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Copper(I) Thiocyanate Networks with Aromatic Diimine Ligands.

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Abstract: A total of five new CuSCN-LL complexes with aromatic diimine ligands, LL= quinoxaline (Qox), quinazoline (Qnz), phthalazine (Ptz), 2-aminopyrazine (2-NH₂Pyz), and 2-methoxypyrazine (2-MeOPyz) have been prepared and characterized by crystallographic methods. The following compounds are reported: (CuSCN)₂(Qox) (**1**), (CuSCN)(Qnz) (**2**), (CuSCN)₂(Ptz) (**3**), (CuSCN)₂(2-NH₂Pyz) (**4**), and (CuSCN)(2-MeOPyz) (**5**). Compounds **1–4** were prepared using an extended aqueous reflux method in the presence of KSCN and ammonia. Compound **5** was prepared by directly reacting solid CuSCN with the liquid ligand. In complexes **2** and **5**, LL is monodentate, while in others LL is bridging bidentate. All network structures are 2-D sheets, consisting of μ_2 -LL-crosslinked CuSCN ladders for **1** and **4**, LL-decorated CuSCN sheets for **2** and **5**, and unusual μ_2 -LL-“stapled” sheets for **3**.

Keywords: Copper thiocyanate complexes; Crystal structures; Diimine ligands; Network structures; Thermogravimetry

1. Introduction

Polymeric and network metal-organic compounds are of interest owing to the wide array of structural motifs they exhibit and their potential applications in gas storage, chemical sensing, catalysis, and separations [1]. Among the advantages offered by metal-organic networks is their convenient formation via self-assembly. Thus, stoichiometrically controlled combinations of metals and ligands tend to react under relatively modest thermal conditions, often forming multiple and/or unexpected product topologies. In addition, insoluble products are readily isolated from reaction mixtures. Of particular interest are metal salts containing bridging inner sphere anions, such as halides, chalcogenides, or pseudo-halides. These salts are themselves robust inorganic network-formers. Their networks can be further expanded through reaction with bridging organic ligands. In contrast, non-coordinating counterions, such as BF_4^- , PF_6^- , ClO_4^- , etc. tend to fill network pores, diminishing network host-guest potential.

Copper(I) thiocyanate is an example of an inner sphere salt, forming 3-D networks in each of its three known polymorphs [2]. In each CuSCN polymorph, tetrahedral coordination of Cu(I) is complemented by tetrahedral geometry at sulfur, resulting from μ_3 -bridging of copper centers. Because both copper and sulfur centers show tetrahedral connectivity, the polymorphs of CuSCN bear a close structural relationship to those of CuI. In the latter, packing of tetrahedral Cu^+ and I^- centers produces either the cubic zinc blende or hexagonal wurtzite forms. Of course, the hexagonal channels in CuSCN networks, unlike those in CuI, are distorted by the length of the thiocyanate ion.

The introduction of organic ligands has been shown to restrict inorganic network formation in CuSCN. Addition of monodentate “capping” ligands (L), such as aromatic amines, typically results in one of three common CuSCN motifs: chains (A), ladders (B), or hexagonal sheets (C), see Chart 1. Type A networks consist of isolated $(\text{CuSCN})_\infty$ chains linked via μ_2 -(N,S)-thiocyanate bridging, with the copper(I) coordination being completed either by pairs of ligand molecules (A) or single ligand molecules (A'). Thus, copper centers are 4-coordinate in Type A, and 3-coordinate in Type A'. Type A polymers

have been identified for L = 2-MePy (Py = pyridine), 3-MePy, 4-MePy, 4-EtPy, 2,4-Me₂Py, and quinoline [3, 4]. Type A' polymers are known for the more hindered L = 2,6-Me₂Py and 2,4,6-Me₃Py [3, 4].

A, CuSCNL_2 ; A', CuSCNL

B, CuSCNL

C, CuSCNL

trans-fusion: zigzag sheet

cis-fusion: square wave sheet

Chart 1. CuSCN Network Motifs.

