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Construction of a Novel Copper(I) Chain Polymer of Hexanuclear $Cu_6(2\text{-}SC_5H_4NH)_6I_6$ Cores with A New (μ_3-S) Mode of Bonding of Pyridine-2-thione and of an Unusual Triangular $Cu_3I_3(dppe)_3(2\text{-}SC_5H_4NH)$ Cluster

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The reactions of copper(I) iodide with pyridine-2-thione ($2\text{-}SC_5H_4NH$) in the presence of a series of diphosphane ligands, $Ph_2P{-}X{-}Ph_2P$ $\{X = -(CH_2)_m-$, $m = 1$(dppm), 2 (dppe), 3 (dppp), 4 (dppb); $-CH{=}CH-$ (dppen)$\}$, yielded an iodo-bridged hexanuclear Cu^I linear polymer, $\{Cu_6(\mu_3\text{-}SC_5H_4NH)_4(\mu_2\text{-}SC_5H_4NH)_2(I_4)(\mu\text{-}I)_2-\}_n\cdot 2nCH_3CN$ (**1**). A similar reaction with 1,2-bis(diphenylphosphino)ethane (dppe) and $2\text{-}SC_5H_4NH$ yielded a triangular cluster, $Cu_3I_3(dppe)_3(2\text{-}SC_5H_4NH)$, **2**. In the chain polymer **1**, three Cu(I) iodide and three $2\text{-}SC_5H_4NH$ ligands combined via bridging S donor atoms to form a boat-shaped trinuclear $Cu_3S_3I_3$ core, and two such cores combined in an inverse manner via four S-donor atoms (μ_3-S) to form a centrosymmetric hexanuclear repeat unit, $Cu_6S_6I_4(\mu\text{-}I)_2$-, which finally formed the iodo-bridged infinite linear chain polymer **1**. Linear chains are separated by the nonbonded acetonitrile molecules. Polymer **1** is the first such example of a linear chain formed by the hexanuclear $Cu_6S_6I_6$ core in copper chemistry as well as in metal–heterocyclic thioamide chemistry. In addition, it has the first μ_3-S mode of neutral pyridine-2-thione ever reported. In the moiety $Cu_3I_3(dppe)_3$ of **2**, two copper(I) centers are bridged by the iodide ligands forming a $Cu(\mu\text{-}I)_2Cu$ core, while a third copper(I) center is terminally bonded to another iodide ligand. Polymer **2** is also rare, and the first triangular cluster of Cu^I with an heterocyclic thioamide.

The importance of sulfur in chemical and biological processes is well recognized.[1] Heterocyclic thioamides, bearing the functional group $-N(H)-C(=S)- \leftrightarrow -N{=}C(-SH)-$, are an important class of sulfur containing organic compounds, which have shown interesting chemical, biochemical, and spectroscopic properties, and structural diversity.[2] Pyridine-2-thiolate ($2\text{-}SC_5H_4N^-$) can bind to a metal or a group of metals via a variety of bonding modes, and this versatility is attributed to the size of the S atom and its proximity to the pyridyl nitrogen.[2,3] The large size of the S atom makes it easier to adopt different angles at this atom in complexes, which is necessary for different geometries. Neutral pyridine-2-thione shows two common bonding modes, (η^1-S) and (μ_2-S), and recently the (μ_4-S) mode has also been reported for silver(I).[3]

The interaction of sulfur containing compounds, such as pyridine-2-thione, with copper(I) halides in a 1:1 molar ratio forms insoluble products of composition $\{CuX(2\text{-}SC_5H_4NH)\}_n$ with unknown structures.[2,4] Phosphane ligands are known to depolymerize insoluble $\{CuX(2\text{-}SC_5H_4NH)\}_n$ compounds into monomers, $[CuX(PPh_3)_2(2\text{-}SC_5H_4NH)]$ (X = Cl, Br),[4,5] or dimers $[Cu_2X_2(\mu\text{-}SC_5H_4NH)_2(R_3P)]$ (X = halide, R = Ph or tolyl group).[6] Among diphosphane ligands, 1,2-bis(diphenylphosphino)-ethane(dppe) formed a P,P′-bridged dimer, $[Cu_2Br_2(\mu\text{-}P,P\text{-}dppe)_2(2\text{-}SC_5H_4NH)_2]$ (dppe = $Ph_2P-CH_2-CH_2-PPh_2$),[7] while 1,3-bis(diphenylphosphino)-propane(dppp) formed monomers, [Cu(X)(HpymS)(dppp)] (HpymS = pyrimidine-2-thione) for X = Cl, Br. For X = I, only the iodo-bridged dimer, $[Cu_2(\mu\text{-}I)_2(dppp)_2]$, with chelating dppp was formed.[8]

