SHORT COMMUNICATION

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Synthesis of an Unprecedented Cu^I Polymer with Alternate $Cu(\mu\text{-}S)_2Cu$ and $Cu(\mu\text{-}Cl)_2Cu$ Cores Bridged by Pyridine-2-carbaldehyde Thiosemicarbazone

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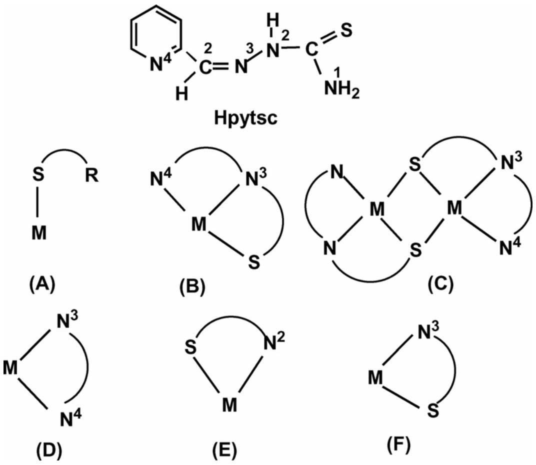
Keywords: Copper; Pyridine-2-carbaldehyde thiosemicarbazone; Polynuclear complexes; Solvent mixture; Bridging ligands

Abstract. Pyridine-2-carbaldehyde thiosemicarbazone $\{(C_5H_5N)(H)C^2{=}N{-}NH{-}C^1({=}S)NH_2$; Hpytsc} formes an unprecedented 1D copper(I) coordination polymer, $\{Cu_4Cl_4(\mu_3\text{-}S,N^4\text{-}Hpytsc)_2\ (PPh_3)_4\}_n$ (**1**) in which pyridyl nitrogen binds to $Cu(\mu\text{-}Cl)_2Cu$ core and sulfur bridges two CuCl units, to form alternate $Cu(\mu\text{-}S)_2Cu$ and $Cu(\mu\text{-}Cl)_2Cu$ cores in the polymer. The Cu···Cu contact in $Cu(\mu\text{-}Cl)_2Cu$ core [3.0877(6) Å] is shorter than in $Cu(\mu\text{-}S)_2Cu$ core [3.1826(6) Å].

Introduction

The interaction of copper with thiosemicarbazones is of current interest from the points of view of the bonding, structure and biological aspects [1–3]. Pyridine-2-carbaldehyde thiosemicarbazone $[(C_5H_4N)(H)C^2{=}N^3N^2H{-}C^1({=}S){-}N^1H_2]$ is a well known N,N,S donor ligand, and has exhibited variable bonding modes in its complexes with several transition metals [1–3]. In case of copper, as a neutral ligand, modes A and B [4, 5], and as an anionic ligand, modes B and C [6, 7] were observed. With other metals, it has shown modes A, B, D (rare), E and F [8–13]. In this communication, we report the first example of a coordination polymer with a thiosemicarbazone ligand [1]. Here, the Hpytsc ligand shows bridging behaviour through pyridyl and thione donor atoms in copper(I) coordination polymer, $[Cu_4Cl_4(\mu_3\text{-}S,N^4\text{-}Hpytsc)_2(PPh_3)_4]_n$ (**1**).



Result and Discussion

Reaction of copper(I) chloride with PPh_3 in 1:1 molar ratio in CH_3CN (10 cm^3) followed by addition of the ligand Hpytsc (1 mol) in $CHCl_3$ (5 cm^3), yielded dark orange-coloured crystals of unusual composition, $[Cu_2Cl_2(PPh_3)_2(Hpytsc)]$. The IR spectroscopic data of **1** confirmed the presence of ν(N–H), ν(C–N), ν(C=C), ν(C=N) and ν(P–C) vibrational modes. The thioamide bands ν(C=S) at 837 and 877 cm^{-1} show marginal shifts relative to the free ligand [14]. An NMR spectrum could not be obtained because of the poor solubility of complex **1** in common organic solvent. The molecular structure of polynuclear complex $[Cu_4Cl_4(\mu_3\text{-}S,N^4\text{-}Hpytsc)_2(PPh_3)_4]_n$ (**1**) reveals the presence of two types of units, $Cu_2(\mu\text{-}Cl)_2$ (unit **A**) and $Cu_2(\mu\text{-}S)_2$ (unit **B**), and the Hpytsc ligand is acting as a bridge between two dimeric units through its pyridyl N^4 and S donor atoms (Scheme 1).