In the case of network types B and C, additional coordination of Cu centers to thiocyanate sulfur produces μ_3 -(N,S,S)-thiocyanate bridging between CuSCN chains. For Type B complexes this results in the formation of $[\text{Cu}_2(\text{SCN})_2]_\infty$ ladders composed of alternating Cu_2S_2 and $\text{Cu}_2(\text{SCN})_2$ rings. Type B ladders have been found for $L = 2\text{-MePy}$, 2-EtPy , and $N\text{-methylpiperidine}$ [3, 4]. While Type B ladders can be envisioned as arising from linked pairs of Type A' chains, Type C networks are likewise formed from series of type A' chains crosslinked in two directions to form 2-D rippled sheets consisting of fused $\text{Cu}_3(\text{SCN})_2\text{S}$ macrocycles. This arrangement is tantamount to extraction of an atom layer from CuSCN and capping of that layer on one or both faces with L ligands. The elongated hexagonal rings fuse in either *trans* (chair-like) or *cis* (boat-like) fashion, yielding zigzag or square-wave cross-sections respectively (see Chart 1). Type C decorated sheets are recognized for $L = 3\text{-ClPy}$ (*trans*), 3-BrPy (*trans*), and $N\text{-methylmorpholine}$ (*cis*) [4].

The use of bridging ligands (LL) with CuSCN results in increased networking in these, and a few other, motifs. Crosslinking of chains by bridging ligands results in expansion of Type A chains into 2-D sheets having stoichiometry $(\text{CuSCN})(\text{LL})$. Type B ladders can be linked together to form 2-D sheets of stoichiometry $(\text{CuSCN})_2(\text{LL})$. Linking can occur in either of two fashions with adjacent ladders related either by mirror or inversion symmetry [5, 6]. Finally, crosslinking of Type C sheets by LL produces 3-D networks. As with the non-bridged sheets, both zigzag (chair) and square wave (boat) topologies are encountered. In some cases, more than one network type can be produced using a particular ligand.

When potentially bidentate pyrazine (Pyz, see Chart 2) ligands are used, a variety of networks are encountered. Known pyrazine networks with CuSCN include (1) 2-D sheets of crosslinked Type A chains, $\text{LL} = \text{Pyz}$, 2-MePyz [7, 8], (2) 2-D sheets of crosslinked Type B ladders, $\text{LL} = 2\text{-MePyz}$ [5, 6], (3) 3-D crosslinked *trans*-fused Type C networks, $\text{LL} = \text{Pyz}$ and $2,5\text{-Me}_2\text{Pyz}$ [9, 10, 11], and (4) a 3-D crosslinked *cis*-fused Type C network, $\text{LL} = 2\text{-Me-3-EtPyz}$ [12]. Two additional bridging Pyz networks are based upon the simple rhomboid Cu_2S_2 building unit. In both $(\text{CuSCN})_2(3\text{-IPyz})$ and $(\text{CuSCN})_2(2,3\text{-Me}_2\text{Pyz})$, Cu_2S_2 rings are linked together by both the SCN tails and the LL ligands. The resulting 3-D networks can be envisioned as being based upon Type B ladders in which the $\text{Cu}_2(\text{SCN})_2$ rings have been

opened, and thus form links in orthogonal directions [13, 14]. Finally, two substituted Pyz ligands have been shown behave in non-bridging monodentate fashion, forming $(\text{CuSCN})(2\text{-NCPyz})_2$, a 1-D Type A chain (2-NCPyz bonds through a ring N) [5], and $(\text{CuSCN})(2\text{-Me-3-EtPyz})$, a 1-D Type B ladder [12].

Chart 2. Ligands (with numbering where needed).

Pyrimidine (Pym) ligands are disadvantaged as bridges by their 120° bite angle, creating difficulties for the crosslinking of sheets. As a result many Pym complexes are monodentate. These include $(\text{CuSCN})(4\text{-HOPym})_2$, which is a Type A chain [5], and $(\text{CuSCN})(4\text{-MePym})$ and $(\text{CuSCN})(5\text{-BrPym})$, both of which are *trans*-fused Type C sheets [5, 8]. Alternatively in the 3-D $(\text{CuSCN})_2(\text{Pym})$ network, bidentate Pym ligands bridge large $\text{Cu}_4(\text{SCN})_2\text{S}_2$ pores in a series of Type A chains that are crosslinked by $\cdots\text{Cu-S-Cu-S}\cdots$ chains [15]. The 3-D $(\text{CuSCN})_2(4\text{-MePym})$ network is altogether different, consisting of orthogonal sets of Type C sheets (both zigzag and square wave type) which are connected by not only through the LL ligand, but also via Cu_3S_3 rings [5]. Pyridazine (Pdz) ligands have not been widely studied with CuSCN. Only the parent ligand complex is known. It fails to bridge, acting in monodentate fashion and forming $(\text{CuSCN})(\text{Pdz})$, a *cis*-fused Type C sheet [16].

