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Article

Versatility of Heterocyclic Thioamides in the Construction of a Trinuclear Cluster [$Cu_3I_3(dppe)_3(SC_5H_4NH)$] and Cu^I Linear Polymers $\{Cu_6(SC_5H_4NH)_6I_6\}_n \cdot 2n CH_3CN$ and $\{Cu^I_6(SC_3H_6N_2)_6X_6\}_n$ ($X = Br, I$)

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Reaction of copper(I) iodide with pyridine-2-thione (2-SC_5H_4NH) and 1,2-bis(diphenylphosphino)ethane (dppe) in a CH_3CN–$CHCl_3$ mixture yielded a triangular cluster, [$Cu_3I_3(\mu_2\text{–P,P-dppe})_3(\eta^1\text{-}SC_5H_4NH)$], **1**. Similar reaction with 2-SC_5H_4NH and a series of diphosphanes, Ph_2P–X–Ph_2P {X = –CH_2– (dppm), –$(CH_2)_3$– (dppp), –$(CH_2)_4$– (dppb), –CH=CH– (dppen)}, gave a novel iodo-bridged hexanuclear Cu^I linear polymer,$\{Cu_6(\mu_3\text{-}SC_5H_4NH)_4(\mu_2\text{-}SC_5H_4\text{-}NH)_2(I_4)(\mu\text{-}I)_2\text{-}\}_n \cdot 2nCH_3CN$, **2**. Reactions of copper(I) iodide/copper(I) bromide with 1,3-imidazolidine-2-thione ($SC_3H_6N_2$) in a CH_3CN–$CHCl_3$ mixture yielded hexanuclear Cu^I linear chain polymers, $[\{Cu_6(\mu_3\text{-}SC_3H_6N_2)_2(\mu_2\text{-}SC_3H_6N_2)_4X_2\text{-}(\mu\text{-}X)_4\}_n]$ (X = Br, **4**; I, **5**). In compound **1**, two iodide atoms and one dppe form the dinuclear $Cu(\mu_2\text{-}I)_2(\mu_2\text{-}dppe)Cu$ core, and two dppe ligands bridge this core with the third Cu(I) center coordinated to 2-SC_5H_4NH via the S atom. The chain polymer **2** has a centrosymmetric hexanuclear central core, $Cu_6S_6I_4(\mu\text{-}I)_2$–, formed by dimerization of six-membered trinuclear motifs, $Cu_3(\mu_2\text{-}SC_3H_6N_2)_3I_3$ via (μ_3-S) bonding modes of the thione ligand, and has four terminal and two bridging iodine atoms in *trans*-orientations. Linear chains are separated by the nonbonded acetonitrile molecules. In **4** and **5**, three copper(I) bromide or copper(I) iodide moieties and three $SC_3H_6N_2$ ligands combined via bridging S donor atoms to form the six-membered trinuclear $Cu_3(\mu_2\text{–}SC_3H_6N_2)_3I_3$ cores which polymerized via S and X atoms in a side-on fashion to form linear chain polymers, $[\{Cu_6(\mu_3\text{-}SC_3H_6N_2)_2(\mu_2\text{-}SC_3H_6N_2)_4X_2(\mu\text{-}X)_4\}_n]$. The ($\mu_3$-S) modes of bonding of neutral heterocyclic thioamides are first examples, as are trinuclear cluster and linear polymers rare examples in copper chemistry.

Introduction

The importance of organosulfur compounds in chemical and biological processes is well recognized, and such compounds have been extensively studied.[1] Heterocyclic thioamides, bearing the functional group $-N(H)-C(=S)- \leftrightarrow -N=C(-SH)-$, constitute an important class of sulfur-containing organic compounds that have been studied for their chemical, biochemical, spectroscopic properties, and structural diversity.[2−13] Neutral pyridine-2-thione (structure

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

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

(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.

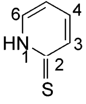
(4) (a) Lobana, T. S.; Bhatia, P. K.; Tiekink, E. R. T. *J. Chem. Soc., Dalton Trans.* **1989**, 749. (b) Lobana, T. S.; Bhatia, P. K. *Ind. J. Chem., Sect. A* **1990**, *29*, 1225.

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

(6) (a) Lobana, T. S.; Castineiras, A. *Polyhedron* **2002**, *21*, 1603. (b) Lobana, T. S.; Paul, S.; Castineiras, A. *Polyhedron* **1997**, *16*, 4023. (c) Karagiannidis, P.; Hadjikakou, S. K.; Aslanidis, P.; Hountas, A. *Inorg. Chim. Acta* **1990**, *178*, 27.

10.1021/ic0484809 CCC: $30.25

I, 2-SC_5H_4NH), the simplest prototype of heterocyclic thioamides, and a sulfur-containing analogue of purine and pyrimidine nucleobases, has shown two modes of bonding (IIIA, IIIB) with Cu^I and several other metals.[2] Mode IIIC is first reported here for compound **2**. Mode IIID with a μ_4-S mode of bonding of neutral 2-SC_5H_4NH has been shown with silver(I) only.[3] Similarly, neutral 1,3-imidazolidine-2-thione (II, $SC_3H_6N_2$) with the functional moiety $-N(H)-C(=S)-N(H)-$ can bind to a metal or a group of metals via η^1-S^{9-12} or μ_2-$S^{10,13}$ bonding modes, and it has shown first μ_3-S mode similar to IIIC for compounds **4** and **5** reported here.



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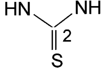

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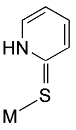

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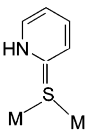

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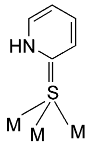
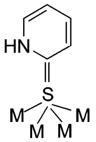


III C



III D

Pyridine-2-thiolate (2-$SC_5H_4N^-$), and its substituted analogues, can bind to a metal, or a group of metals, via a variety of bonding modes in dimeric, tetrameric, and hexameric complexes.[8a-g] This versatility of pyridine-2-thione is attributed to the size of 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. The coordination chemistry of anionic imdtH_2 is limited, however.[13]

The reactions of pyridine-2-thione with copper(I) halides in a 1:1 molar ratio gave insoluble products of composition $\{CuX(2\text{-}SC_5H_4NH)\}_n$ with unknown structures.[2,4] Phosphane ligands 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 $[Cu_2X_2(\mu\text{-}SC_5H_4NH)_2(R_3P)_2]$ (X = halide, R = Ph or tolyl group).[6] Among diphosphane ligands, only dppe formed a P,P′-bridged dimer, $[Cu_2Br_2(\mu\text{-P,P-dppe})_2(2\text{-}SC_5H_4NH)_2]$, **6** (dppe = $Ph_2P-CH_2-CH_2-PPh_2$).[7a] The reaction behavior of copper(I) iodide with 2-SC_5H_4NH in the presence of diphosphanes is unknown, though a related ligand, namely, pyrimidine-2-thione, in the presence of 1,3-bis(diphenylphosphino)propane(dppp) formed monomers, [Cu(X)(HpymS)(dppp)] (HpymS = pyrimidine-2-thione) for X = Cl, Br, and an iodo-bridged dimer, $[Cu_2(\mu\text{-}I)_2(dppp)_2]$, for X = I, with chelating dppp.[7b] Recently it was observed that iodide and alkane spacers connecting Ph_2P groups of diphosphanes played an important role in forming unusual Cu^I polymers with bis(diphenylselenophosphinyl)alkanes.[14ab]