In unit **A**, the copper(I) atom is bonded to two chlorine [Cu–Cl, 2.3817(7), 2.6752(11) Å] and one phosphorus atoms of PPh_3 [Cu–P, 2.012(7) Å] and the other coordination site is occupied by pyridine nitrogen atom of Hpytsc [Cu(1)–N(11), 2.0564(19) Å]. The sulfur atom of the same Hpytsc ligand bridges two $[CuCl(PPh_3)]_2$ units at Cu–S distance of 2.3663(6) Å to form a second unit (**B**). Copper atom in unit **B** is further coordinated to a terminal chlorine atom [Cu–Cl, 2.3085(7) Å], and one terminal phosphorus atom of PPh_3 [Cu–P, 2.2341(6) Å], and thereby yielding a polymeric chain (Figure 1). The Cu···Cu contacts in unit **A** [3.0877(6) Å], and unit **B** [3.1826(6) Å] are similar to the literature reports [4]. The bond angles of unit **A**, P–Cu–Cl [110.88(2), 114.66(2)°] and Cl–Cu–Cl [99.93(2)°] are similar to the analogous halogen

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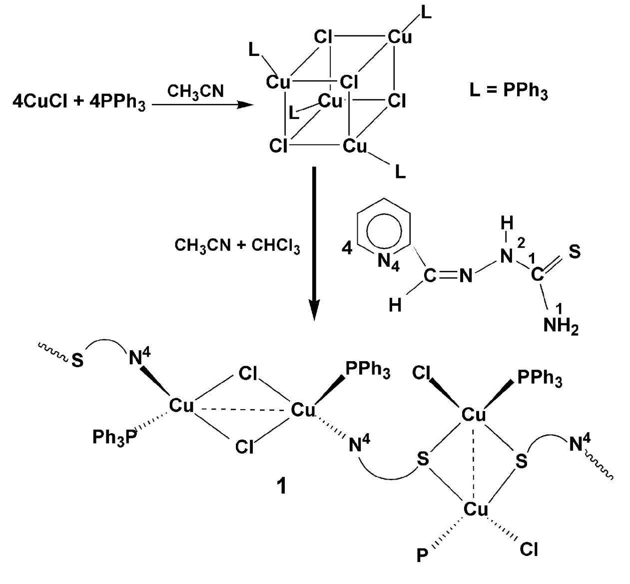

Scheme 1.

bridged dimers in literature [4]. In contrast, core bond angles of unit **B**, P–Cu–S [114.35(2), 106.85(2)°] and S–Cu–S [97.67(2)°] are shorter than in analogous complex [$Cu_2(\mu$-S-$Hbtsc)_2Cl_2(PPh_3)_2$] [P–Cu–S, 118.76(2), 107.15(2)°, S–Cu–S, 107.833(17)°] [4].

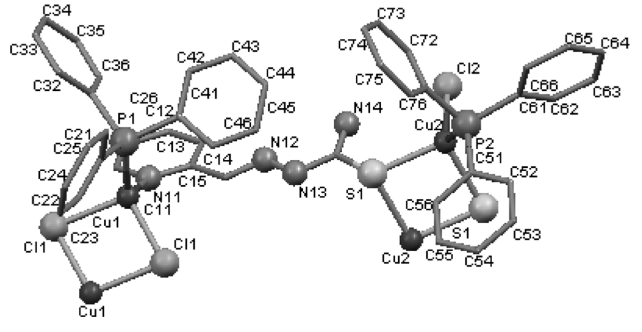

Figure 1. Repeat unit of polymer [$Cu_4Cl_4(\mu_3$-S,N^{11}-$Hpytsc)_2(PPh_3)_4]_n$ (**1**) (hydrogen atoms removed for clarity).

The packing diagram of complex **1** shows the presence of intramolecular hydrogen bonding between terminal chlorine with amino hydrogen (Cl···HNH, 2.829 Å) in unit **B** yielding a linear chain. Two linear chains are interlinked by CH···π interactions involving phenyl rings of PPh_3 (2.792 Å) and chlorine atom (2.806 Å), resulting in formation of 2D network in *ab* plane (Figure 2).

For *X* = Br as an anion, a polymer [$Cu_4Br_4(\mu_3$-S, N^1-$Hpytsc)_2(PPh_3)_4 \cdot CH_3CN \cdot H_2O]_n$ (**2**) similar to **1** is formed. In addition, a protonated product [$CuBr_2(\eta^1$-S-Hpytsc-$N^1H^+)(PPh_3)] \cdot H_2O$ (**3**) was also isolated (Figure 3). For *X* = I, an iodo-bridged dimer, [$Cu_2(\mu$-$I)_2(\eta^1$-S-$Hpytsc)_2(PPh_3)_2$] (**4**) was obtained. Complex **2** showed similar bonding behaviour as in **1** (Figure 4) and the bond parameters are similar (see Supporting Information). The complexes are stable to air and moisture for several weeks. It may be pointed out here that