Herein we present the synthesis and structure of five new CuSCN-aromatic diimine compounds containing LL = quinoxaline (Qox), quinazoline (Qnz), phthalazine (Ptz), 2-aminopyrazine (2-NH₂Pyz) and 2-methoxypyrazine (2-MeOPyz). The closely related Qox, Qnz and Ptz were found to show

networking behavior with CuSCN that differed greatly from that of their single-ring analogs: Pyz, Pym, and Pd_z, respectively.

2. Experimental

2.1 Materials and Methods

All reagents were purchased from Aldrich or Acros and used without purification, except for quinoxaline (Qox), which was sublimed before use. Commercial CuSCN (Aldrich) was shown by FTIR to consist solely of the α -phase [17]. IR spectra were collected on a Shimadzu IRTracer-100 instrument using a diamond ATR probe (spectra shown in Supporting Information). Analyses for C, H, and N were carried out by Atlantic Microlabs, Norcross, GA. Atomic absorption analyses for Cu were carried out using a Perkin-Elmer AAnalyst 700 as previously described [18]. Thermogravimetric analyses (TGA) were conducted using a TA Instruments Q500 in the dynamic (variable temp.) mode with a maximum heating rate of 50 °C/min. to 800 °C under 50 mL/min. N₂ flow.

2.2 Syntheses

(CuSCN)₂(Qox), **1**. CuSCN (121 mg, 1.00 mmol) was suspended in 20 mL deionized water containing 146 mg (1.5 mmol) KSCN and 0.5 mL 17 M NH₃ (8.5 mmol) under Ar purge. Qox (70 mg, 0.54 mmol) was added to the suspension, which quickly took on a red-orange color. The suspension was refluxed for 72 h. The red solid product was collected via filtration, washed with deionized water, and dried under vacuum (123 mg, 66%). IR (cm⁻¹): 2086 (strong), 1500, 1362, 1207, 1049, 867, 764 (strong). Anal. Calcd for C₁₀H₆Cu₂N₄S₂: Cu, 34.03; C, 32.17; H, 1.62; N, 15.00. Found: Cu, 33.93; C, 31.40; H, 1.66; N, 14.45. TGA calcd for CuSCN: 65.2%. Found: 66.3% (140–190 °C).

(CuSCN)(Qnz), **2**. The procedure for **1** was followed using Qnz (133 mg, 1.02 mmol) in the place of Qox. A yellow solid was collected (145 mg, 57%). IR (cm⁻¹): 2113 (strong), 1616, 1574, 1489, 1373, 1211, 926, 791, 745 (strong), 633. Anal. Calcd for C₉H₆CuN₃S₁: Cu, 25.24; C, 42.93; H, 2.40; N, 16.69.

Found: Cu, 27.08; C, 41.28; H, 2.27; N, 16.08. TGA calcd for CuSCN: 48.3%. Found: 51.9% (125–170 °C).

(CuSCN)₂(Ptz), **3**. The procedure for **1** was followed using Ptz (70 mg, 0.54 mmol) in place of Qox. A yellow solid was collected (87 mg, 46%). IR (cm⁻¹): 2137 (strong, sharp), 1574, 1447, 1377, 1308, 1273, 1219, 914, 741 (strong). Anal. Calcd for C₁₀H₆Cu₂N₄S₂: Cu, 34.04; C, 32.17; H, 1.62; N, 15.00. Found: 34.89; C, 31.33; H, 1.58; N, 14.51. TGA calcd for CuSCN: 65.2%. Found: 66.6% (200–250 °C).

(CuSCN)₂(2-NH₂Pyz), **4**. The procedure for **1** was followed using 2-NH₂Pyz (65 mg, 0.68 mmol) in place of Qox. A yellow solid was collected (106 mg, 63%). IR (cm⁻¹): 3418, 3317, 2102 (strong), 1616 (strong), 1593, 1528 (strong), 1435, 1215, 1029, 817, 768. Anal. Calcd for C₆H₅Cu₂N₅S₂: Cu 37.56; C, 21.30; H, 1.49; N, 20.70. Found: Cu, 36.32; C, 20.41; H, 1.38; N, 19.73. TGA calcd for CuSCN: 71.9%. Found: 74.0% (115–220 °C).

