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Synthesis of 1D $\{Cu_6(\mu_3\text{-}SC_3H_6N_2)_4(\mu\text{-}SC_3H_6N_2)_2(\mu\text{-}I)_2I_4\}_n$ and 3D $\{Cu_2(\mu\text{-}SC_3H_6N_2)_2(\mu\text{-}SCN)_2\}_n$ Polymers with 1,3-Imidazolidine-2-thione: Bond Isomerism in Polymers

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The reaction of copper(I) iodide with 1, 3-imidazolidine-2-thione ($SC_3H_6N_2$) in a 1:2 molar ratio (M/L) has formed unusual 1D polymers, $\{Cu_6(\mu_3\text{-}SC_3H_6N_2)_4(\mu\text{-}SC_3H_6N_2)_2(\mu\text{-}I)_2I_4\}_n$ (**1**) and $\{Cu_6(\mu_3\text{-}SC_3H_6N_2)_2(\mu\text{-}SC_3H_6N_2)_4(\mu\text{-}I)_4I_2\}_n$ (**1a**). A similar reaction with copper(I) bromide has formed a polymer $\{Cu_6(\mu_3\text{-}SC_3H_6N_2)_2(\mu\text{-}SC_3H_6N_2)_4(\mu\text{-}Br)_4Br_2\}_n$ (**3a**), similar to **1a**, along with a dimer, $\{Cu_2(\mu\text{-}SC_3H_6N_2)_2(\eta^1\text{-}SC_3H_6N_2)_2Br_2\}$ (**3**). Copper(I) chloride behaved differently, and only an unsymmetrical dimer, $\{Cu_2(\mu\text{-}SC_3H_6N_2)(\eta^1\text{-}SC_3H_6N_2)_3Cl_2\}$ (**4**), was formed. Finally, reactions of copper(I) thiocyanate in 1:1 or 1:2 molar ratios yielded a 3D polymer, $\{Cu_2(\mu\text{-}SC_3H_6N_2)_2(\mu\text{-}SCN)_2\}_n$ (**2**). Crystal data: **1**, $C_9H_{18}Cu_3I_3N_6S_3$, triclinic, $P\bar{1}$, $a = 9.6646(11)$ Å, $b = 10.5520(13)$ Å, $c = 12.6177(15)$ Å, $\alpha = 107.239(2)°$, $\beta = 99.844(2)°$, $\gamma = 113.682(2)°$, $V = 1061.8(2)$ Å^3, $Z = 2$, $R = 0.0333$; **2**, $C_4H_6CuN_3S_2$, monoclinic, $P2_1/c$, $a = 7.864(3)$ Å, $b = 14.328(6)$ Å, $c = 6.737(2)$ Å, $\beta = 100.07(3)°$, $V = 747.4(5)$, $Z = 4$, $R = 0.0363$; **3**, $C_{12}H_{24}Br_2Cu_2N_8S_4$, monoclinic, $C2/c$, $a = 19.420(7)$ Å, $b = 7.686(3)$ Å, $c = 16.706(6)$ Å, $\beta = 115.844(6)°$, $V = 2244.1(14)$ Å^3, $Z = 4$, $R = 0.0228$; **4**, $C_{12}H_{24}Cl_2Cu_2N_8S_4$, monoclinic, $P2_1/c$, $a = 7.4500(6)$ Å, $b = 18.4965(15)$ Å, $c = 16.2131(14)$ Å, $\beta = 95.036(2)°$, $V = 2225.5(3)$ Å^3, $Z = 4$, $R = 0.0392$. The 3D polymer **2** exhibits 20-membered metallacyclic rings in its structure, while synthesis of linear polymers, **1** and **1a**, represents an unusual example of I (**1a**)–S (**1**) bond isomerism.

Introduction

Coordination chemistry of heterocyclic thioamides with the $-NH-C(=S)- \leftrightarrow -N=C(-SH)-$ functional moiety has shown novel bonding modes, leading to structural diversity, and the compounds exhibit interesting chemical, biochemical, and spectral properties.[1−15] In regards to structural diversity, copper(I), being a soft Lewis acid, has formed oligomers and polymers of diverse coordination networks with soft Lewis bases,[16] and the study of such inorganic−organic coordination networks is a current area of wide interest for developing new materials that may exhibit conducting, catalytic, and magnetic exchange properties.[17a−j]

Among the heterocyclic thioamides, pyridine-2-thione and its substituted derivatives make up the most studied group of ligands.[1−15,18−24] In comparison to pyridine-2-thiones, 1,3-

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(1) (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) Garcia-Vazquez, J. A.; Romero, J.; Sousa, A. *Coord. Chem. Rev.* **1999**, *193*, 691. (f) Akrivos, P. D. *Coord. Chem. Rev.* **2001**, *213*, 181.

(2) Antolini, L.; Cristiani, F.; Devillanova, F. A.; Diaz, A.; Verani, G. *J. Chem. Soc., Dalton Trans.* **1983**, 1261.

(3) (a) Battaglia, L. P.; Corradi, A. B.; Devillanova, F. A.; Verani, G. *Transition Met. Chem.* **1979**, *4*, 264. (b) Devillanova, F. A.; Verani, G.; Battaglia, L. P.; Corradi, A. B. *Transition Met. Chem.* **1980**, *5*, 362. (c) Weiniger, M. S.; Hunt, G. W.; Amma, E. L. *J. Chem. Soc., Chem. Commun.* **1970**, 1140. (d) Ramaprabhu, S.; Lucken, E. A. C.; Bernardinelli, G. *J. Chem. Soc., Dalton Trans.* **1995**, 115. (e) Hussain, M. S.; Al-Afaj, A. P.; Hossain, M. L. *Transition Met. Chem.* **1990**, *15*, 264. (f) Raper, E. S.; Creighton, J. R.; Wilson, J. D.; Clegg, W.; Milne, A. *Inorg. Chim. Acta* **1989**, *155*, 85. (g) Battaglia, L. P.; Corradi, A. B.; Nardelli, M.; Tani, M. E. V. *J. Chem. Soc., Dalton Trans.* **1976**, 143.

(4) Jones, P. G.; Guy, J. J.; Sheldrick, G. M. *Acta Crystallogr., Sect. B* **1976**, *32*, 3321.

(5) Al-Arfaj, A. R.; Reibenspies, J. H.; Isab, A. A.; Hussain, M. S. *Acta Crystallogr., Sect. C* **1998**, *54*, 51.

(6) Cannas, M.; Devillanova, F. A.; Marongiu, G.; Verani, G. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2383.

(7) Raper, E. S.; Wilson, J. D.; Clegg, W. *Inorg. Chim. Acta* **1992**, *194*, 51.

(8) Stocker, F. B.; Britton, D. *Acta Crystallogr., Sect. C* **2000**, *56*, 798.

(9) Herland, P.; Lundeland, M.; Maroy, K. *Acta Chem. Scand. A* **1976**, *A30*, 719.

(10) Cayton, R. H.; Chisholm, M. H.; Putilina, E. F.; Folting, K. *Polyhedron* **1993**, *12*, 2627.