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 in the presence of diphosphanes and of copper(I) iodide/copper(I) bromide with 1,3-imidazolidine-2-thione in a mixture of solvents have been carried out. In this paper we report synthesis, spectroscopy, and X-ray crystallographic studies of the triangular cluster, $Cu_3I_3(\mu_2\text{-dppe})_3(2\text{-}SC_5H_4NH)$ **1**, linear chain polymers,$\{Cu_6(\mu_3\text{-}SC_5H_4NH)_4(\mu_2\text{-}SC_5H_4NH)_2\text{-}(I_4)(\mu\text{-}I)_2-\}_n\cdot 2nCH_3CN$ **2** and $[\{Cu_6(\mu_3-SC_3H_6N_2)_2(\mu_2-SC_3H_6N_2)_4X_2(\mu\text{-}X)_4\}_n]$ (X = Br, **4**, I, **5**).[14c] The construction of supramolecular metal complexes containing copper(I) and silver(I) is a very interesting area, in view of formation of unusual metal clusters and multidirectional networks, some of which display conducting properties.[14d]

Experimental Section

General Materials and Techniques. Copper(I) iodide was prepared by the reduction of $CuSO_4\cdot 5H_2O$ using SO_2 in the presence of NaI in water.[15a] Bis(diphenylphosphino)methane(dppm), 1,3-bis-(diphenyl-phosphino)propane (dppp), 1,2-cis-bis(diphenylphosphino)ethane (dppen), pyridine-2-thione (2-SC_5H_4NH), and 1,3-imidazolidine-2-thione (imdtH_2) were purchased from Sigma-Aldrich, Ltd. 1,2-Bis(diphenylphosphino)ethane (dppe) and 1,4-bis(diphenylphosphino)butane (dppb) were prepared from PPh_3 by the lithiation method.[15b] The elemental analyses (C, H, N) were obtained with a Carlo-Erba 1108 microanalyzer from University of Santiago, Spain. The melting points were determined with a Gallenkamp electrically heated apparatus. IR spectra were recorded using KBr pellets on a FTIR-NICOLET 320 Fourier Transform Spectrophotometer in the 4000−400 cm^{-1} range. ^1H NMR spectra of complexes were recorded on an AL-300 FT JEOL spectrometer operating at a frequency of 300 MHz in $CDCl_3$ with TMS as internal reference.

$Cu_3I_3(dppe)_3(2\text{-}SC_5H_4NH)$, 1. To a solution of copper(I) iodide (0.025 g, 0.13 mmol) in dry acetonitrile (5 mL) was added a solution of pyridine-2-thione (0.015 g, 0.13 mmol) in acetonitrile (5 mL) followed by stirring for 1 h when deep yellow colored precipitates were formed. To these precipitates, a solution of dppe (0.052 g, 0.13 mmol) in acetonitrile−chloroform mixture (10 mL) was added followed by stirring for 4 h. The light yellow colored solution

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(7) (a) Cox, P. J.; Aslanidis, P.; Karagiannidis, P. *Polyhedron* **2000**, *19*, 1615. A. (b) Aslanidis, P.; Cox, P. J.; Divanidis, S.; Tsipis, A. C. *Inorg. Chem.* **2002**, *41*, 6875.

(8) (a) Garcia-Vazquez, J. A.; Romero, J.; Castro, R.; Sousa, A.; Rose, D. J.; Zubieta, J. *Inorg. Chim. Acta* **1997**, *260*, 221. (b) Kitagawa, S.; Munakata, M.; Shimono, H.; Matsuyama, S.; Masuda, H. *J. Chem. Soc., Dalton Trans.* **1990**, 2105. (c) Block, E.; Gernon, M.; Kang, H.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1342. (d) Garcia-Vazquez, J. A.; Romero, J.; Louro, M. L.; Sousa, A.; Zubieta, J. *J. Chem. Soc., Dalton Trans.* **2000**, 559. (e) Constable, E. C.; Elder, S. E.; Palmer, C. A.; Raithby, P. R.; Tocher, D. A. *Inorg. Chim. Acta* **1996**, *252*, 281. (f) Perez-Lourido, V.; Garica-Vazquez, V.; Romero, J.; Louro, M. S.; Sousa, A.; Zubieta, J. *Inorg. Chim. Acta* **1998**, *271*, 1. (g) Castro, R.; Romero, J.; Garcia-Vazquez, J. A.; Sousa, A.; Chang, Y. D.; Zubieta, J. *Inorg. Chim. Acta* **1996**, *245*, 119.

(9) Al-Arfaj, A. R.; Reibenspies, J. H.; Isab, A. A.; Hussain, M. S. *Acta Crystallogr.* **1998**, *C54*, 51.

(10) Battaglia, L. P.; Corradi, A. B.; Nardelli, M.; Tani, M. E. V. *J. Chem. Soc., Dalton Trans.* **1976**, 143.

(11) Stocker, F. B.; Britton, D. *Acta Crystallogr.* **2000**, *C56*, 798.

(12) Friedrichs, S.; Jones, P. G. *Acta Crystallogr.* **1999**, *C55*, 1625.

(13) (a) Raper, E. S.; Wilson, J. D.; Clegg, W. *Inorg. Chim. Acta* **1992**, *194*, 51. (b) Jones, P. G.; Friedrichs, S. *Chem. Commun.* **1999**, 1365.

(14) (a) Lobana, T. S.; Rimple; Castineiras, A.; Turner, P. *Inorg. Chem.* **2003**, *42*, 4731. (b) Lobana, T. S.; Hundal, G. *J. Chem. Soc., Dalton Trans.* **2002**, 2203. (c) Lobana, T. S.; Sharma, R.; Bermejo, E.; Castineiras, A. *Inorg. Chem.* **2003**, *42*, 7728**.** (d) Munakata, M.; Wu, L. P.; Kuroda-Sowa, T. *Adv. Inorg. Chem.* **1999**, *46*, 174

(15) (a) *Handbook of Preparative Inorganic Chemistry*, 2nd ed.; Brauer, G., Ed.; Academic Press: New York, 1965; Vol. 2. (b) Aguiar, A. M.; Beisler, J. *J. Org. Chem.* **1964**, *29*, 1660.