(CuSCN)(2-MeOPyz), **5**. CuSCN (100 mg, 0.82 mmol) was stirred in 500 µL neat 2-MeOPyz (5.18 mmol) under Ar for 3 d at ambient temp. A yellow solid was collected by filtration, washed with ethyl ether, and dried under vacuum (154 mg, 81%). IR (cm⁻¹): 2123 (strong, sharp), 1587, 1529 (strong), 1471, 1438, 1398, 1311, 1284, 1195, 1145, 1060, 1014 (weak), 1004 (strong, sharp), 837, 759, 617. Anal. Calcd for C₆H₆CuN₃O₁S₁: Cu 27.42; C 31.10; H, 2.61; N, 18.13. Found: Cu, 26.48; C, 31.12; H, 2.42; N, 17.95. TGA calcd for CuSCN: 52.5%. Found: 53.9% (75–105 °C).

2.3 Crystallizations

Single crystals were grown from suspensions similar to those used in the bulk syntheses. Crystals of **1**, **2**, **3** and **4** were grown as follows: Deionized water (35 mL) containing CuSCN (121 mg, 1.00 mmol) and KSCN (97 mg, 1.00 mmol) was degassed using Ar. To this suspension, NH₃ (17 M) was added drop-wise until most of the solid had dissolved (about 1 mL total). The ligand (66 mg Qox, 131 mg Qnz, 66 mg Ptz, or 54 mg 2-NH₂Pyz) was then added and the solution was briefly stirred. It was then refluxed under Ar for 72 h without stirring. Crystals were observed on the surface of the aqueous layer within 24 h, but were left to grow over another 48 h. They were collected by filtration and washed with deionized water.

Crystals of **5** were grown differently: CuSCN (100 mg, 0.82 mmol) was partially dissolved in 5 mL 1 M NH₃ (aq) under Ar. 2-MeOPyz (50 μ L, 0.52 mmol) was dissolved in 3 mL EtOH and layered on top of the aqueous suspension and sealed in a 5 mm i.d. tube. Crystal growth became apparent after about two weeks when the solid emitted green upon exposure to UV light.

2.4 X-ray data collection, structure solutions and refinements

All X-ray measurements were made using graphite-monochromated Cu K α radiation on a Bruker-AXS three-circle diffractometer, equipped with a SMART Apex II CCD detector. All data were collected at 100 K. Initial space group determination was based on a matrix consisting of 120 frames. The data were corrected for Lorentz and polarization [19] effects and absorption using SADABS [20]. All structures were solved using direct methods or intrinsic phasing. Structure solution, refinement and the calculation of derived results were performed using the SHELXTL [21] package of software and ShelXle [22]. Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in theoretical positions.

3. Results and Discussion

3.1 Synthesis and characterization

The complexes of CuSCN with diimine ligands, LL = Qox, Qnz, Ptz, 2-NH₂Pyz, and 2-MeOPyz (**1–5**) were prepared and studied. An aqueous procedure was effective for the synthesis of four of the five complexes described herein. Thiocyanate ion and ammonia were used as mineralization and phase-transfer agents to partially solubilize CuSCN in aqueous medium. A prolonged three-day reflux was required to ensure complete conversion of CuSCN to the network product. TGA and powder X-ray diffraction analysis indicated the presence of residual CuSCN when shorter reflux times were used, or when no ammonia was added. Compounds **1–4** formed readily under these conditions, with the resulting suspensions taking on their characteristic color within seconds or minutes but complete conversion requiring several days. Additionally, the H₂O/KSCN/NH₃ reaction conditions enabled the convenient growth of single crystals for all four compounds when stirring of the mixture was omitted. The slow pace

of the reaction due to the very limited aqueous solubility of CuSCN thus proved to be advantageous for crystal growth.

Pure samples of **5** could not be prepared under aqueous conditions, and were only accessible by stirring CuSCN in the neat ligand at room temperature. This method has previously been used to prepare monodentate ligand complexes of CuSCN, yielding bulk powders when stirred and crystals when heated without stirring [4]. In order to grow crystals of this compound, CuSCN was fully dissolved in relatively concentrated aqueous ammonia and the ligand in ethanol solution layered on top of CuSCN solution [9].