(11) Crumbliss, A. L.; Gestaut, L. J.; Rickard, R. C.; McPhail, A. T. *J. Chem. Soc., Chem. Commun.* **1974**, 545.

(12) Nardelli, M.; Fava, G.; Musatti, A.; Manfredotti, A. *Acta Crystallogr.* **1966**, *21*, 910.

(13) Friedrichs, S.; Jones, P. G. *Acta Crystallogr., Sect. C* **1999**, *55*, 1625.

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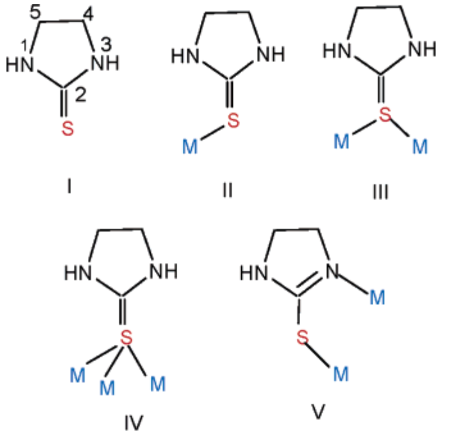
Chart 1



imidazolidine-2-thione (**I**, $SC_3H_6N_2$) with the functional moiety −N(H)−C(=S)−N(H)− has been much less investigated.[2−15] Chart 1 shows η^1-S (**II**) and μ_2-S (**III**) as common modes of neutral 1,3-imidazolidine-2-thione,[2−9,12−14] and as an anionic ligand, it coordinates in a bridging μ-N,S mode (**V**).[10,15]

Recently, we have reported the first μ_3-S bonding modes of pyridine-2-thione and 1,3-imidazolidine-2-thione (mode **IV**).[25] In the case of the latter ligand, this mode was observed in copper(I) linear polymers, namely, $\{Cu_6(\mu_3\text{-}SC_3H_6N_2)_2(\mu\text{-}SC_3H_6N_2)_4(\mu\text{-}X)_4X_2\}_n$ (X = I, **1a**; Br, **3a**; Tables 1 and 2).[25] In a continuation of our interest on the interaction of heterocyclic thioamides, in this paper we report on linear 1D polymer $\{Cu_6(\mu_3\text{-}SC_3H_6N_2)_4(\mu\text{-}SC_3H_6N_2)_2(\mu\text{-}I)_2I_4\}_n$ (**1**) and 3D polymer $\{Cu_2(\mu\text{-}SC_3H_6N_2)_2(\mu\text{-}SCN)_2\}_n$ (**2**) as well as dimeric complexes $\{Cu_2(\mu\text{-}SC_3H_6N_2)_2(\eta^1\text{-}SC_3H_6N_2)_2Br_2\}$ (**3**) and $\{Cu_2(\mu\text{-}SC_3H_6N_2)(\eta^1\text{-}SC_3H_6N_2)_3Cl_2\}$ (**4**).[3g]

Table 1. Crystallographic Data for Compounds **1**−**3**

parameter	1	2	3
empirical formula	$C_9H_{18}Cu_3I_3N_6S_3$	$C_4H_6CuN_3S_2$	$C_{12}H_{24}Br_2Cu_2N_8S_4$
molecular mass	877.79	223.77	695.53
temp, K	103(2)	293(2)	103(2)
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$C2/c$
a, Å	9.6646(11)	7.864(3)	19.420(7)
b, Å	10.5520(13)	14.328(6)	7.686(3)
c, Å	12.6177(15)	6.737(2)	16.706(6)
α, deg	107.239(2)	90	90
β, deg	99.844(2)	100.07(3)	115.844(6)
γ, deg	113.682(2)	90	90
V, Å^3	1061.8(2)	747.4(5)	2244.1(14)
Z	2	4	4
D_{calcd}, Mg m^{-3}	2.746	1.882	2.059
μ(Mo Kα), mm^{-1}	7.640	3.394	5.846
no. of reflns collected	8252	1433	7301
no. of unique reflns, R_{int}	5001, 0.0538	1313, 0.0463	2688, 0.0329
no. of reflns obsd [$I > 2\sigma(I)$]	4704	1118	2416
final indices, R1, wR2	0.0333, 0.0884	0.0363, 0.0931	0.0228, 0.0547

Table 2. Bond Lengths (Å) and Angles (deg) for Compounds **1**−**3**[a]

	Compound 1		
Cu(1)−S(1)	2.3133(10)	Cu(2)−S(2)	2.3352(10)
Cu(1)−S(1)$^{\#}$	2.5544(10)	Cu(2)−I(3)$^{\#}$	2.7086(6)
Cu(1)−S(3)	2.2839(10)	Cu(3)$^{\#}$−I(3)$^{\#}$	2.5756(6)
Cu(1)−I(1)	2.5646(6)	Cu(3)$^{\#}$−S(2)	2.5150(10)
Cu(3)−S(2)	2.3325(10)	Cu(2)−I(2)	2.5857(6)
Cu(3)−S(2)$^{\#}$	2.5150(10)	Cu(2)−S(1)	2.3303(10)
Cu(3)−I(3)	2.5756(6)	S(1)−C(11)	1.724(4)
Cu(3)−S(3)	2.2901(11)	S(2)−C(21)	1.720(4)
Cu(2)···Cu(3)	2.7273(7)	S(3)−C(31)	1.705(4)
Cu(1)···Cu(1)$^{\#}$	3.294(1)	S(2)−Cu(3)−S(2)$^{\#}$	100.87(3)
Cu(3)···Cu(3)$^{\#}$	3.091(1)	Cu(3)−S(2)−Cu(3)$^{\#1}$	79.13(3)
S(1)−Cu(1)−S(1)$^{\#1}$	95.00(3)	Cu(2)−S(2)−Cu(3)$^{\#}$	68.31(3)
Cu(1)−S(1)−Cu(1)$^{\#1}$	85.00(3)	S(2)−Cu(2)−I(3)$^{\#}$	114.34(3)
Cu(1)−S(1)−Cu(2)	132.05(4)	Cu(3)$^{\#}$−I(3)$^{\#}$−Cu(2)	62.083(17)
Cu(3)−S(2)−Cu(2)	127.36(4)	S(2)−Cu(3)$^{\#}$−I(3)	116.66(3)
Cu(1)−S(3)−Cu(3)	133.94(5)		
	Compound 2		
Cu(1)−S(3)	2.3701(16)	S(2)−Cu(1)$^{\#1}$	2.4061(15)
Cu(1)−S(2)	2.3851(16)	S(2)−C(9)$^{\#1}$	1.722(5)
Cu(1)−S(2)$^{\#1}$	2.4061(15)	S(3)−C(8)$^{\#2}$	1.666(5)
Cu(1)−Cu(1)$^{\#1}$	2.8002(15)	Cu(1)−N(6)	1.982(4)
S(3)−Cu(1)−S(2)	114.02(6)	C(9)$^{\#1}$−S(2)−Cu(1)$^{\#1}$	101.10(16)
S(3)−Cu(1)−S(2)$^{\#1}$	105.37(5)	C(8)$^{\#2}$−S(3)−Cu(1)	98.71(17)
S(2)−Cu(1)−S(2)$^{\#1}$	108.47(5)	Cu(1)−S(2)−Cu(1)$^{\#1}$	71.53(5)
C(9)$^{\#1}$−S(2)−Cu(1)	102.66(16)	N(6)−Cu(1)−S(3)	103.52(13)
		N(6)−Cu(1)−S(2)	111.39(13)
	Compound 3		
Cu−S(1B)	2.269(1)	Br−Cu	2.488(1)
Cu−S(1A)$^{\#1}$	2.371(1)	S(1B)−C(1B)	1.699(2)
Cu−S(1A)	2.374(1)	S(1A)−C(1A)	1.707(2)
Cu−Cu$^{\#1}$	2.707(1)		
S(1B)−Cu−S(1A)$^{\#1}$	106.17(3)	S(1B)−Cu−Br	121.32(3)
S(1B)−Cu−S(1A)	112.49(2)	S(1A)$^{\#1}$−Cu−Br	111.99(3)
S(1A)$^{\#1}$−Cu−S(1A)	110.41(3)	S(1A)−Cu−Br	93.98(2)
C(1A)−S(1A)−Cu	114.32(8)	C(1B)−S(1B)−Cu	107.42(8)
Cu$^{\#1}$−S(1A)−Cu	69.59(3)	C(1A)−S(1A)−Cu$^{\#1}$	110.51(7)