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(1) Oae, S. *Organic Sulfur Chemistry: Structure and Mechanism*; CRC Press Inc.: Boca Raton, FL, 1992. Miller, A.; Krebs, B. *Sulfur, Its Significance for Chemistry, for Geo-, Bio-, and Cosmosphere and Technology*; Elsevier: Amsterdam, 1984.

(2) Raper, E. S. *Coord. Chem. Rev.* **1985**, *61*, 115. Raper, E. S. *Coord. Chem. Rev.* **1996**, *153*, 199. Raper, E. S. *Coord. Chem. Rev.* **1994**, *129*, 91. Raper, E. S. *Coord. Chem. Rev.* **1997**, *165*, 475. Garcia-Vazquez, J. A.; Romero, J.; Sousa, A. *Coord. Chem. Rev.* **1999**, *193–195*, 691. Akrivos, P. D. *Coord. Chem. Rev.* **2001**, *213*, 181.

(3) Su, W.; Hong, M.; Weng, J.; Liang, Y.; Zhao, Y.; Cao, R.; Zhou, Z.; Chan, A. S. C. *Inorg. Chim. Acta* **2002**, *331*, 8 and references therein.

(4) Lobana, T. S.; Bhatia, P. K.; Tiekink, E. R. T. *J. Chem. Soc., Dalton Trans.* **1989**, 749.

(5) Karagiannidis, P.; Aslanidis, P.; Kessissoglou, D. P.; Krebs, B.; Dartmann, M. *Inorg. Chim. Acta* **1989**, *156*, 47.

(6) Lobana, T. S.; Castineiras, A. *Polyhedron* **2002**, *21*, 1603.

(7) Cox, P. J.; Aslanidis, P.; Karagiannidis, P. *Polyhedron* **2000**, *19*, 1615.

10.1021/ic034770y CCC: $25.00

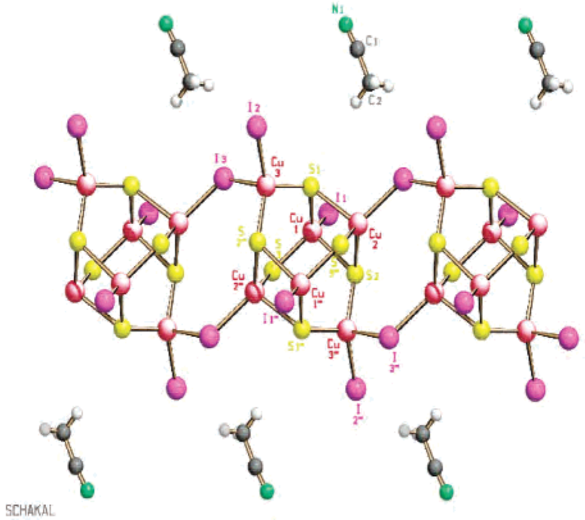
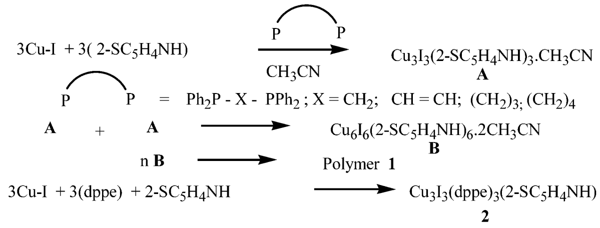


Figure 1. Linear chain of **1** without pyridine rings.