All compounds were characterized via elemental analysis and found to be with acceptable range. Thermogravimetric analysis (TGA) was carried out on all complexes. The results shown in Figure S1 revealed loss of the diimine ligands at modest temperatures, commencing between 80 and 200 °C. The thermal stability ranking of the complexes based on TGA results was: **5** < **2** < **1** < **4** < **3**. Thus bidentate ligand binding in complexes **1**, **3**, and **4** imparted greater stability than monodentate binding seen in **2** and **5**. No plateaus that might indicate the formation of metastable phases were observed during ligand loss. In all cases, CuSCN had formed by about 250 °C and then decomposed near 400–450 °C.

3.2. Description of X-Ray Structures

Crystal structures were solved for all complexes. The resulting structures generally fall into two of the recognized categories for CuSCN networks: bridged ladders (Type B, see Chart 1) and 2-D sheets (Type C). Crystallographic data are summarized in Table 1. Selected bond distances and angles for all complexes are given in Table S1. Thermal ellipsoid drawings of the asymmetric units for all compounds are found in the Supporting Information.

Compound **1** crystallized as long red needles that solved in centrosymmetric monoclinic space group $P2_1/n$. Network diagrams are shown in Figure 1. The asymmetric unit consists of $(\text{CuSCN})_2(\text{Qox})$. In **1**, Type B CuSCN ladders are bridged by Qox ligands. The thiocyanate sulfur atoms bridge pairs of Cu atoms to form alternating rhomboid cyclic Cu_2S_2 and $\text{Cu}_2(\text{SCN})_2$ dimers. The gross structure of **1** bears much resemblance to $(\text{CuI})_2\text{Qox}$ [18], with the SCN anion acting as the μ_3 bridging ligand in place of

iodide. Copper atoms in **1** show distorted tetrahedral S_2N_2 coordination environments: $100.56(8)$ – $128.49(8)^\circ$. As with all such complexes, Cu–NCS is significantly shorter than Cu–N_{aromatic} ($1.975(3)$ and $1.983(3)$ Å vs. $2.019(3)$ and $2.032(3)$ Å). The CuSCN ladders propagate along the *a*-axis. The ladders repeat along the *b*-axis as they are bridged by Qox. Pairs of CuSCN chains are linked in an anti-parallel fashion to form the ladder motif, with Qox ligands forming the steps in a square wave pattern in the sheets when viewed from the side. The Qox groups are sufficiently displaced from one another along rows such that the nearest centroid⋯centroid distance is approximately 4.14 Å, ruling out π -stacking. A very close Cu⋯Cu interaction of $2.7305(6)$ Å is noted across the Cu_2S_2 rhombus. This distance falls within the van der Waals radius sum for copper (2.8 Å) and is correlated with relatively acute angles at S of $67.79(3)$ and $70.17(3)^\circ$. Similar behavior is noted for the Cu_2I_2 rhombs in $(CuI)_2Qox$ [18], and is also apparent in other CuSCN ladder networks. [5, 6, 23].

Figure 1. Network formation for **1**. CuSCN atoms shown as ball and stick, and Qox atoms as wireframe. Hydrogen atoms are omitted. Top: view along *c*-axis, bottom: view along *a*-axis. Color scheme for all X-ray figures: orange = Cu, yellow = S, grey = C, blue = N, red = O. Selected bond lengths (Å) and angles (°): Cu–SCN = 2.3185(9), 2.2788(9), 2.4641(9), 2.5641(9), Cu–NCS = 1.975(3), 1.983(3), Cu–N_{arom} = 2.019(3), 2.032(3), Cu···Cu = 2.7305(6), Cu–S–C = 93.99(11), 106.04(11), C–N–Cu = 161.7(3), 162.9(3), Cu–S–Cu = 67.79(3), 70.17(3).

The 1:1 CuSCN:Qnz compound **2** crystallized as small yellow plates. The structure was solved in the non-centrosymmetric monoclinic space group *Cc*. A network diagram are shown in Figure 2. As has previously been observed for CuSCN complexes of Pym ligands, this first-reported Qnz complex contains only monodentate ligands. It forms a *trans*-fused Type C network (see Chart 1). Thus, the gross structure of **2** bears much resemblance to the parent CuSCN networks, essentially comprising a series of exfoliated sheets consisting of elongated, fused Cu₃(SCN)₂S rings. Zigzag (CuS)_∞ chains run parallel to the *b*-axis and the 2-D sheets run parallel to the crystallographic *b,c* plane. The 4-coordinate Cu atoms have a S₂N₂ coordination sphere, in which one of the nitrogen atoms is associated with the monodentate Qnz ligand. Angles around Cu are very close to tetrahedral: 106.30(19)–112.4(3)°. Each copper atom is capped by a monodentate Qnz ligand, all of which are located on a single sheet face. The Qnz ligands along individual zigzag (CuS)_∞ chains are canted in identical positions and are π -stacked with identical centroid-centroid distances of 3.764 Å between adjacent carbocyclic rings and between adjacent heterocyclic rings. The cant angle of the Qnz rings alternates between adjacent (CuS)_∞ chains, with an inter-planar angle of 44.62°. All the sheets are identically aligned, such that the carbocyclic Qnz rings lie relatively close to the undecorated side of the adjacent sheet. This results in several close interactions between ring hydrogens

