation of several significant species.

Supplementary Information

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC 1405753 for **1**, 1405754 for **2**, 1405755 for **3** and 1405756 for **4** (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>). ESI mass data area in Supplementary Information is available at www.ias.ac.in/chemsci.

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