Table 1. Crystallographic Data for Compounds **1**, **2**, **4**, and **5**

parameters	1	2	4	5
empirical formula	$C_{83}H_{77}Cu_3I_3P_6NS$	$C_{17}H_{18}Cu_3I_3N_4S_3$	$C_9H_{18}Br_3Cu_3N_6S_3$	$C_9H_{18}Cu_3I_3N_6S_3$
molecular mass	1877.65	945.85	736.82	877.79
temp, K	293(2)	293(2)	150(2)	150(2)
cryst syst	orthorhombic	triclinic	triclinic	triclinic
space group	P2(1)2(1)2(1) (no. 19)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a, Å	11.611(2)	8.047(2)	7.595(2)	7.883(2)
b, Å	23.191(4)	13.454(3)	11.968(3)	12.164(3)
c, Å	32.917(5)	13.770(3)	12.225(3)	12.615(3)
α, deg	90	64.097(3)	68.016(4)	68.835(4)
β, deg	90	79.996(4)	74.724(4)	73.432(4)
γ, deg	90	81.448(4)	87.670(4)	87.814(4)
V, $Å^3$	8864(2)	1316.1(5)	991.9(4)	1078.4(5)
Z	4	2	2	2
D_{calc}, Mg/m^3	1.406	2.387	2.467	2.703
μ(Mo Kα)/mm^{-1}	1.929	6.172	9.551	7.522
no. unique reflns, R_{int}	18160, 0.1258	5354, 0.0459	4589, 0.0381	4872, 0.0514
no. of reflections	6605	3967	4100	4744
observed ($I > 2\sigma(I)$) final R indices	R1 = 0.0724 wR2 = 0.1624	R1 = 0.0342 wR2 = 0.0828	R1 = 0.0225 wR2 = 0.0539	R1 = 0.0328 wR2 = 0.0885

formed was allowed to evaporate at room temperature, and a light yellow colored crystalline solid was obtained (yellow, 0.050 g, 60%, mp 206−208 °C). Anal. Calcd for $C_{83}H_{77}Cu_3I_3P_6NS$: C, 53.1; H, 4.10; N, 0.74. Found: C, 52.9; H, 3.94; N, 0.71. The complex is soluble only in hot acetonitrile and poorly soluble in chloroform. The crystals for X-ray study were grown from acetonitrile. IR bands (KBr pellets): ν(C−S) 1133 (m), ν(N−H) 3165 (m), ν(P−C_{Ph}) 1097s cm^{-1}. NMR data (δ, ppm; $CDCl_3$): 2.62 (m, 12H, CH_2), 6.62−7.62 (py + C_6H_5).

$Cu_6I_6(2\text{-}SC_5H_4NH)_6\}_n\cdot 2nCH_3CN\}$, 2. To a solution of copper(I) iodide (0.025 g, 0.13 m mol) in dry acetonitrile (5 mL) was added solid pyridine-2-thione (0.015 g, 0.13 mmol), followed by stirring for 1 h, when deep yellow colored precipitates were formed. A solution of 1,4-bis(diphenylphosphino)butane (dppb) (0.055 g, 0.13 mmol) in chloroform (10 mL) was added to the precipitates followed by stirring for 2 h, when a bright yellow colored solution was formed. The slow evaporation of the solution at room temperature for 2 days with volume left to about 10 mL formed yellow crystals of dimer **3a** (see below) and the filtrate upon further allowing it to evaporate at room temperature for overnight to volume of mother liquor around 4−5 mL, gave crystals of polymer **2** (orange, 0.020 g, 45%, mp 140−142 °C). Anal. Calcd for $C_{34}H_{30}Cu_6I_6N_8S_6$: C, 21.57; H 1.90; N 5.92. Found: C, 21.84; H, 1.86; N, 5.70. IR bands (KBr pellets): υ(C−S) 1130 (s), 1115 (sh), υ(N−H) 3235 (w) cm^{-1}. NMR data (δ, ppm; $CDCl_3$): δ 7.56 (s, br), 7.47 (s, br, 3H, H-6), 7.28 (t, br, 3H, H-4), 6.95 (t, br, 3H, H-3) 6.60 (t, br, 3H, H-5), 13.20 (sb, 3H, NH), 2.01(s) (3H, CH_3CN).

$[Cu_2(\mu\text{-}I)_2(dppb)_2]$, 3a. Yellow-colored precipitates of **3a** (0.036 g, 46%, mp 250−255 °C). Anal. Calcd for $C_{56}H_{56}Cu_2I_2P_4$: C, 54.50; H 4.54. Found: C, 54.03; H, 4.46.

$[Cu_2(\mu\text{-}I)_2(dppp)_2]$, 3b. Mp 240−245 °C. Anal. Calcd for $C_{54}H_{52}Cu_2I_2P_4$: C, 53.7; H, 4.31. Found: C, 53.0; H, 4.33.

$[Cu_2(\mu\text{-}I)_2(dppm)_2]$, 3c. Mp 200−210 °C. Anal. Calcd for $C_{50}H_{44}Cu_2I_2P_4$: C, 52.2; H, 3.82. Found: C, 52.9; H, 4.01.

$[Cu_2(\mu\text{-}I)_2(dppen)_2]$, 3d. Mp 205−210 °C. Anal. Calcd for $C_{52}H_{44}Cu_2I_2P_4$: C, 53.15; H, 4.30. Found: C, 53.30; H, 4.16.

$[\{Cu_6(\mu_3\text{-}SC_3H_6N_2)_2(\mu_2\text{-}SC_3H_6N_2)_4Br_2(\mu\text{-}Br)_4\}_n]$ 4. A solution of 1,3-imidazolidine-2-thione (0.025 g, 0.25 mmol) in acetonitrile (10 mL) was added to a solution of copper(I) bromide (0.018 g, 0.12 mmol) in dry acetonitrile (10 mL) followed by stirring for 30 min at room temperature. To this clear solution was added chloroform (5 mL) and the contents stirred for a further period of 2 h. The slow evaporation of the solution at room temperature to about 5 mL formed white crystals of **4** (yield, 0.012 g, 40%). Mp 180−185 °C. Anal. Calcd for $C_9H_{18}Br_3Cu_3N_6S_3$: C, 14.7; H, 2.44; N, 11.41. Found: C, 14.6; H, 2.44; N, 11.06. The complex is very poorly soluble in $CHCl_3$ and CH_3CN. IR bands (KBr pellets): υ(C−S) 1030 (m), 975(m), υ(N−H) 3290 (m), υ(C−N) 1510 (m) cm^{-1}. NMR data (δ, ppm, CDCl3): δ 6.52 (2H, NH), 3.79, 3.77 (4H, CH_2). Ligand NMR data: δ 6.40 (2H, br. NH), 3.59 (4H, CH_2).

$[\{Cu_6(\mu_3\text{-}SC_3H_6N_2)_2(\mu_2\text{-}SC_3H_6N_2)_4I_2(\mu\text{-}I)_4\}_n]$ 5. A solution of 1,3-imidazolidine-2-thione (0.027 g, 0.26 mmol) in acetonitrile (10 mL) was added to a solution of copper(I) iodide (0.025 g, 0.13 mmol) in acetonitrile (10 mL), followed by stirring for 30 min at room temperature. To this solution was added chloroform (5 mL) and the contents stirred for a further period of 2 h. The slow evaporation of the solution at room temperature to about 5 mL formed white crystals of **5** (yield, 0.014 g, 35%). Mp 190−195 °C. Anal. Calcd for $C_9H_{18}Cu_3I_3N_6S_3$: C, 12.3; H, 2.04; N, 9.56. Found: C, 12.9; H, 2.13; N, 9.91. The complex is very poorly soluble in $CHCl_3$ and CH_3CN. IR bands (KBr pellets): υ(C−S) 1040 (s), 985(m), υ(N−H) 3160 (m), υ(C−N) 1465 (s) cm^{-1}. NMR data (δ, ppm, CD_3CN): δ 7.03 (2H, NH), 3.69 (4H, CH_2).