and thiocyanate: $H6\cdots C1 = 3.025 \text{ \AA}$, $H6\cdots S1 = 2.864 \text{ \AA}$, $H5\cdots N1 = 3.154 \text{ \AA}$, $H5\cdots C1 = 3.337 \text{ \AA}$. In the current structure, Qnz coordinates only through the 3-position nitrogen atom (see Chart 2). This allows the long axis of the ligand to point outward from the CuSCN sheet.

Figure 2. Network formation in **2**, viewed down the a,b -axis bisector. CuSCN atoms shown as ball and stick, and Qnz atoms as wireframe. Hydrogen atoms are omitted. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$): Cu–SCN = 2.345(2), 2.349(2), Cu–NCS = 1.953(8), Cu–N_{arom} = 2.057(7), Cu–S–C = 104.8(3), 108.3(3), C–N–Cu = 177.5(7), Cu–S–Cu = 106.60(8).

Compound **3** crystallized as yellow plates, solving in the centrosymmetric orthorhombic space group $Pbcn$. Network diagrams are shown in Figure 3. As was the case with **2**, compound **3** formed Type C 2-D CuSCN sheets consisting of 10-membered $Cu_3(SCN)_2S$ rings. However, rather than having LL ligands either monodentate or bridging between sheets, the Ptz ligands bridge pairs of Cu atoms within single sheets. This produces five-membered Cu_2N_2S rings that project obliquely from the faces of the sheets, an effect we describe as ligand “stapling”. The stapling effect of the Ptz ligands between pairs copper atoms draws these pairs relatively close together. Thus, the stapled $Cu\cdots Cu = 3.042 \text{ \AA}$, while the non-stapled $Cu\cdots Cu = 3.889 \text{ \AA}$. Furthermore, the stapled Cu–S–Cu bond angle is $77.083(16)^\circ$, while the

non-stapled Cu–S–Cu angle is $109.84(2)^\circ$. The stapling strain is also reflected in large deviations from ideal tetrahedral angles around Cu, ranging from $93.58(4)^\circ$ to $134.53(7)^\circ$. Stapling also introduces significant strain into the Type C 10-membered rings, half of which are chairs, while the other half are twist boats, the two forms alternating along edge-sharing rows. This type of bridging causes the sheet to become significantly distorted compared to other known Type C structures, such as **2** or **5**. The CuSCN chains, which propagate roughly parallel to the *b*-axis are modestly distorted. However, the CuS chains, which propagate parallel the *a*-axis, are highly distorted by the stapling effect of the Ptz ligands.

Figure 3. Network formation in **3**. CuSCN atoms shown as ball and stick, and Ptz atoms as wireframe. Hydrogen atoms are omitted. Top: view along *c*-axis, center: view along *a*-axis, bottom: view along *b*-axis. Selected bond lengths (Å) and angles ($^\circ$): Cu–SCN = 2.3641(5), 2.3883(5), 2.3994(5), 2.4814(5), Cu–NCS = 1.9035(18), 1.9272(17), Cu–N_{arom} = 2.0038(16), 2.0839(16), Cu $\cdots$ Cu = 3.0417(4), Cu–S–C =

100.11(7), 100.69(6), 100.70(7), 102.25(7), C–N–Cu = 173.56(16), 177.13(16), Cu–S–Cu = 77.083(16), 109.84(2).