In order to understand the complexity of the interaction of copper(I) halides with heterocyclic thioamides, a series of reactions of copper(I) iodide with pyridine-2-thione, and diphosphane ligands, have been carried out. In a reaction of copper(I) iodide with pyridine-2-thione, and 1,4-bis(diphenylphosphino)butane (dppb) in $CH_3CN-CHCl_3$, an orange crystalline product of empirical formula $Cu_3I_3(2\text{-}SC_5H_4NH)_3\cdot CH_3CN$ (**A**) was formed.[9] The X-ray crystallography of compound **A** has shown that it existed as an iodo-bridged hexanuclear Cu^I inear chain polymer, $\{Cu_6(\mu_3\text{-}SC_5H_4NH)_4(\mu_2\text{-}SC_5H_4NH)_2(I_4)(\mu\text{-}I)_2-\}_n\cdot 2nCH_3CN$ (**1**) (Figure 1).[10] It is remarkable to note that other diphosphanes as listed in Scheme 1 also formed the same polymer **1** except the dppe ligand which formed another unusual triangular cluster, $Cu_3I_3(dppe)_3(2\text{-}SC_5H_4NH)$ (**2**).[11] Neither of the products is analogous to known compounds as already discussed.[2]

Scheme 1



Polymer **1** is the first example of a linear chain formed by hexanuclear $Cu_6S_6I_6$ cores in copper chemistry, and also it has the first μ_3-S mode of coordination by neutral $2\text{-}SC_5H_4NH$ ever reported.[2,3] In the literature, it is known that copper(I) with neutral $2\text{-}SC_5H_4NH$ has formed monomeric or dimeric complexes,[2,4−8] and with anionic $2\text{-}SC_5H_4N^-$ and its substituted analogues, it formed dimeric,[12] tetrameric, and hexameric complexes,[13] but no polymer is known in both the forms of pyridine-2-thione.[2,3]

The formation of polymer **1** is unprecedented,[2−8] and this is significant, as it provides a new method to transform insoluble materials such as $\{CuI(2\text{-}SC_5H_4NH)\}_n$ into new and interesting compounds. Whereas the dppe ligand formed the triangular cluster **2**, all other diphosphane ligands listed in Scheme 1 provided a solution phase in which CuI and $2\text{-}SC_5H_4NH$ rearrange into polymer **1**. Further, selective intercalation of acetonitrile molecules beween chains of **1** in the presence of diphosphane is significant and helps in crystallization of the insoluble $\{CuI(2\text{-}SC_5H_4NH)\}_n$ compound. Compound **2** is also the first triangular cluster of Cu^I with a heterocyclic thioamide.[2]

In polymer **1**, three copper(I) iodide and three $2\text{-}SC_5H_4NH$ ligands combined via bridging S donor atoms, to form an orange crystalline product of empirical formula $Cu_3I_3(2\text{-}SC_5H_4NH)_3.CH_3CN$ (**A**). It has a boat-shaped trinuclear $Cu_3S_3I_3$ core (terminal iodine atoms), and two such cores combined in an inverse manner via four S-donor atoms (μ_3-S) to form the centrosymmetric hexanuclear central core, $Cu_6S_6I_4(\mu\text{-}I)_2-$ {i.e., repeat unit **B**}, which has four terminal and two bridging iodide ligands, in *trans*-orientations. The

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(8) Aslanidis, P.; Cox, P. J.; Divanidis, S.; Tsipis, A. C. *Inorg. Chem.* **2002**, *41*, 6875.

(9) Synthesis of **1**: A solution of pyridine-2-thione (0.015 g, 0.13 mmol) in acetonitrile (5 mL) was added to a solution of copper(I) iodide (0.025 g, 0.13 mmol) in dry acetonitrile (5 mL) followed by stirring for 1 h when deep yellow precipitates were formed. A solution of 1,4-bis(diphenylphosphino)butane (dppb) (0.055 g, 0.13 mmol) in a $CH_3CN-CHCl_3$ mixture (10 mL) was added to the precipitates followed by stirring for 2 h when a bright yellow solution was formed. The slow evaporation of the solution at room temperature formed light orange crystals of **1** in 45% yield. Mp 140−142 °C. Anal. Calcd for $C_{17}H_{15}Cu_3I_3N_4S_3$: C 21.57, H 1.90, N 5.92. Found(%): C 21.84, H 1.86, N 5.70. The complex is partly soluble in chloroform and nearly insoluble in cold CH_3CN. IR bands (KBr pellets): ν(C−S), 1130 (s), 1115 (sh); ν (N−H), 3235 cm^{-1}.