X-ray Crystallography. Data were collected using a Bruker SMART CCD 1000 diffractometer, using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) from a sealed tube. The data integration and reduction were undertaken with SAINT and XPREP.[16] A yellow plate crystal of **1** {or an orange needle crystal of **2**}was mounted on a glass fiber, and diffraction data were collected at 291(2) K. A multiscan absorption correction using SADABS was applied to the data for **1** and **2** (transmission factors, 0.910−0.658 for **1**; 1.000−0.327 for **2**).[17] The structures of **1** and **2** were solved by the direct methods using the program SHELXS-97[18] and refined using SHELXL-97.[19] The non-hydrogen atoms were modeled with anisotropic displacement parameters, and in general, a riding model was used for hydrogen atoms. N−H hydrogen atoms for **1** and **2** were initially positioned at sites determined from difference maps. Atomic scattering factors taken

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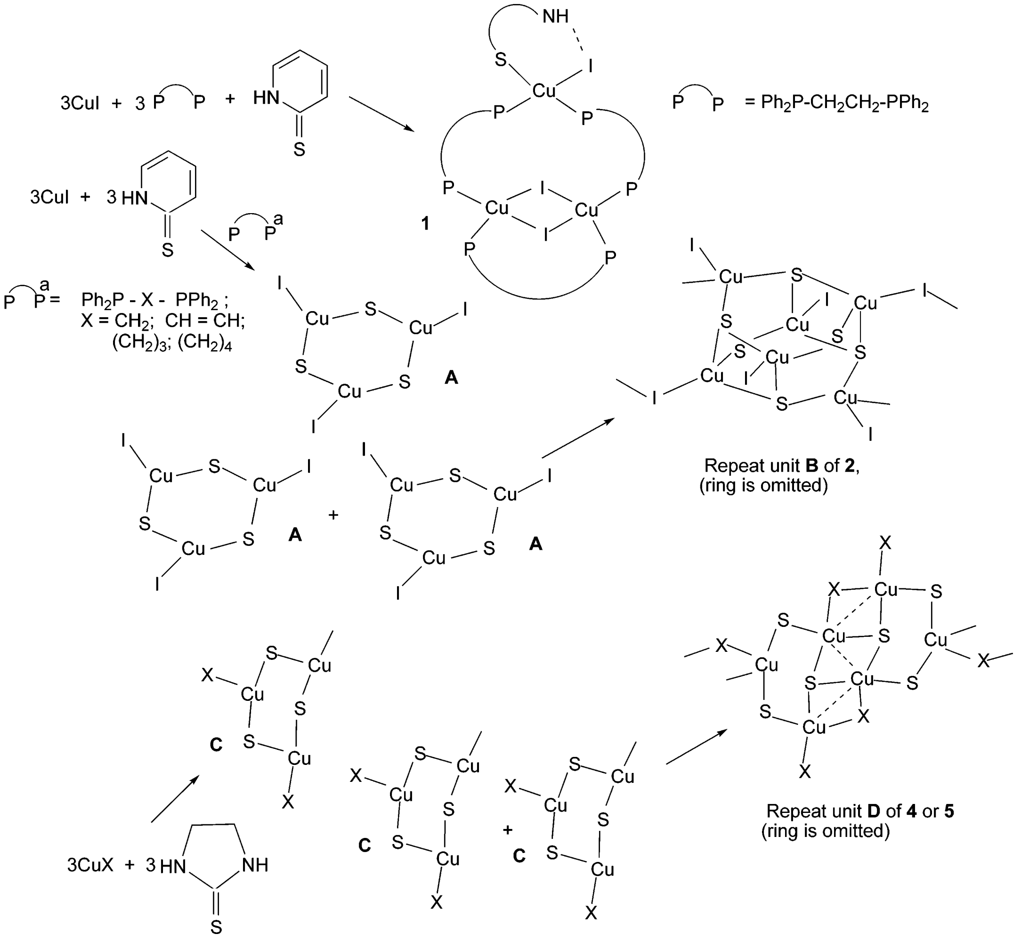
(16) Bruker. SMART, SAINT and XPREP. *Area Detector Control and data Integration and reduction Software*; Bruker Analytical X-ray Instruments, Inc.: Madison, WI, 1995.

(17) Sheldrick, G. M. SADABS. *Program for Empirical Absorption Correction of Area Detector Data*; University of Goettingen: Germany, 1997.

(18) Sheldrick, G. M. *Acta Crystallgr., Sect. A* **1990**, *46*, 467.

(19) Sheldrick, G. M. SHELXL-97. *Program for the Refinement of Crystal Structures*; University of Goettingen: Germany, 1997.

Scheme 1



from "International Tables for X-ray Crystallography",[20] while molecular graphics were taken from PLATON[21] and SCHAKAL.[22]

Data for the isostructural complexes **4** and **5** were collected at 150 K, with crystal cooling in a cold nitrogen gas stream from an Oxford Cryosystems Cryostream. A colorless prismatic crystal of **4** [or **5**] attached with Exxon Paratone N to a short length of fiber supported on a thin piece of copper wire inserted in a copper mounting pin. A Gaussian absorption correction[16,22b] was applied to the data in each case. The structure was solved by the direct methods with SIR97[16] and extended and refined with SHELXL-97.[19] The amine hydrogens were located and modeled with isotropic displacement parameters. A depiction of the oligomeric structure generated with ORTEP3[22c] and showing 50% displacement ellipsoids is given in Figure 3. A summary of the crystal data, experimental details, and refinement results are listed in Table 1.

Results and Discussion

Synthesis. Scheme 1 shows the formation of the triangular cluster **1** and Cu^I-linear chain polymers **2**, **4**, and **5**.

The reaction of copper(I) iodide with pyridine-2-thione in a 1:1 molar ratio in CH_3CN formed an insoluble product of empirical composition, $\{CuI(2\text{-}SC_5H_4NH)\}_n$ (presumably a polymer of unknown structure), which reacted with dppe in $CH_3CN-CHCl_3$ and formed an unusual triangular cluster, $Cu_3I_3(dppe)_3(2\text{-}SC_5H_4NH)$ **1**. The insoluble product $\{CuI(2\text{-}SC_5H_4NH)\}_n$ suspended in CH_3CN reacted with dppb in $CHCl_3$ and formed a light-orange compound of the composition $Cu_3I_3(2\text{-}SC_5H_4NH)_3{\cdot}CH_3CN$ (**A**), and X-ray crystallography showed that it is a polymer, $\{Cu_6I_6(2\text{-}SC_5H_4NH)_6\}_n{\cdot}2nCH_3CN$ (**2**, Figure 2). Other diphosphanes as listed in Scheme 1 also formed polymer **2**. Similarly, copper(I) iodide and 1,3-imidazolidine-2-thione ($SC_3H_6N_2$) in a 1:1 molar ratio in acetonitrile formed an insoluble product of empirical composition, $\{CuI(SC_3H_6N_2)\}_n$, (presumably a polymer of unknown structure). This reaction carried out in a 1:2 molar ratio (metal:ligand), followed by addition of chloroform-yielded crystals of empirical composition, $Cu_3X_3(SC_3H_6N_2)_3$ (**C**), and X-ray crystallography showed that it existed as a unusual Cu^I linear chain polymer, **5**. Copper(I) bromide also formed similar polymer, **4**. In Scheme 1, **B** and **D** are suggested as repeat units that formed polymers **2**, **4**, and **5**.