The Ptz ligands alternate between faces of the sheet, producing a roughly square wave pattern in which each wave contains a Cu–S–Cu–S unit. There is no evidence of π -stacking between Ptz ligands or interactions between the sheets. There are two orientations of the Ptz group, their ring planes lying at angles of 15.9° to one another. The Ptz planes are found to lie at angles of 50.5° and 51.0° with respect to the CuSCN sheet plane (calculated using the nearly-parallel CuSCN units). The bridging behavior of Ptz is noteworthy when compared with its single-ring analog Pdz [14]. The known network (CuSCN)(Pdz) is composed of *cis*-fused Type C sheets with Pdz acting as a monodentate capping ligand, as is seen herein for Qnz in the *trans*-fused Type C complex **2**. In contrast to **3**, neither of the monodentate Pdz or Qnz structures show meaningful evidence of strain in the sheet arrangements, bond lengths or bond angles.

Compound **4** crystallized as orange blocks that solved in the centrosymmetric triclinic space group *P*–1. Network diagrams for **4** are shown in Figure 4. The crystallographically independent unit consists of (CuSCN)(2-NH₂Pyz)_{0.5}. Because the 2-NH₂Pyz ligand in **4** is centered on an inversion center, the NH₂ substituent is disordered over two positions (see Supporting Information). As was seen for **1**, the networking in compound **4** is composed of a series of crosslinked Type B ladders, which propagate parallel to the *a*-axis. Linking of the ladders by 2-NH₂Pyz occurs in a direction parallel to the *a,c*-axis bisector. Unlike compound **1**, the Cu··Cu separation of 3.0032(10) Å in the Cu₂S₂ dimers is too large to be considered bonding. Correspondingly, the rhomboid dimer Cu–S–Cu angle of 72.89(2)° was larger than those seen in **1**. Viewed from the side, the sheets in **4** show a zigzag pattern. The Cu₂S₂ units lie in like orientation and are bridged by LL units across oppositely oriented Cu centers. In **1**, by way of contrast, the Cu₂S₂ units lie alternating orientations, creating a square wave pattern (see Figure 1).

Figure 4. Network arrangement in **4**. CuSCN atoms shown as ball and stick, and 2-NH₂Pyz atoms as wireframe. Hydrogen atoms are omitted. Top: view along *b*-axis, bottom: view along *a*-axis. Ligand disorder has been omitted. Selected bond lengths (Å) and angles (°): Cu–SCN = 2.3572(11), 2.6803(13), Cu–NCS = 1.921(4), Cu–N_{arom} = 1.997(4), Cu···Cu = 3.0031(16), Cu–S–C = 96.78(13), 102.04(15), C–N–Cu = 163.8(3), Cu–S–Cu = 72.87(4).

Compound **5** crystallized as small colorless blades, solving in the centrosymmetric orthorhombic space group *Pnnm*. A network diagram is shown in Figure 5. The networking structure consists of Type C

sheets with *cis* ring fusions. As was the case with Qnz in **2**, 2-MeOPyz acts as a monodentate ligand. However, in **5**, 2-MeOPyz ligands are present on both faces of the CuSCN sheet, similar to monodentate complexes (CuSCN)(2-Me-3-EtPyz) and (CuSCN)(Pdz) [10, 14]. The *cis*-fused boat conformation of the CuSCN rings allows for ligand decoration on both faces of the sheets, which in the case of **5** run parallel to the *a,c* plane. All CuSCN chains lie directly on a mirror plane, but for the 2-MeOPyz ligand only atoms N1 (coordinated to Cu) and C3 (*meta* to N1) lie directly on a mirror plane. The remaining atoms C1, C2, C4, N2, O1, and C5 are slightly displaced to either side of a mirror plane, resulting in two-site disorder (see Supporting Information). There is no evidence of interactions between the sheets, or of π -stacking in the structure.

Figure 5: Network formation in **5**, viewed down the *c*-axis. CuSCN atoms shown as ball and stick, and 2-MeOPyz atoms as wireframe. Hydrogen atoms are omitted. Disordered 2-MeOPyz positions have been omitted. Selected bond lengths (Å) and angles (°): Cu–SCN = 2.3513(5), Cu–NCS = 1.944(3), Cu–N_{arom} = 2.041(3), Cu–S–C = 102.69(6), C–N–Cu = 170.0(2), Cu–S–Cu = 108.55(3).