[a] Symmetry transformations used to generate equivalent atoms. Compound **1**: #, $-x + 1, -y, -z + 1$. Compound **2**: #1, $-x + 1, -y, -z$; #2, $x, -y - {}^1/_2, z - {}^1/_2$. Compound **3**: #1, $-x + 1, -y + 1, -z + 1$.

Experimental Section

General Materials and Techniques. Copper(I) halides and copper(I) thiocyanate were prepared by the reduction of $CuSO_4 \cdot 5H_2O$ using SO_2 in the presence of stoichimetric NaCl, NaBr, NaI, or NaSCN in water.[26] The ligand 1,3-imidazolidine-2-thione was

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(14) Cavalca, L.; Nardelli, M.; Fava, G. *Acta Crystallogr.* **1960**, *13*, 125.

(15) Jones, P. G.; Friedrichs, S. *Chem. Commun.* **1999**, 1365.

(16) (a) Hanton, L. R.; Richardson, C.; Robinson, W. T.; Turnbull, J. M. *Chem. Commun.* **2000**, 2465. (b) Zhang, Q.-F.; Leung, W.-H.; Xin, X. Q.; Fun, H. K. *Inorg Chem.* **2000**, *39*, 417. (c) Ahlrichs, R.; Besinger, J.; Eichhoefer, A.; Fenske, D.; Gbureck, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3929. (d) Zhang, J.; Xiong, R. G.; Zuo, J. L.; You, X. Z. *Chem. Commun.* **2000**, 1495. (e) Zhang, J.; Xiong, R. G.; Zuo, J. L.; Che, C. M.; You, X. Z. *J. Chem. Soc., Dalton Trans.* **2000**, 2898. (f) Aakeroy, C. B.; Beatty, A. M.; Lorimer, K. R. *J. Chem. Soc., Dalton Trans.* **2000**, 3869. (g) Graham, P. M.; Pike, R. D.; Sabat, M.; Bailey, R. D.; Pennington, W. T. *Inorg Chem.* **2000**, *39*, 5121. (h) Lobana, T. S.; Sharma, R.; Bermejo, E.; Castineiras, A. *Inorg. Chem.* **2003**, *42*, 7728. (i) Lobana, T. S.; Rimple; Castineiras, A.; Turner, P. *Inorg. Chem.* **2003**, *42*, 4731. (j) Lobana, T. S.; Hundal, G. *J. Chem. Soc., Dalton Trans* **2002**, 2203.

(17) (a) Fortin, D.; Drouin, M.; Harvey, P. D. *Inorg. Chem.* **2000**, *39*, 2758 and references cited therein. (b) Carlucci, L.; Ciani, G.; Moret, M.; Proserpio, D. M.; Rizzato, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 1506. (c) Robson, R.; Abrahams, B. F.; Batten, S. R.; Gable, R. W.; Hoskins, B. F.; Liu, J. *Supramolecular Architecture*; American Chemical Society: Washington, DC, 1992; Chapter 19. (d) Munakata, M.; Wu, L. P.; Kuroda-Sowa, T. *Adv. Inorg. Chem.* **1999**, *46*, 173. (e) Janiak, C. *Angew. Chem., Int. Ed.* **1997**, *36*, 1431. (f) Mitzi, D. B. *Prog. Inorg. Chem.* **1999**, *48*, 1. (g) Clearfield, A. *Prog. Inorg. Chem.* **1998**, *47*, 371. (h) Kingsborough, R. P.; Swager, T. M. *Prog. Inorg. Chem.* **1999**, *48*, 123. (i) Cheng, Y.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1996**, *35*, 7339. (j) Cheng, Y.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1996**, *35*, 342.

(18) Kitagawa, S.; Munakata, M.; Shimono, H.; Matsuyama, S.; Masuda, M. *J. Chem. Soc., Dalton Trans.* **1990**, 2105.

(19) Block, E.; Gernon, M.; Kamg, H.; Zubieta, J. *Angew. Chem., Int. Ed.* **1988**, *27*, 1342.

(20) Constable, E. C.; Elder, S. M.; Palmer, C. A.; Raithby, P. R.; Tocher, D. A. *Inorg. Chim. Acta* **1996**, *252*, 281.

procured from Sigma Aldrich Ltd. The C, H, and N elemental analyses were obtained with a Carlo-Erba 1108 microanalyzer. The preparation of copper(I) salts and their complexes was carried out under aerobic condtions; however, dry solvents were used. The melting points were determined with a Gallenkamp electrically heated apparatus. IR spectra were recorded using KBr pellets on a Pye Unicam SP3-300. IR spectra were in the 4000−200-cm^{-1} range. ^{1}H NMR spectra were recorded in $CH_3CN\text{-}d_3$ on a JEOL JNM-LA 300 WB Fourier transform (FT) spectrometer from Osaka City University, Osaka, Japan, or on a JEOL AL-300 FT spectrometer operating at a frequency of 300 MHz in $CHCl_3\text{-}d$ with tetramethylsilane as the internal reference.

$\{Cu_6(\mu_3\text{-}SC_3H_6N_2)_4(\mu\text{-}SC_3H_6N_2)_2(\mu\text{-}I)_2I_4\}_n$ (1). 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 were stirred for a further period of 2 h. The reduction of volume to nearly half of its original volume by evaporation of the solution at room temperature formed prismatic crystals of polymer $\{Cu_6(\mu_3\text{-}SC_3H_6N_2)_2(\mu\text{-}SC_3H_6N_2)_4(\mu\text{-}I)_4I_2\}_n$ (**1a**).[25] After the filtrate was allowed to slowly evaporate to almost dryness, needle-shaped colorless crystals of identical composition, $\{Cu_6(SC_3H_6N_2)_6I_6\}_n$ (**1**), were formed (yield: 0.010 g, 26%). Mp: 160−165 °C. Anal. Calcd for $C_9H_{18}Cu_3I_3N_6S_3$: C, 12.30; H, 2.04; N, 9.56. Found: C, 12.85; H, 2.10; N, 9.90. The complex is very poorly soluble in $CHCl_3$ and CH_3CN. IR bands (KBr, cm^{-1}): ν(N−H) 3205(w), 3134(m), ν(C−H) 3000(m), 2890(w), ν(C−N) 1597(s), 1533(m), ν(C−S) 885(s). NMR data (δ, ppm; $CDCl_3$): δ 3.79 (4H, CH_2).