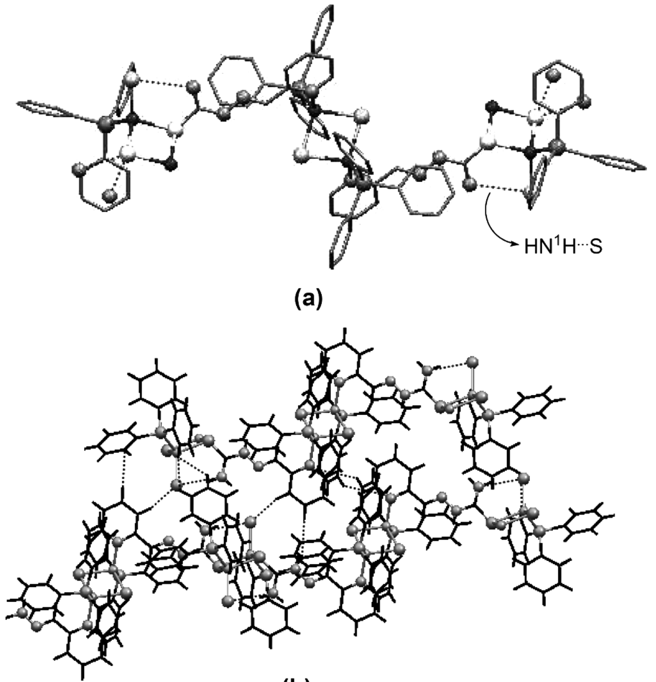

Figure 2. Packing diagram of complex [$Cu_4Cl_4(\mu_3$-S, N^{11}-$Hpytsc)_2(PPh_3)_4]_n$ (**1**) (a) 1D chain, (b) 2D network.

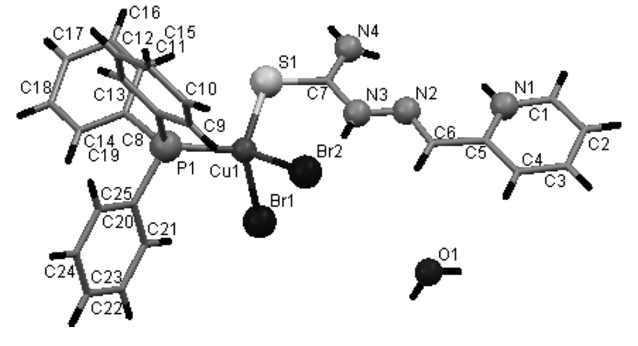

Figure 3. Molecular structure of [$CuBr_2(\eta^1$-S-Hpytsc-$N^1H^+)(PPh_3)] \cdot H_2O$ (**3**).

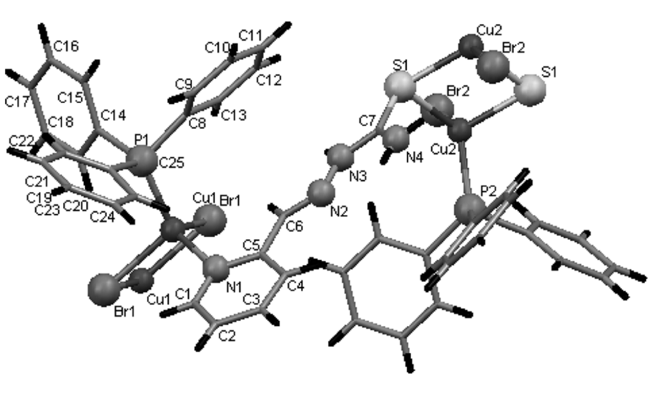

Figure 4. Repeat unit of polymer {$Cu_4Br_4(\mu_3$-S,N^1-$Hpytsc)_2(PPh_3)_4\}_n$ (**2**) (solvent molecules have been removed for clarity, see Supporting Information).

reactions of Cu_4X_4 clusters (X = Cl, Br) with bidentate 1, 3-bis(diphenylphosphanyl)propane (dppp) in presence of pyrimidine-2-thione ligand (pymSH) yielded mononuclear complexes, [CuX(η^1-S-pymSH)(η^2-P,P-dppp)] [15]. Reactions of [$Cu_4X_4(L_4)$] cubanes (L = PPh_3, o-tolyl$_3$P) with N,S-donor ligands such as pymSH and 1,3-thiazolidine-2-thione have also formed mononuclear complexes [16, 17].

Conclusions

The ligand Hpytsc in $CH_3CN/CHCl_3$ mixture has formed novel polynuclear complexes **1** and **2** with copper(I) chloride/bromide exhibiting unprecedented bridging by Hpytsc ligand. The complexes are stable to air and moisture for several weeks. It may be noted that the reactions of Hpytsc with copper(I) halides in CH_3CN has formed only mononuclear complexes of type, [CuX(η^1-S-Hpytsc)$(PPh_3)_2$] (X = Cl, Br, I) [4], and addition of chloroform to the reaction mixture did not give any significant change in bonding and nuclearity of the complexes.