4. Conclusions

We have reported the synthesis of five new CuSCN-aromatic diimine networks. Compounds **1–4** were formed via reflux in dilute aqueous ammonia, while **5** was prepared by reacting CuSCN directly in the neat ligand. The diimines (LL) Qnz and 2-MeOPyz acted exclusively as monodentate capping ligands, producing 1:1 (CuSCN)(LL) stoichiometry in **2** and **5**, respectively. Diimines Qox, Ptz and 2-NH₂Pyz acted as μ_2 -bridging ligands, and produced (CuSCN)₂(LL) networks **1**, **3**, and **4**. Networks based on CuSCN ladders (**1** and **4**) and hexagonal sheets of fused Cu₃(SCN)₂S rings (**2**, **3**, and **5**) were observed. In the ladder networks Cu...Cu distances within the Cu₂S₂ rhombs were found lie near the van der Waals sum, representing either potentially bonding (**1**) or non-bonding interaction (**4**). Hexagonal sheet networks **2** and **5** exemplify *trans*-fusion of chair rings leading to zigzag rippled sheets and *cis*-fusion of boat rings leading to square wave rippled sheets, respectively. Of particular note is the intra-sheet bridging behavior exhibited by Ptz in **3**. This “stapling” of sheets provides a contrast to crosslinking. It also introduces significant ring strain into the network, leading to buckled sheets of *trans*-fused alternating chair and twist boat rings. This stapling behavior stands in contrast to the known monodentate (CuSCN)(Pd₂) complex, and appears to be unprecedented.

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Appendix A. Supplementary data: CCDC 1460757–1460761 contains the supplementary crystallographic data for **1–5**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Supplementary data associated with this article can be found, in the online version.

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Table 1. Crystal and Structure Refinement Data.

complex	1	2	3
CCDC deposit no.	1460758	1460757	1460759
color and habit	orange prism	yellow plate	yellow block
size, mm	$0.39 \times 0.10 \times 0.07$	$0.18 \times 0.12 \times 0.05$	$0.22 \times 0.17 \times 0.12$
formula	$\text{C}_{10}\text{H}_6\text{Cu}_2\text{N}_4\text{S}_2$	$\text{C}_9\text{H}_6\text{CuN}_3\text{S}$	$\text{C}_{10}\text{H}_6\text{Cu}_2\text{N}_4\text{S}_2$
formula weight	373.39	251.77	373.39
space group	$P2_1/n$ (#14)	Cc (#9)	$Pbca$ (#61)
a , Å	5.86660(10)	21.6629(4)	13.3325(3)
b , Å	17.5548(4)	3.76380(10)	10.8446(2)
c , Å	11.7576(3)	11.2315(2)	16.6635(3)
α , deg	90	90	90
β , deg	97.8520(10)	101.4430(10)	90
γ , deg	90	90	90
volume, Å ³	1199.53(5)	2118.51(6)	3837.12(16)
Z	4	4	8
ρ_{calc} , g cm ⁻³	2.068	1.863	2.059
F_{000}	736	504	1472
$\mu(\text{Cu K}\alpha)$, mm ⁻¹	2.068	1.863	2.059
temperature, K	100(2)	100(2)	100(2)
residuals: ^a R ; R_w	0.0330; 0.0843	0.0432; 0.1328	0.0201; 0.0577
goodness of fit	1.049	1.091	1.055
Flack	—	0.03(4)	—

^a $R = R_I = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ for observed data only. $R_w = wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$ for all data.

Table 1. Cont'd.

complex	4	5
CCDC deposit no.	1460761	1460760
color and habit	yellow block	colorless blade
size, mm	$0.21 \times 0.21 \times 0.08$	$0.36 \times 0.09 \times 0.04$
formula	$\text{C}_6\text{H}_5\text{Cu}_2\text{N}_5\text{S}_2$	$\text{C}_6\text{H}_6\text{CuN}_3\text{OS}$
formula weight	338.35	231.74
space group	$P\bar{1}$ (#2)	$Pn\bar{1}m$ (#58)
a , Å	5.75360(10)	10.4822(2)
b , Å	6.66110(10)	20.7412(4)
c , Å	7.16720(10)	3.81760(10)
α , deg	103.5560(10)	90
β , deg	97.6900(10)	90
γ , deg	110.9560(10)	90
volume, Å ³	242.097(7)	830.00(3)
Z	1	4
ρ_{calc} , g cm ⁻³	2.321	1.855
F_{000}	166	464
$\mu(\text{Cu K}\alpha)$, mm ⁻¹	9.206	5.690
temperature, K	100(2)	100(2)
residuals: ^a R ; R_w	0.0485; 0.1279	0.0276; 0.0707
goodness of fit	1.162	1.055
Flack	—	—

^a $R = R_I = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ for observed data only. $R_w = wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$ for all data.