$\{Cu_2(\mu\text{-}SC_3H_6N_2)_2(\mu\text{-}SCN)_2\}_n$ (2). A solution of 1,3-imidazolidine-2-thione (0.025 g, 0.25 mmol) in acetonitrile (10 mL) was added to a suspension of copper(I) thiocyanate (0.029 g, 0.24 mmol) in acetonitrile (10 mL), followed by stirring for 2 h at room temperature until a clear solution was obtained, which on slow evaporation at room temperature yielded light-yellow prismatic crystals of **2** (yield: 0.035 g, 67%). Mp: 158−160 °C. Anal. Calcd for $C_8H_{12}Cu_2N_6S_4$: C, 21.5; H, 2.68; N, 18.79. Found: C, 21.8; H, 2.70; N, 18.34. IR bands (KBr, cm^{-1}): ν(N−H) 3300(s), ν(C−H) 2940(w), ν(C−N) 1482(s), $\nu(C{-}S)_{thione}$ 895(s). IR and NMR bands for SCN: ν(C≡N) 2060(s), $\nu(C{-}S)_{SCN}$ 725(m); δ(SCN) 470(m). NMR data (δ, ppm; CD_3CN): δ 6.66 (2H, NH), 3.65 (4H, CH_2).

$\{Cu_2(\mu\text{-}SC_3H_6N_2)_2(\eta^1\text{-}SC_3H_6N_2)_2Br_2\}$ (3). 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 acetonitrile (10 mL) followed by stirring for 30 min at room temperature. To this clear solution was added chloroform (5 mL), and the contents was stirred for a further period of 2 h. The reduction of volume to nearly half of its original volume by evaporation of the solution at room temperature formed prismatic crystals of polymer $\{Cu_6(\mu_3\text{-}SC_3H_6N_2)_2(\mu\text{-}SC_3H_6N_2)_4(\mu\text{-}Br)_4Br_2\}_n$ (**3a**).[25] Allowing the filtrate to slowly evaporate at room temperature to almost dryness gave crystals of dimer **3** (0.012 g, 28%). Mp: 160−162 °C. Anal. Calcd for $C_{12}H_{24}Br_2Cu_2N_8S_4$: C, 20.7: H, 3.45; N, 16.11. Found: C, 20.0; H, 3.41; N, 16.24. IR bands (KBr, cm^{-1}): ν(N−H) 3230(m), ν(C−H) 2830 (mbr), ν(C−N) 1518(s), 1491(s), ν(C−S) 910(m).

$[Cu_2(\mu\text{-}SC_3H_6N_2)(\eta^1\text{-}SC_3H_6N_2)_3Cl_2]$ (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) chloride (0.012 g, 0.12 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 was stirred for a further period of 2 h. The slow evaporation of the solution at room temperature formed white needles of **4** (yield: 0.016 g, 68%). Mp: 159−160 °C. Anal. Calcd for $C_{12}H_{24}Cl_2Cu_2N_8S_4$: C, 23.76; H, 3.96; N, 18.48. Found: C, 24.26; H, 3.90; N, 18.81. IR bands (KBr, cm^{-1}): ν(N−H) 3195(s), ν(C−H) 2920(m), ν(C−N) 1540(s), 1490(w), ν(C−S) 920(m).

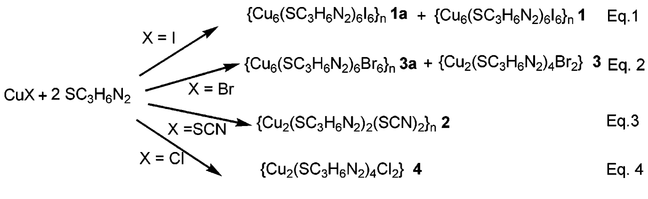
Ligand imdtH$_2$ Data. IR: ν(N−H) 3283(s), 3248(s), ν(C=S) 920(s); ν(C−N) 1518(s), 1491(s), ν(C−H) 2881−3000(ws). NMR: δ 6.40 (2H, br NH), 3.59 (4H, CH_2).

X-ray Crystallography. The data for **2** were collected at room temperature, 293(2) K, on a Siemens P4 diffractometer. The $\theta-2\theta$ technique was used to measure the intensities, up to a maximum of $2\theta = 50°$, with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). Cell parameters were refined using 25 reflections in the θ range 10−12.5° using *XSCANS*.[27] The data were corrected for Lorentz and polarization factors. An empirical ψ absorption correction was applied. The structure was solved by direct methods and refined by full-matrix least-squares methods based on F^2. All H atoms were refined anisotropically. H atoms were fixed geometrically and were not refined. Scattering factors from *International Tables for X-ray Crystallography* were used.[28] Data reduction, structure solution, refinement, and molecular graphics were performed using *SHELXTL-PC*[29] and *WinGX*.[30]

The crystals of **1**, **3**, and **4** were mounted on an automatic Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator and Mo Kα radiation (λ = 0.710 73 Å). The unit cell dimensions and intensity data were measured at 103(2) K for **2** and **3** and 93(2) K for **4**. The structure was solved by direct methods and refined by full-matrix least squares based on F^2 with anisotropic thermal parameters for non-H atoms using *XCAD-49* (data reduction) and *SHELXL* (absorption correction, structure solution refinement, and molecular graphics).[31] The H atoms were calculated in structure factor calculations in their idealized positions.

Results and Discussion

Synthesis. The stoichiometric chemical equations for the preparation of complexes are shown in eqs 1−4. The reaction of copper(I) iodide with 1,3-imidazolidine-2-thione in a 1:2 molar ratio in acetonitrile/chlorofom has formed 1D polymers, **1** and **1a**.[25] Likewise, copper(I) bromide has formed a polymer, **3a**,[25] similar to **1a**, and a dimer, **3**. The reaction of copper(I) chloride, anticipated to form a polymer similar to **1a/1**, instead yielded an unsymmetrical dimer, **4**, with a



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(21) Garcia-Vazquez, J. A.; Romero, J.; Pedrares, A. S.; Louro, M. L.; Sousa, A.; Zubieta, J. *J. Chem. Soc., Dalton Trans.* **2000**, 559.

(22) Kitagawa, S.; Kawata, S.; Nozaka, Y.; Munakata, M. *J. Chem. Soc., Dalton Trans.* **1993**, 1399.