Structure of Triangular Cluster 1. In triangular cluster **1** (Figure 1, Table 2), two iodide atoms and one dppe ligand form the dinuclear $Cu(\mu_2\text{-}I)_2(\mu_2\text{-}dppe)Cu$ core, and two dppe ligands bridge this core with the third Cu(I) center to which

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[20] *International Tables for X-ray Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1995; Vol. C.

[21] Spek, A. L.; PLATON. *A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2000.

[22] (a). Keller, E. SCHAKAL-97. *A Computer Program for the Graphic Representation of Molecular and Crystallographic Models*; 1997. (b). Coppens, P.; Leiserowitz, L., Rabinovich, D. *Acta Cryst.* **1965**, *18*, 1035. (c). Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565. (d). Altomare A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Cryst.* **1999**, *32*, 115.

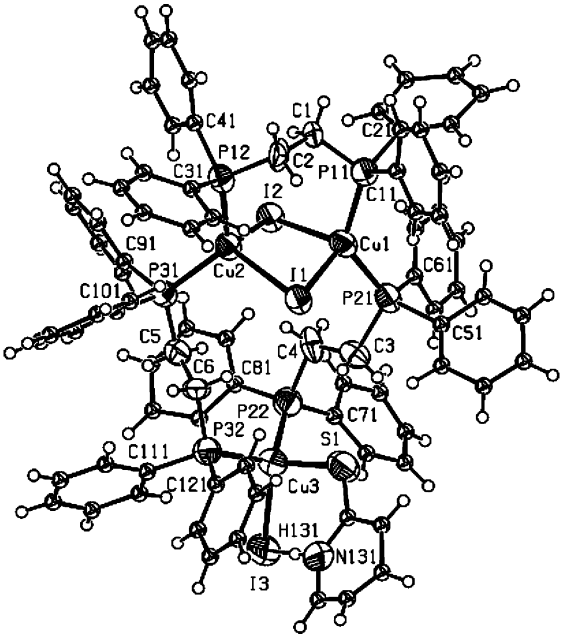

Figure 1. The structure of triangular cluster **1** with numbering scheme.

one 2-SC_5H_4NH is also coordinated via an S atom. In the dinuclear core, the Cu−I−Cu and I−Cu−I bond angles of ca. 72 and 105°, respectively are close to the theoretically predicted values[6] of ca. 70 and 105°. Further, the Cu(1)···Cu(2) separation of 3.199(3) Å is more than twice the van der Waals radius of Cu, viz., 2.80 Å[2424,25] but less than that (3.263(4) Å) observed in a sulfur-bridged dimer $[Cu_2(2\text{-}SC_5H_4NH)_2I_2(p\text{-}tol_3P)_2]$,[6b] **7**. The Cu(3)−S(1)−C(132) angle of ca. 114° is similar to that observed in **7** (ca. 116°)[6b] or $[CuCl(PPh_3)_2(2\text{-}SC_5H_4NH)]$, **8**, (ca. 113°),[4a] characteristic of S-bonded 2-SC_5H_4NH with NH···X hydrogen bonding.[2−4]

Terminal and bridging Cu−I bond distances, 2.700−2.740 Å, are less than the sum of radii of the Cu^+ and I^- (2.97 Å)[24] but longer than the terminal Cu−I distances {2.603(2) Å} observed in compound **7**.[6b] The Cu− P bond distances, 2.238−2.282 Å, are comparable with that, 2.243(3) Å, observed in **7**. The Cu(3)−S(1) bond distance (2.359(6) Å) is shorter than those observed in **7** (Cu−S, 2.393(4) and 2.425(4) Å)[6b] or **8** (Cu−S, 2.374(2) Å).[4a] Finally, the C(132)−S(1) bond distance of 1.652(18) Å is comparable to those in **7** (d(C−S), 1.690(12) Å)[6b] or **8** (d(C−S), 1.692(9) Å).[4a] The NH···I bond distance of 2.96 Å showed very weak hydrogen bonding (sum of van der Waals radii, H···I, 3.24 Å). The seven-memebered metallacyclic ring, formed by the bridging dppe across the dinuclear Cu(μ-I)$_2$Cu core, is puckered with the longest C(1)−C(2) distance of 1.616(19) Å.

Structures of Linear Polymers 2, 4, and 5. The atomic numbering scheme of polymer **2** is shown in Figure 2a, while Figure 2b shows a linear view of the polymer. Three Cu(I) iodide and three 2-SC_5H_4NH ligands are believed to combine via bridging S donor atoms to form a boat-shaped six-membered trinuclear $Cu_3S_3I_3$ core of $Cu_3I_3(2\text{-}SC_5H_4NH)_3 \cdot CH_3CN$ (**A**) species. Two six-membered trinuclear $Cu_3S_3I_3$ cores combine 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 iodine atoms in trans orientations. The repeat unit (**B**) combines to another repeat unit via bridging iodine atoms, and this process finally formed the infinite linear chain polymer **2**. The bond parameters of CH_3CN molecules essentially indicate the nonbonded nature. The presence of CH_3CN molecules between chains appears essential to form the crystals in the presence of diphosphanes.

Table 2. Bond Lengths (Å) and Angles (deg) for Compounds **1**, **2**, **4**, and **5**