(10) Crystallographic data for **1**: $C_{17}H_{18}I_3N_4S_3Cu_3$, $M = 945.85$, triclinic, $a = 8.047(2)$ Å, $b = 13.454(3)$ Å, $c = 13.770(3)$ Å, $a = 64.097(3)°$, $\beta = 79.996(4)°$, $\gamma = 81.448(4)°$, $U = 1316.1(5)$ Å^3, $T = 293$ K, space group $P\bar{1}$ (No. 2), $\rho_{calcd} = 2.387$ g cm^{-3}, $Z = 2$, μ(Mo Kα) = 6.172 mm^{-1}, 13160 reflections measured on a Bruker SMART CCD 1000 diffractometer, 5354 unique ($R_{int} = 0.0459$) which were used in all calculations. The final R1 was 0.0342 for 5354 reflections [$I > 2.0\sigma(I)$], and wR2 was 0.0904 (all data). For **2**: $C_{83}H_{77}Cu_3I_3P_6NS$, $M = 1877.65$, orthorhombic, $a = 11.6109(18)$ Å, $b = 23.191(4)$ Å, $c = 32.917(5)$ Å, $U = 8864(2)$, $T = 293$ K, space group $P2_12_12_1$ (No. 19), $\rho_{calcd} = 1.406$ g cm^{-3}, $Z = 2$, μ(Mo Kα) = 1.929 mm^{-1}, 50635 reflections measured on a Bruker SMART CCD 1000 diffractometer, 18160 unique ($R_{int} = 0.1258$) which were used in all calculations. The final R1 was 0.0724 for 18160 reflections [$I > 2.0\sigma(I)$], and wR2 was 0.2126 (all data). The structures were solved by the direct methods using the program SHELXS-97 and refined by full-matrix least-squares techniques against F^2 using the SHELXL-97.

(11) Synthesis of **2**: A solution of pyridine-2-thione (0.015 g, 0.13 mmol) in acetonitrile (5 mL) was added to a solution of copper(I) iodide (0.025 g, 0.13 mmol) in dry acetonitrile (5 mL), followed by stirring for 1 h when deep yellow precipitates were formed. To these precipitates, a solution of dppe (0.052 g, 0.13 mmol) in an acetonitrile−chloroform mixture (10 mL) was added, followed by stirring for 4 h. The light yellow solution formed was allowed to evaporate at room temperature, and a light yellow crystalline solid was obtained. Yield, 60%. Mp 206−208 °C. Anal. Found: C 52.9, H 3.94, N 0.71. Calcd for $C_{83}H_{77}Cu_3I_3P_6NS$: C 53.1, H 4.10, N 0.74%. The complex is soluble only in hot acetonitrile and poorly soluble in chloroform. The crystals for X-ray study were grown from acetonitrile.

(12) Perez-Lourido, P.; Garcia-Vazquez, J. A.; Romero, J.; Louro, M. S.; Sousa, A.; Zubieta, J. *Inorg. Chim. Acta* **1998**, *271*, 1. Castro, R.; Romer, J.; Garcia-Vazquez, J. A.; Sousa, A.; Chang, Y. D.; Zubieta, J. *Inorg. Chim. Acta* **1996**, *245*, 119.