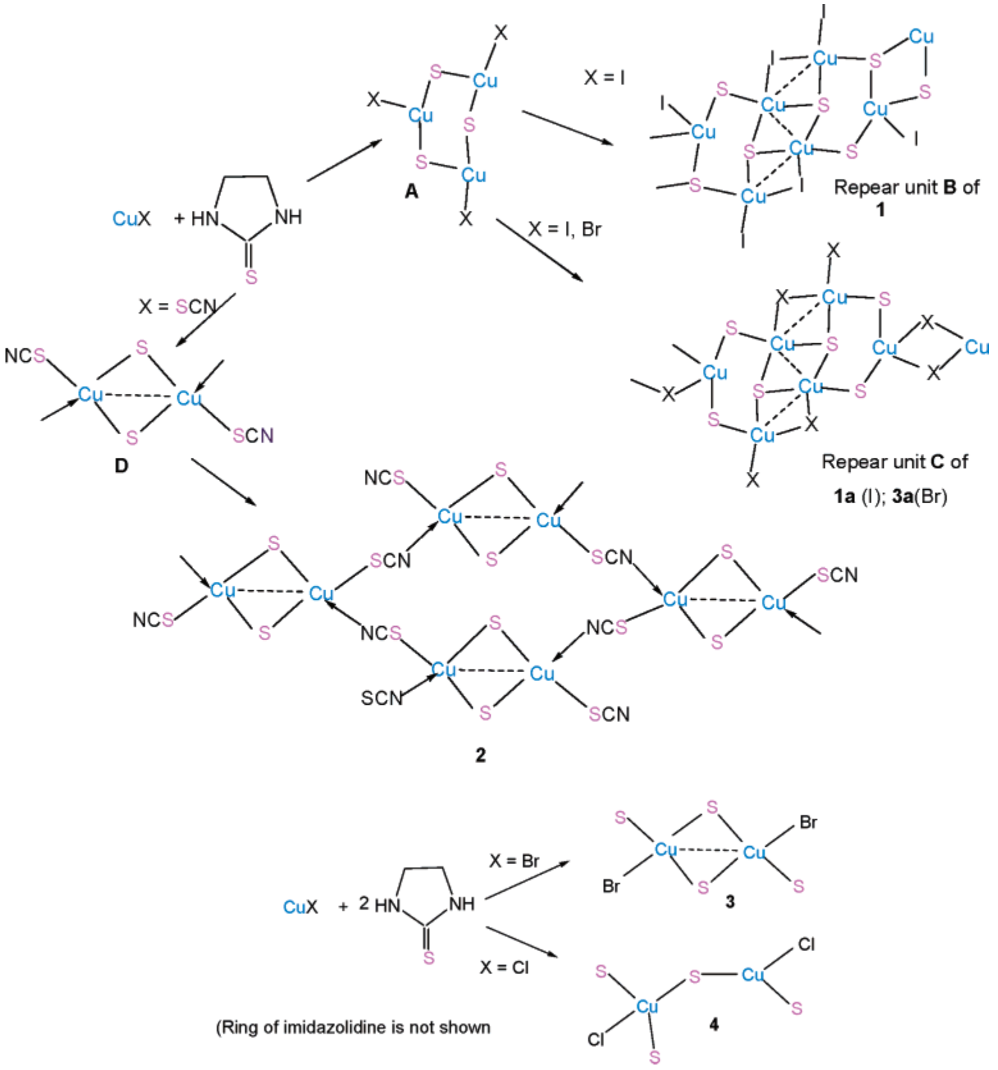
(23) Castro, R.; Duran, M. L.; Garcia-Vazquez, J. A.; Romero, J.; Sousa, A.; Castellano, E. E.; Schpector, J. Z. *J. Chem. Soc., Dalton Trans.* **1992**, 2559.

(24) Kitagawa, S.; Nozaka, Y.; Munakata, M.; Kawata, S. *Inorg. Chim. Acta* **1992**, *197*, 169.

(25) Lobana, T. S.; Sharma, R.; Sharma, R.; Mehra, S.; Castineiras, A.; Turner, P. *Inorg. Chem.* **2005**, *44*, 1914.

(26) Brauer, G. *Handbook of Preparative Inorganic Chemistry*, 2nd ed.; Academic Press: New York, 1965; Vol. 2.

Scheme 1



structure identical with that reported[3g] in the literature (see the Supporting Information). The reaction of copper(I) thiocyanate with $SC_3H_6N_2$ in a 1:1 or 1:2 molar ratio in acetonitrile or a acetonitrile/chloroform mixture has invariably formed a novel 3D polymer, **2**, unlike linear-chain polymers **1**, **1a**, and **3a**.

The formation of polymers (Scheme 1) is believed to take place as follows. Three copper(I) iodide units and three μ_2-S atoms of three $SC_3H_6N_2$ ligands form a six-membered ring (species **A**, Scheme 1) with terminal I atoms. Two such rings (**A**) combined in side-on fashion via μ_3-S and I atoms to generate species **B (**Scheme 1), which combined with another repeat unit **B** via an S atom to generate polymer **1**. Similarly, when repeat units **C** combined via halogen atoms (I and Br), the formation of polymers **1a** and **3a** occurred.[25] Copper(I) thiocyanate has probably initially formed a dimeric species **D**, via S atoms of two $SC_3H_6N_2$ ligands, with S-bonded SCN anions. The dimeric species **D** linked via free N ends of SCN anions to generate polymer **2**. The formation of **3** and **4** occurred via bridging by S atoms of 1,3-imidazolidine-2-thione.

Crystal Structures. Compound **1** crystallized in a triclinic system with space group $P\bar{1}$, while compound **2** as well as dimers **3** and **4** have monoclinic crystal systems. Figures 1, 6, 9, and 11 depict molecular structures with numbering schemes of compounds **1**, **3**, **4**, and **2**, respectively; other figures depict packing, H bonding, etc.

Compound 1. Figure 1 shows the repeat unit **B** of polymer **1** along with its numbering scheme, while Figure 2 shows a 1D polymeric chain running in the *ac* plane with its central axis parallel to the *a* axis. A look at Figure 2 reveals that there are four μ_3-S, two μ-S, two μ-I, and four terminal η^1-I atoms per hexanuclear unit $\{Cu_6(SC_3H_6N_2)_6I_6\}$. Each of Cu(1) and $Cu(1)^{\#}$ is bonded to two μ_3-S, one μ-S, and one terminal η^1-I atoms; each of Cu(2) and $Cu(2)^{\#}$ is bonded to two μ_3-S, one terminal η^1-I, and one bridging μ-I atoms, and finally each of Cu(3) and $Cu(3)^{\#}$ is bonded to two μ_3-S, one

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(27) *XSCANS*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1994.

(28) *International Tables for X-ray Crystallography*; Kluwer: Dordrecht, The Netherlands, 1995; Vol. C.

(29) Sheldrick, G. M. *SHELXTL-PC*, release 5.03; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1995.