Compound **1**			
Cu(1)−P(11)	2.238(5)	Cu(2)−P(31)	2.263(4)
Cu(1)−P(21)	2.247(5)	Cu(2)−I(2)	2.703(2)
Cu(1)−I(1)	2.700(2)	Cu(2)−I(1)	2.723(2)
Cu(1)−I(2)	2.739(2)	Cu(3)−P(32)	2.281(5)
Cu(2)−P(12)	2.260(5)	Cu(3)−P(22)	2.282(5)
Cu(1)−I(1)−Cu(2)	72.28(6)	Cu(3)−I(3)	2.707(2)
Cu(2)−I(2)−Cu(1)	72.00(6)	I(1)−Cu(1)−I(2)	104.54(7)
P(11)−Cu(1)−P(21)	130.19(17)	I(1)−Cu(2)−I(2)	104.89(7)
P(12)−Cu(2)−P(31)	122.88(17)	Cu(3)−S(1)−C(132)	113.7(8)
Compound **2**			
Cu(1)−S(1)	2.3060(15)	Cu(2)−S(3)*	2.2970 (14)
Cu(1)−S(2)	2.5871(16)	Cu(2)−I(3)*	2.5867 (9)
Cu(1)−S(3))	2.3005(15)	Cu(3)−S(2)*	2.2750(15)
Cu(1)−I(1)	2.5932(9)	Cu(3)−S(1)	2.3134(15)
Cu(2)−S(1)	2.5643 (16)	Cu(3)−I(2)	2.5776(9)
Cu(2)−S(2)	2.3062 (15)	Cu(3)−I(3)	2.9094(10)
S(1)−Cu(1)−I(1)	119.59(4)	S(1)−Cu(2)−S(2)	103.31(5)
S(2)−Cu(1)−I(1)	104.53(4)	Cu(1)−S(1)−Cu(2)	76.64(5)
S(3)−Cu(1)−S(1)	110.09(5)	Cu(1)−S(2)−Cu(2)	76.18(5)
S(3)−Cu(1)−S(2)	97.86(5)	Cu(3)−S(1)−Cu(2)	125.17(6)
S(3)−Cu(1)−I(1)	118.08(5)	Cu(3)−S(1)−Cu(1)	114.16(6)
S(1)−Cu(1)−S(2)	102.61(5)		
Compound **4**			
Cu(1)−S(1)	2.2842(9)	Cu(3)−Br(2)	2. 4938(7)
Cu(1)−S(3)	2.2910(9)	Cu(3)−Br(3)	2. 4631(7)
Cu(1)−Br(1)	2.5525(6)	Cu(2)−S(1)	2.2758(9)
Cu(1)−Br(1)*	2.4839(6)	Cu(3)−S(3)	2. 3540(10)
Cu(2)−Br(2)	2.4359(6)	Cu(3)−S(2)	2. 3483(9)
Cu(3)−S(2)−Cu(2)*	71.67(2)	S(2)−Cu(3)−Br(2)	109.97(2)
Cu(3)−Br(2)−Cu(2)*	71.559(19)	S(2)−Cu(2)*−Br(2)	114.54(3)
Cu(1)−Br(1)−Cu(1)*	83.24(2)	Br(1)−Cu(1)−Br(1)*	96.76(2)
Compound **5**			
Cu(1)−S(1)	2.3108(14)	Cu(3)−I(3)	2.6236(9)
Cu(1)−S(3)	2.2998(14)	Cu(1)−I(1)*	2.6392(8)
Cu(1)−I(1)	2.7133(9)	Cu(2)−S(1)	2.2894(14)
Cu(2)−I(2)	2.5913(8)	Cu(3)−S(3)	2.3865(14)
Cu(3)−I(2)	2.6587(10)	Cu(3)−S(2)	2.3454(14)
Cu(3)−S(2)−Cu(2)*	73.19(4)	S(2)−Cu(3)−I(2)	110.95(4)
Cu(3)−I(2)−Cu(2)*	67.98(2)	S(2)−Cu(2)*−I(2)	114.29(4)
Cu(1)−I(1)−Cu(1)*	79.0(4)	I(1)−Cu(1)−I(1)*	101.0(4)

In the hexameric unit $Cu_6S_6I_4(\mu\text{-}I)_2$, each of Cu(1), Cu(1)*, Cu(2), and Cu(2)* atoms are bonded to three S atoms and one I atom (CuS_3I cores), while each of the Cu(3) and Cu(3)* atoms are bonded to two S atoms and two I atoms (CuS_2I_2 cores). The iodine atoms bonded to Cu(2) and Cu(2)* bridge the two adjacent hexameric units on both sides of the central unit, and likewise two iodine atoms from adjacent hexameric units bridge the central unit. This leads to the formation of two eight-membered puckered metallacyclic rings of $Cu_4I_2S_2$ core, on both sides of the central unit. Four sulfur atoms

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(23) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* 1**997**, *62*, 7512.

(24) *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; Huheey, J. E., Keiter, E. A., Keiter, R. L., Eds.; Harper Collins College Publishers: New York, 1993.

(25) Lobana, T. S.; Mahajan, R.; Castineiras, A. *Trans. Met. Chem.* **2001**, *26*, 440.

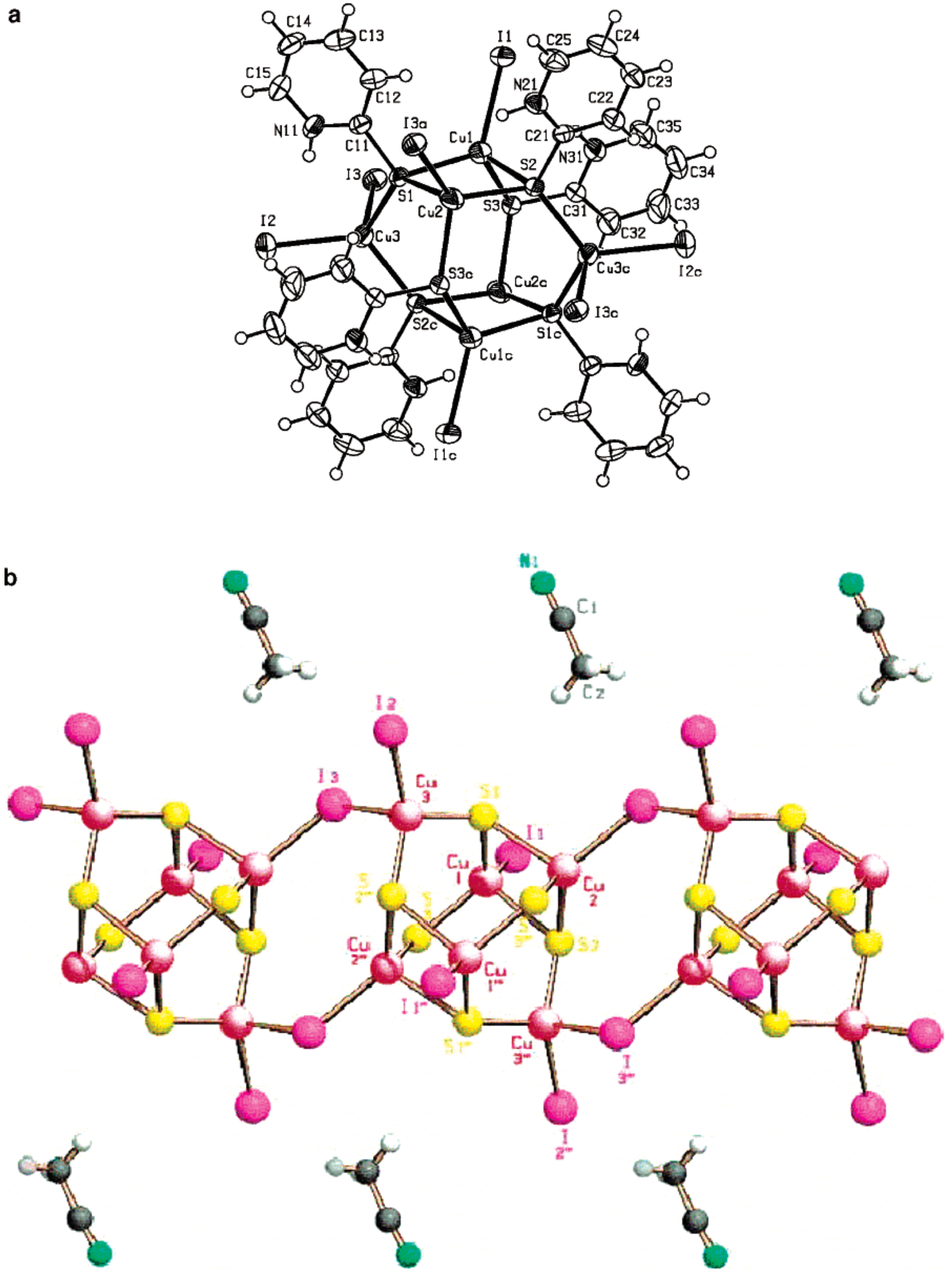

Figure 2. (a) Hexanuclear repeat unit **B** of polymer **2**. (b) Linear chain of polymer **2** along *a* axis (pyridyls omitted for clarity).