(13) Garcia-Vazquez, J. A.; Romero, J.; Castro, R.; Sousa, A.; Rose, D. J.; Zubieta, J. *Inorg. Chim. Acta* **1997**, *260*, 221. Kitagawa, S.; Munakata, M.; Shimono, H.; Matsuyama, S.; Masuda, H. *J. Chem. Soc., Dalton Trans.* **1990**, 2105. Block, E.; Gernon, M.; Kang, H.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1342. Garcia-Vazquez, J. A.; Romero, J.; Louro, M. L.; Sousa, A.; Zubieta, J. *J. Chem. Soc., Dalton Trans.* **2000**, 559. Constable, E. C.; Elder, S. E.; Palmer, C. A.; Raithby, P. R.; Tocher, D. A. *Inorg. Chim. Acta* **1996**, *252*, 281.

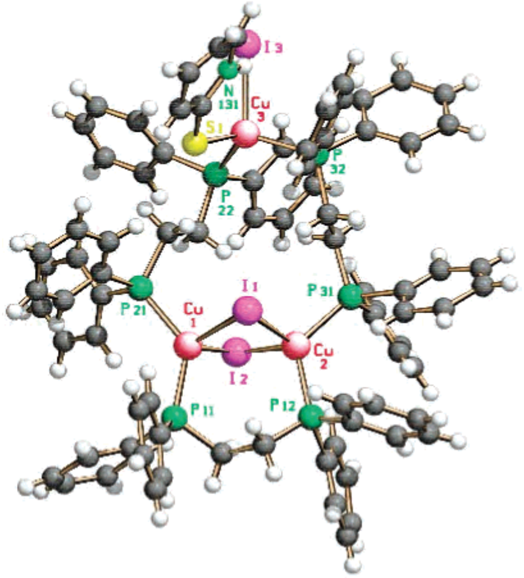

Figure 2. Structure of triangular cluster **2** with numbering scheme.

repeat unit (**B**) combined via bridging iodine ligands to another repeat unit and, finally, formed the infinite linear chain polymer **1**. In the hexameric unit, each of four Cu atoms, Cu(1), Cu(1)*, Cu(2), and Cu(2)*, are bonded to three sulfur atoms and one iodine atom, while each of other two copper atoms, Cu(3), Cu(3)*, are bonded to two sulfur atoms and two iodine atoms. The iodide ligands, bonded to Cu(2) and Cu(2)* atoms, bridge the two adjacent hexameric units on both sides of the central unit, and likewise, two iodide ligands from adjacent hexameric units bridge the central unit. This led to the formation of two eight membered puckered metallacyclic rings of $Cu_4I_2S_2$ core on both sides of the central unit. Thus, four copper atoms {Cu(1), Cu(1)*, Cu(2), Cu(2)*} have CuS_3I cores, and other two Cu atoms {Cu(3), Cu(3)*} have CuS_2I_2 cores. Four sulfur atoms {S(1), S(1)*, S(2), S(2)*} act as μ_3-S donor atoms, and other two S atoms {S(3), S(3)*} act as μ_2-S donor atoms. The Cu$\cdots$Cu bond distances are >3.8 Å, except that (3.027(1) Å) in the four-membered rings formed by Cu(1), S(1), Cu(2), and S(2) and centrosymmetic Cu(2)*, S(2)*, Cu(1)*, and S(1)* atoms, and thus show no metal−metal interaction.[6] CH_3CN is nonbonded.

In the moiety, $Cu_3I_3(dppe)_3$, of triangular cluster **2**, two copper(I) centers are bridged by the iodide ligands forming a rhombic Cu(μ-I)$_2$Cu core,[10,11] while the third copper(I) is terminally bonded to another iodide ligand (Figure 2). The dinuclear Cu(μ-I)$_2$Cu core is bridged by one dppe ligand, and each copper is further connected to a third Cu center via two bridging dppe ligands, thus forming the triangular cluster **2**. In the dinuclear Cu(μ-I)$_2$Cu core, the Cu(1)$\cdots$Cu(2) separation is 3.199(3) Å, while Cu(1)$\cdots$Cu(3) and Cu(2)$\cdots$Cu(3) separations are 6.503(3) and 6.440(3) Å, respectively.

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Supporting Information Available: X-ray crystal data in CIF format {CCDC numbers 190225, 208445}. This material is available free of charge via the Internet at http://pubs.acs.org.

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