(30) Win, G. X.; Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

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

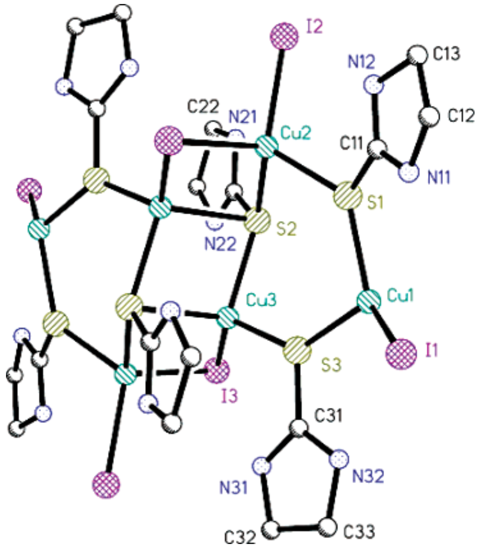

Figure 1. Structure of repeat unit **B** of 1D polymer **1** showing the numbering scheme.

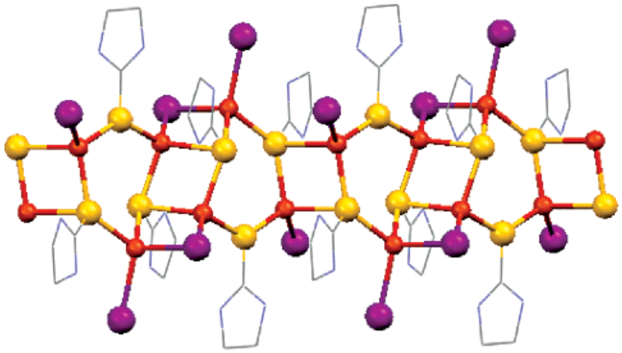

Figure 2. 1D polymeric chain of **1** running along the *ac* plane with its central axis parallel to the *a* axis.

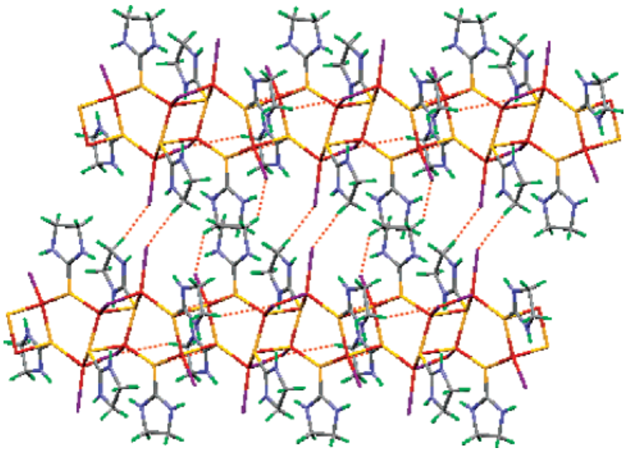

Figure 3. H bonding in **1** between two adjacent chains (stairs) giving rise to a 2D H-bonded lattice in the *bc* plane.

μ-S, and one μ-I atoms. Thus, in polymer **1**, there are two units, tetranuclear $Cu_4S_2I_2$ and dinuclear Cu_2S_2, that alternate to build this polymer. Further, the $Cu_4S_2I_2$ core has three subunits, a central homobridged Cu(μ-S)$_2$Cu core shared by two heterobridged Cu(μ-I)(μ-S)Cu cores, from top and bottom sides. Also, this central homobridged Cu(μ-S)$_2$Cu core has two shared six-membered rings (Cu_3S_3 cores) on either side in the horizontal direction. Figure 3 shows H bonding between two adjacent chains, giving rise to a 2D lattice in the *bc* plane. If we ignore heterobridged Cu(μ-I)(μ-S)Cu cores, the ladder-type skeleton results, as shown in Figure 4.

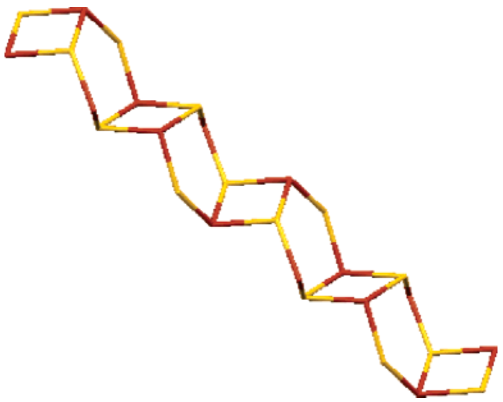

Figure 4. Ladder arrangement formed by four- and six-membered rings of **1**.

In the formation of polymer **1a** (Figure 5), the combining of repeat units **C** occurred via I atoms (Scheme 1). Here, there are two units, tetranuclear $Cu_4S_2I_2$ and dinuclear Cu_2I_2, that alternate to build this polymer. There are two μ_3-S, four μ-S, four μ-I, and two terminal η^1-I atoms per hexanuclear unit $\{Cu_6(SC_3H_6N_2)_6I_6\}$. Thus, **1a** and **1** represent rare examples of I$-$S bond isomerism.

The Cu$\cdots$Cu distances in the tetranuclear $Cu_4S_2I_2$ core of polymer **1** are 2.727(1) and 3.091(1) Å in the heterobridged Cu(μ-I)(μ-S)Cu and central homobridged Cu(μ-S)$_2$Cu cores, respectively, and the former contact is less than twice the sum of the van der Waals radii of Cu atoms, 2.80 Å.[32] Likewise, the dinuclear Cu_2S_2 core of polymer **1** has the longest Cu$\cdots$Cu contact of 3.294(1) Å. The corresponding distances in the tetranuclear $Cu_4S_2I_2$ core of polymer **1a** are 2.936(1) Å in the heterobridged Cu(μ-I)(μ-S)Cu moiety and 2.729(1) Å in the central homobridged Cu(μ-S)$_2$Cu moiety.[25] Thus, Cu$\cdots$Cu distances within tetranuclear $Cu_4S_2I_2$ cores of polymers **1** and **1a** are different. The Cu_2S_2 central core of polymer **1** forms a parallelogram with unequal Cu$-$S distances [Cu(3)$-$S(2), 2.3325(10) Å; Cu(3)$-$S(2)$^{\#}$, 2.5150(10) Å]. The angles Cu(3)$-$S(2)$-$Cu(3)$^{\#1}$ and S(2)$-$Cu(3)$-$S(2)$^{\#}$ within the Cu(μ-S)$_2$Cu core are 79.13(3) and 100.87(3)°, respectively, characteristic of such cores.[25] The angles Cu(1)$-$S(1)$-$Cu(1)$^{\#1}$ and S(1)$-$Cu(1)$-$S(1)$^{\#}$ are 85.00(3) and 95.00(3)°, respectively, within the dinuclear core Cu(μ-S)$_2$Cu. In regards to the heterobridged Cu(μ-I)(μ-S)Cu core, the angles at Cu, S, and I atoms are 114.34(3)$-$116.66(3)° (at Cu), 68.31(3)° (at S), and 62.083(17)° (at I), which are different, as expected, because of the difference in the bridging atoms. The C$-$S bond distances, 1.705(4)$-$1.724(4) Å, reveal considerable double-bond character.[32] The geometry around each Cu atom is distorted tetrahedral.