(S(1), S(1)*, S(2), S(2)*) act as μ_3-S donor atoms, and the other two S atoms (S(3) and S(3)*) act as μ_2-S donor atoms. The geometry around each Cu center is distorted tetrahedral, and the angles around Cu vary over a wide range, ca. 98−123°. The variation of bond angles around S is more widespread, ca. 76−125° in view of the large angular flexibility at the S donor atom. The Cu−S−C bond angles are typical of S-bonded neutral SC_5H_4NH.[2] The Cu···Cu bond distance is 3.027(1) Å in the four-membered rings of $Cu(\mu\text{-}S)_2Cu$ cores, which is close to similar distance (2.795−3.160 Å) observed in $Cu_6(2\text{-}SC_5H_4N)_6$.[8b] The angles at Cu and S atoms of the four-membered rings are ca. 103 and 76.5°, which are typical of S-bridged dinuclear complexes containing such rings.[6]

The CuS_3I cores have two short and one long Cu−S bond distances, while in the CuS_2I_2 cores, both Cu−S distances

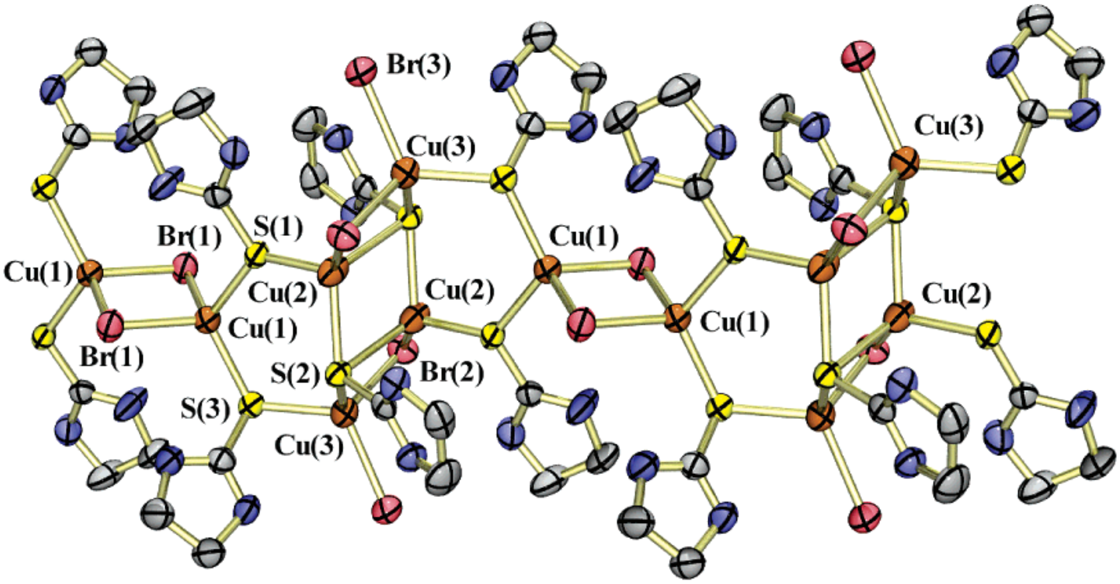

Figure 3. Structure of polymer **4** showing the numbering scheme and 50% displacement ellipsoids. Hydrogen atoms have been omitted for clarity.

are similar to the shorter Cu−S distances of CuS_3I core (Table 2). All these Cu−S bond distances are shorter than the sum of radii of Cu^+ and S^{2-} (2.61 Å: Cu^+, 0.91 Å; S^{2-}, 1.70 Å}[19] but somewhat longer than in $Cu_6(2\text{-}SC_5H_4N)_6$[8b] with anionic ligands. The terminal Cu−I bond distances of the $Cu_6S_6I_6$ core lie in the close range, 2.578−2.593 Å (Table 2), which are close to the terminal Cu−I (2.603 Å) bond distance in **7**.[6b] Two iodines of $Cu_6S_6I_6$ core involved in bridging the adjacent hexameric units form longer bonds (Cu(3)−I(3), 2.909(1) Å). All these Cu−I bond distances are less than the sum of radii of Cu^+ and I^- (2.97 Å).[19] The C−S bond distances, 1.728−1.737 Å, reveal considerable double-bond character,[2] (cf. d(C−S) = 1.764 Å) in $Cu_6(2\text{-}SC_5H_4N)_6$}.[8b]

The polymeric complexes **4** and **5** are isostructural, and the same numbering has been used for both; a depiction of **4** is given in Figure 3. The formation of polymers **4** and **5** is believed to take place via six-membered trinuclear $Cu_3S_3X_3$ cores of $Cu_3X_3(\mu_2{-}SC_3H_6N_2)_3$ species **C** having three bridging S atoms and three terminal X atoms. Two units of species **C** interacted via two S and two X groups, in side-on fashion unlike inverse fashion as in **2**, forming the repeat unit $Cu_6(\mu_3\text{-}SC_3H_6N_2)_2(\mu_2\text{-}SC_3H_6N_2)_4X_2(\mu_2\text{-}X)_4$ (**D**). Two halide ligands of repeat unit **D** interact with other repeat units forming the infinite polymers **4** and **5**. The repeat unit, $Cu_6(\mu_3\text{-}SC_3H_6N_2)_2(\mu_2\text{-}SC_3H_6N_2)_4X_2(\mu_2\text{-}X)_4$ (**D**), comprises two components: steplike tetranuclear $Cu_4S_2X_2$ cores involving two μ_3-S and two μ_2-X bridges and a dinuclear Cu_2X_2 core. Each of Cu(2) and Cu(2)* atoms are bonded to three S and one X atoms; each of Cu(3) and Cu(3)′ atoms, as well as Cu(1) and Cu(1)′ atoms are bonded to two sulfur atoms and two halogen atoms. In the repeat unit, **D**, only two halogen atoms are terminally bonded: the ones bonded to Cu(3) and Cu(3)′ atoms.