Experimental Section

Synthesis of 1: PPh_3 (0.066 g, 0.25 mmol) was added to a solution of copper(I) chloride (0.025 g, 0.25 mmol) in CH_3CN, followed by stirring for 1 h. A colourless precipitate formed to which the ligand Hpytsc (0.045 g, 0.25 mmol) and $CHCl_3$ (5 mL) were added. The mixture was heated under reflux and a dark orange solution formed, which on slow evaporation resulted in the formation of orange-coloured crystals of **1** (Yield 52 %, M.p. 205–207 °C). $C_{43}H_{38}Cl_2Cu_2N_8P_2S_2\cdot 0.25CHCl_3$: calcd. C 55.69, H 4.10, N 6.00; found C 55.46, H 3.97, N 6.09. Main **IR** peaks (KBr): $\tilde{\nu}$ = ν(N–H) 3357 (m), 3300 (s), 3215 (b); (–NH_2–) 3138 (b); (–NH–) ν(C–H) 3088 (s), 3061 (s); ν(C=N) + δNH_2 + ν(C=C) 1601 (s), 1558 (s), 1533 (s), 1490 (s); ν(C=S) 877 (s), 837 (s) (thioamide moiety); ν(C–N) 1118 (s), 1076 (s); ν(P–C_{Ph}) 1095 (s) cm^{-1}. The complex proved to be poorly soluble in $CHCl_3$.
Complexes **2**–**4** were prepared similarly.

Data for 2: (Yield 26 %, M.p. 215–218 °C). $C_{43}H_{38}Br_2Cu_2N_8P_2S_2\cdot 0.5CHCl_3\cdot 0.5CH_3CN$: calcd. C 47.76, H 3.75, N 9.46; found C 47.73, H 4.15, N 9.10. Main **IR** peaks (KBr): $\tilde{\nu}$ = ν(N–H) 3401 (s), 3300 (m), 3277 (b); (–NH_2–) 3134 (b) (–NH–); ν(C–H) 3099 (s), 3070 (w); ν(C=N) + δNH_2 + ν(C=C) 1660 (s), 1610 (s), 1525 (s), 1452 (s); ν(C–S) 897 (s), 879 (s), 810 (s) (thioamide moiety); ν(C–N) 1128 (s); ν(P–C_{Ph}) 1095 (s) cm^{-1}. The complex is poorly soluble in $CHCl_3$ and CH_3CN.
For the syntheses of complexes **3** and **4**, see Supporting Information

Crystallographic Data for 1: $C_{43}H_{38}Cl_2Cu_2N_4P_2S$, M = 902.75, triclinic, a = 902.75 Å, b = 13.2593(11) Å, c = 19.0132(19) Å, α = 109.286(4)°, β = 91.745(4)°, γ = 109.882(3)°, V = 2122.1(3) $Å^3$, space group $P\bar{1}$ (No. 2); T = 100(2) K, $\rho_{calcd.}$ = 1.413 $Mg\cdot m^{-3}$, Z = 2; μ(Mo-K_α) = 1.288 mm^{-1}, 49444 reflections measured with a CCD area detector diffractometer with graphite-monochromated Mo-K_α radiation, unique 9710 (R_{int} = 0.0414). The final R_1 is 0.0359 and wR_2 is 0.0815.

Crystallographic Data for 2: $C_{44.32}H_{41.34}Br_2Cu_2N_{4.66}$ $P_2SO_{0.68}$, M = 1031.02, monoclinic, a = 9.6779(15) Å, b = 13.275(2) Å, c = 19.103(3) Å, α = 109.412(3)°, β = 90.473(3)°, γ = 109.924(3)°, V = 2155.7(6) $Å^3$, space group $P2_1/n$; T = 100(2) K, $\rho_{calcd.}$ = 1.588 $Mg\cdot m^{-3}$, Z = 2; μ(Mo-K_α) = 3.002 mm^{-1}, 22264 reflections measured with a Bruker AXS SMART APEX CCD diffractometer with graphite-monochromated Mo-K_α radiation, unique 10649 (R_{int} = 0.0406). The final R_1 is 0.0559 and wR_2 is 0.1288.

For the crystallographic data of complexes **3** and **4**, see Supporting Information

CCDC-728182 (**1**), 728183 (**2**), 728184 (**3**) and -666766 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Selected bond lengths and angles for complexes **1**–**4**. Syntheses and crystallographic data of complexes **3** and **4**.

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