Dimers. As discussed earlier, the reaction of copper(I) bromide with $SC_3H_6N_2$ formed a polymer, **3a**,[25] and a dimer,

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

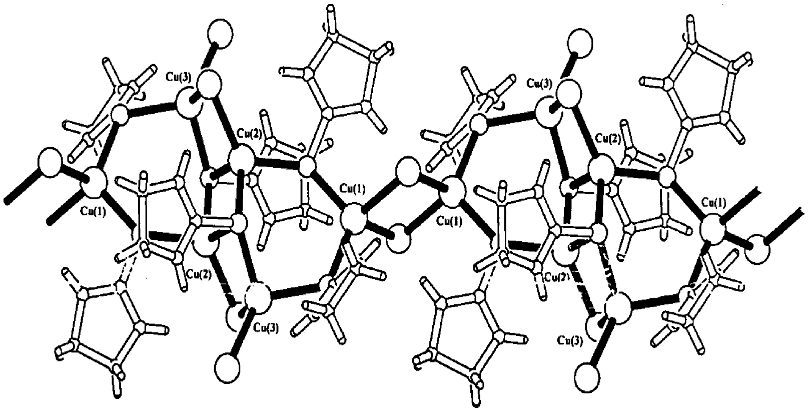

Figure 5. Structure of **1a** showing a 1D polymeric chain.[25]

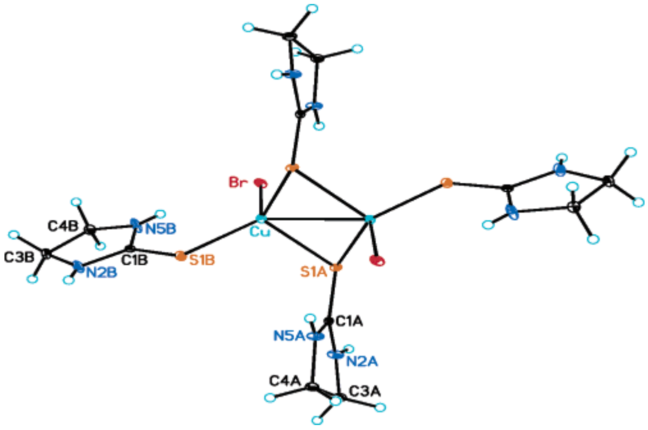

Figure 6. Structure of dimer **3** showing the numbering scheme.

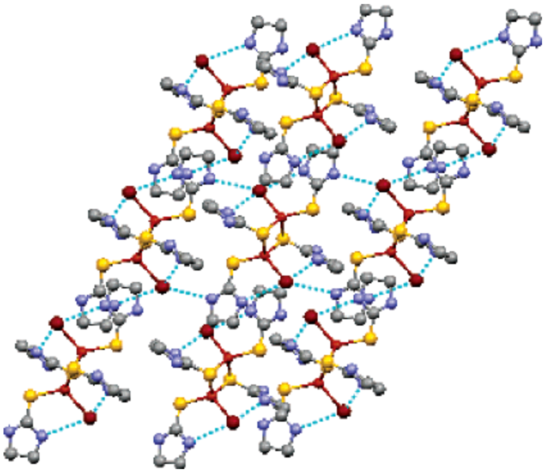

Figure 7. H-bonded polymeric view of dimer **3**.

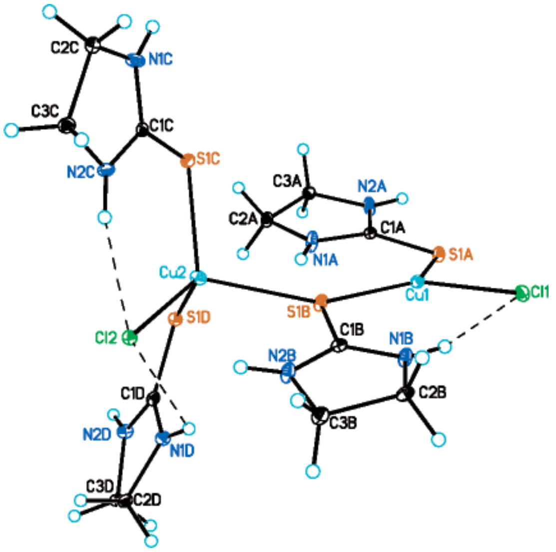

Figure 8. Structure of dimer **4** showing the numbering scheme.

3. The structure of polymer **3a** is identical with that of **1a** (see Figure 5).[25] The structure of **3** consists of a symmetrical sulfur-bridged dimer (Figure 6), formed by two bridging imidazolidine ligands, with two terminal bromide and two thione ligands. It has tetrahedral CuS_3Br coordination cores. The Cu−S distances are not equal [2.269(1) and 2.374(1) Å], and thus the Cu_2S_2 core forms a parallelogram, with angles at Cu and S within the core being 110.41(3)° and 69.59(3)°, respectively.[25] The similar cores of polymer **1** have different Cu−S distances and angles within the Cu_2S_2 cores as discussed. The Cu···Cu bond distance of 2.707(1) Å is smaller than those in polymers **1** and **1a.** The Cu−Br bond distance [2.488(1) Å] is close to the terminal Cu−Br distance, 2.436(1) Å, in **3a**.[25] The C−S bond distances, 1.699(2)−1.707(2) Å, support the double-bond character of the C═S bonds.[32] The geometry around each Cu atom is distorted tetrahedral. H bonding between Br and the imidazole rings is shown in Figure 7.

The structure of unsymmetrical dimer **4** formed by the reaction of copper(I) chloride with $SC_3H_6N_2$ is shown in Figure 8, which is similar to that reported in the literature[3g] and is only briefly given in this paper for comparison purposes (see the Supporting Information for more details).

3D Polymer 2. Two 1,3-imidazolidine-2-thione ligands and two CuSCN moieties combined via thione S to form a dimeric repeat unit, $\{Cu_2(\mu_2\text{-}SC_3H_6N_2)_2(SCN)_2\}$ (**C**), with S-bonded SCN ligands (Figure 9). The unequal Cu−S distances [2.3851(16) and 2.4061(15) Å] form a parallelogram with a Cu_2S_2 central core, and the angles within the $Cu(\mu_2\text{-}S)_2Cu$ core are 71.53(5) and 108.47(5)° at S and Cu atoms, respectively, characteristic of such cores.[25] Repeat units **C** combine with other **C** units via free N donor atoms of SCN to form the polymer **2** [Cu−S(SCN) distance, 2.3701(16) Å; Cu−N(SCN), 1.982(4) Å]. The C−S distances of the 1,3-imidazolidine-2-thione and SCN ligands are 1.722(5) and 1.666(5) Å, respectively, with the former

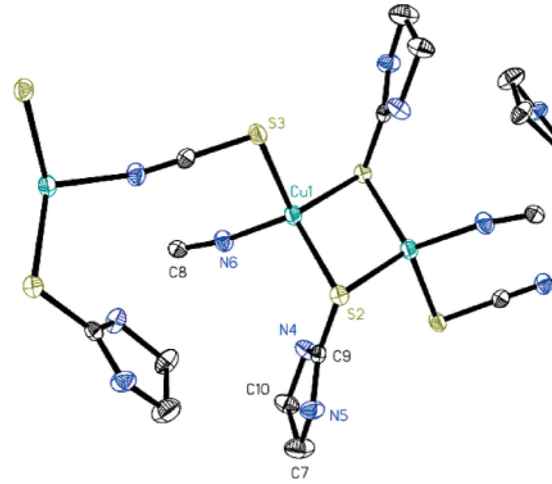

Figure 9. Numbering scheme of polymer **2**.