The steplike tetranuclear $Cu_4S_2Br_2$ core of **4** has a Cu···Cu bond distance of 2.8826(7) Å, in hetero-bridged Cu(μ_2-Br)-(μ_2-S)Cu moiety, and it is 2.7356(9) Å in homo-bridged Cu(μ_2-S)$_2$Cu moiety. The corresponding Cu···Cu distances in **5** are 2.9356(11) Å in hetero-bridged Cu(μ_2-I)(μ_2-S)Cu moiety and 2.7292(14) Å in homo-bridged Cu(μ_2-S)$_2$Cu moiety. The Cu−S distances of the Cu(μ_2-S)$_2$Cu core are unequal (**4**: Cu(2)−S(2), 2. 3213(9), Cu(2)−S(2)*, 2.5663(9) Å; **5**, Cu(2)−S(2), 2. 3457(14), Cu(2)−S(2)*, 2.5695(15) Å), and four-membered rings form parallelograms (S−Cu−S: 67.85(3) **4**, 67.28(4)° **5**; Cu−S−Cu: 112.15(3)°, **4**, 112.72(4)° **5**) (Table 2). There is remarkable similarity of two Cu(μ_2-S)$_2$Cu moieties in two polymers. In the hetero-bridged Cu(μ_2-X)(μ_2-S)Cu moieties, since the Cu−X and Cu−S distances are unequal, the four-membered rings do not form parallelograms. Further, the S−Cu−X, Cu−X−Cu, and Cu−S−Cu angles of hetero-bridged Cu(μ_2-X)(μ_2-S)Cu moieties lie in the ranges, ca. 109−114, 67−71, and 71−73°, respectively (Table 2). The Cu(μ_2−X)$_2$Cu cores also form parallelograms with Cu−X−Cu and X−Cu−X bond angles of ca. 79−83 and 96−101°, respectively. It may be noted that the angles at Cu, S, or X atoms of the various dimeric cores discussed above are similar to the theoretically predicted values[6] of ca. 70 and 105°. Finally, in the six-membered rings formed by Cu_3S_3 cores, the angles at S(1), S(2), and S(3) lie in the range ca. 116−129° in both the polymers **4** and **5** (Table 2); while the angles at Cu(1), Cu(2), and Cu(3) lie in the range 97−115°. However, the angles at S(1) and Cu(1) atoms are the largest. The C−S bond distances, 1.699−1.733 Å, reveal considerable double bond character.[2]

Spectroscopy. The IR spectrum of 2-SC_5H_4NH shows the υ(N−H) at 3190 (w) cm^{-1}, which shifted to 3165 cm^{-1} in compound **1** and to 3235 (w) cm^{-1} in compound **2**. The ν(C−S) peak at 1138 cm^{-1} of the free 2-SC_5H_4NH shifted to 1133 cm^{-1} in compound **1** and for dppe a characteristic ν(P−C_{Ph}) peak at 1097s cm^{-1} in the complex confirmed its presence. For compound **2**, the shift of the diagnostic υ(C−S) peak from 1135 (s) cm^{-1} to a split band at 1130 (s), 1115 (sh) cm^{-1}, took place. The ν(C−N) peak of CH_3CN could not be located, and the possibility is that it evaporated during pellet formation in KBr. For **4** and **5**, some characteristic bands due to υ(N−H) and υ(C−S) were observed (cf. Experimental Section).

The ^{1}H NMR spectrum of **1** in $CDCl_3$ (poorly soluble) showed peaks due to $-CH_2-$ protons of alkane moiety of dppe at δ 2.62 ppm. The pyridyl and phenyl protons showed multiplets in the region, δ 6.62 to 7.62 ppm; the NH proton signal was too broad to be detected. The proton NMR spectrum of the partially soluble compound **2** in $CDCl_3$ showed a NH proton signal at 13.20 ppm vs free ligand signal at 13.40.[6b] The presence of methyl signal of CH_3CN was shown at 2.01 ppm, a region characteristic of the free CH_3CN.[18] Pyridyl H(3), H(4), and H(5) protons shifted to high field and were broad peaks due to two types of 2-SC_5H_4NH ligands in compound **2** (cf. Experimental Section). Interestingly, H(6) protons did not merge, and two broad singlets at 7.56 and 7.47 ppm were clearly visible. The proton NMR spectrum of compound **4** in $CDCl_3$ and of **5** in CD_3CN showed the bands due to CH_2 and NH protons at low field vis-à-vis free ligand as listed in Experimental Section.

Conclusion

In summary, copper(I) iodide and pyridine-2-thione in the presence of diphosphanes formed unusual cluster **1** and linear polymer **2**, which has acetonitrile between its chains. The dimeric complexes, $[Cu_2(\mu_2\text{-}I)_2(\text{diphosphanes})_2]$ **3a−d**, were also isolated during the formation of **2**. Unlike pyridine-2-thione, the ligands 1,3-imidazolidine-2-thione and pyrimidine-2-thione did not form polymers similar to **2** in the presence of diphosphanes; rather only dimers $(Cu_2(\mu_2\text{-}I)_2(\text{diphosphanes})_2)$ **3a−d** were formed. However, 1,3-imidazolidine-2-thione and copper(I) iodide and bromide have formed unusual linear polymers **4** and **5**, but no such polymer was formed by pyrimidine-2-thione. Dimers involve iodide bridging with chelating diphosphanes, as verified by X-ray crystallography for $(Cu_2(\mu_2\text{-}I)_2(\text{dppp})_2)$.[7b]

In the formation of **2**, the use of CH_3CN alone gave a higher amount of **3a** dimer (80%) and low amount of polymer **2** (15%). The addition of $CHCl_3$ to the reaction mixture (CH_3CN:$CHCl_3$, 1:2 v/v) increased amount of **2** (45%) vis-à-vis dimer (45%). Though CH_3CN intercalates between polymer chains and is necessary for polymer formation, the ligand dppb is more soluble in $CHCl_3$ and thus solvates it more extensively leaving behind CuI and SC_5H_4NH to polymerize. In the absence of $CHCl_3$, dppb preferentially binds CuI and forms a dimer first and a lower amount of **2** results. The dppp is relatively more soluble in CH_3CN and thus **2** (45%) and **3b** (45%) were formed in equal quantity; however, the addition of $CHCl_3$ (CH_3CN:$CHCl_3$, 1:2 v/v) enhanced the yields, **2** (75%) and **3b** (15%). In the case of dppm and dppen, due to their higher solubility in CH_3CN, the polymer **2** in 50−55% and dimers **3c** and **3d** in 40−50% yields were isolated either in CH_3CN alone or in the solvent mixture (CH_3CN:$CHCl_3$, 1:2 v/v). Finally, in the case of dppp and dppb ligands, dimers **3a** and **3b** were formed first and from filtrate polymer **2** was isolated, while in case of dppm and *cis*-dppen ligands, polymer **2** was formed first and dimers **3c** and **3d** formed later from the mother liquor.

The formation of unusual triangular cluster **1** and linear polymer **2** in the presence of diphosphanes in $CH_3CN-CHCl_3$ medium and also of **4** and **5** in the presence of $CH_3CN-CHCl_3$ is significant, and it demonstrates the role of diphosphanes (**2**) and solvents such as chloroform (**4** and **5**) in the construction of novel polymers.

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Supporting Information Available: X-ray crystal data in CIF format (CCDC numbers are 190225, 208445, 225476, and 225477). This material is available free of charge via the Internet at http://pubs.acs.org.

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