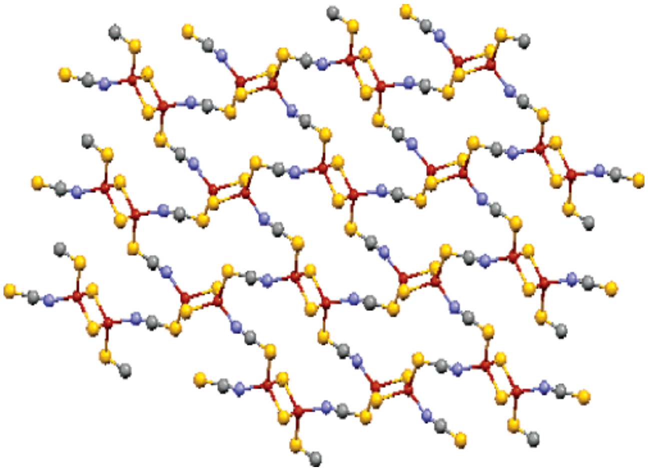

Figure 10. 3D coordination polymer formed because of bridging bidentate coordination by −SCN groups (rings and H atoms are omitted for clarity).

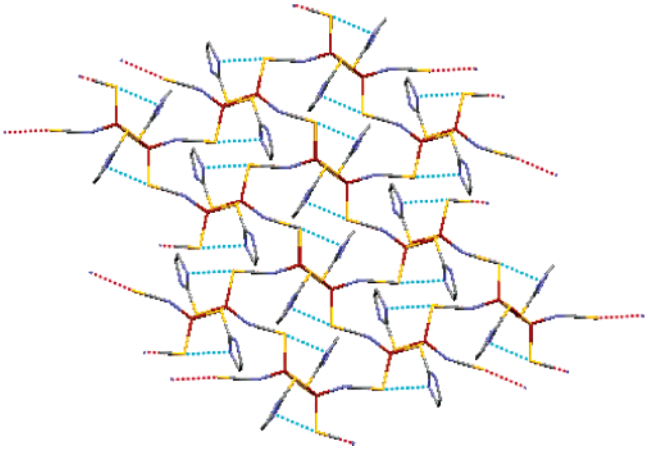

Figure 11. H-bonding interactions in **2** [N4···S3, 3.264 Å, between the imidazolidine ring and the thiocyanate group; S3···centroid of ring, 3.779 Å].

distance being similar to that in **1**. The Cu···Cu distance at 2. 8002(15) Å is less than the similar distance in polymer **1** but equal to the sum of the van der Waals radii of Cu atoms, at 2.80 Å.[32] The angles at Cu vary over a wide range, ca. 71.53(5)−114.02(6)°, suggesting distorted tetrahedral geometry around each Cu atom. A significant feature of the structure of **2** lies in the observation that it has 20-membered metallacyclic rings (Figure 10). The H-bonding interactions in **2** [between imidazole and thiocyanate groups, N4···S3, 3.264(1) Å; S3···imidazole ring S3···centroid, 3.779(1) Å] are shown in Figure 11.

IR and NMR Spectroscopies. The main characteristic IR peaks of complexes of 1,3-imidazolidine-2-thione are listed in the Experimental Section. The ν(N−H) peaks in free imdtH$_2$ at 3283(s) and 3248(s) cm^{-1} undergo low-energy shifts in complexes **1**, **3,** and **4**, while in compound **2**, it moves to higher energy.[33−35] The most significant diagnostic peak due to the ν(C=S) peak in a free ligand at 920 cm^{-1} shifts to a low-energy region, 885−895 cm^{-1}, in complexes **1** and **2**, the shift is small in compound **3**, and it is unchanged in **4**. The peaks due to ν(C−H) and ring ν(C−N) are not significantly changed. The thiocyanate peaks due to ν(C−S), ν(C−N), and δ(SCN) bands of the thiocyanate moiety occur at 725, 2060, and 470 cm$^{-1,}$ respectively, and support its bridging nature. NMR spectra of compounds **1** and **2** were recorded although the solubility was very low. The S-bridged polymer **1** showed a very weak peak due to CH$_2$ protons at δ 3.79 ppm, which is at low field relative to the free ligand CH$_2$ peak at δ 3.59 ppm; its NH protons could not be identified probably because of the low solubility of the complex (cf. the ligand NH proton signal at δ 6.40 ppm). The thiocyanate-based polymer **2** also has shown peaks at δ 6.66 (NH) and 3.65 (CH$_2$) ppm in CD$_3$CN. Thus, both of the polymers undergo deshielding for their NH and CH$_2$ protons.

Conclusion

In the reactions of copper(I) salts with 1,3-imidazolidine-2-thione, the anions have influenced the bonding properties of the thione ligand. Copper(I) iodide formed 1D linear polymers, exhibiting I−S bond isomerism in unusual linear polymers: $\{Cu_6(\mu_3\text{-}SC_3H_6N_2)_4(\mu_2\text{-}SC_3H_6N_2)_2(\mu\text{-}I)_2I_4\}_n$ (**1**) and $\{Cu_6(\mu_3\text{-}SC_3H_6N_2)_2(\mu_2\text{-}SC_3H_6N_2)_4(\mu\text{-}I)_4I_2\}_n$ (**1a**). Copper(I) bromide yielded 1D polymer **3a**, similar to **1a**, and a dimer $\{Cu_2(\mu\text{-}SC_3H_6N_2)_2(\eta^1\text{-}SC_3H_6N_2)_2Br_2\}$ (**3**). Finally, copper(I) chloride only formed an unsymmetrical dimer $\{Cu_2(\mu\text{-}SC_3H_6N_2)(\eta^1\text{-}SC_3H_6N_2)_3Cl_2\}$ (**4**). Polymers **1**, **1a**, and **3a** exhibited a new μ_3-S bonding mode. The thiocyanate anion yielded another novel 3D polymer **2** with the formation of 20-membered metallacyclic rings. The crystal formation of compounds **1/1a**, **3a/3**, and **4** was favored in the mixed solvents CH$_3$CN/CHCl$_3$, and for **2**, either this mixture or CH$_3$CN alone was suitable.

Acknowledgment. Financial help from CSIR New Delhi and research facilities to R.S. by the Guru Nanak Dev University are gratefully acknowledged.

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(33) Dwarkanath, K.; Satyanarayana, D. N. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2699.

(34) Dwarkanath, K.; Satyanarayana, D. N. *Indian J. Chem.* **1979**, *18A*, 2699.

(35) Devillanova, F. A.; Verani, G. *J. Chem. Soc. A* **1978**, 24.

Supporting Information Available: X-ray crystal data in CIF format [CCDC numbers are 298899−298902 for compounds **1**−**4**, respectively; these data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K., tel +441223 336408, fax +44 1223 336033] and crystallographic data, bond lengths and angles, and structure for compound **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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