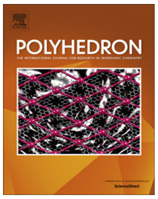
Polyhedron 115 (2016) 257–263

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly



Copper(I) thiocyanate networks with aromatic diimine ligands

Gerardo Ayala, Tristan A. Tronic, Robert D. Pike *

Department of Chemistry, College of William and Mary, Williamsburg, VA 23187, United States

A R T I C L E   I N F O

Article history:
Received 12 March 2016
Accepted 12 May 2016
Available online 19 May 2016

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

A B S T R A C T

A total of five new CuSCN-LL complexes with aromatic diimine ligands, LL = quinoxaline (Qox), quinazoline (Qnz), phthalazine (Ptz), 2-aminopyrazine (2-NH_2Pyz), 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-NH_2Pyz) (**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**.

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 pseudohalides. 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 $(CuSCN)_\infty$ 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-Me_2Py, and quinoline [3,4]. Type A′ polymers are known for the more hindered L = 2,6-Me_2Py and 2,4,6-Me_3Py [3,4].

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 $[Cu_2(SCN)_2]_\infty$ ladders composed of alternating Cu_2S_2 and $Cu_2(SCN)_2$ rings. Type B ladders have been found for L = 2-MePy, 2-EtPy, and N-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 $Cu_3(SCN)_2S$ 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

---

* Corresponding author.

http://dx.doi.org/10.1016/j.poly.2016.05.030
0277-5387/

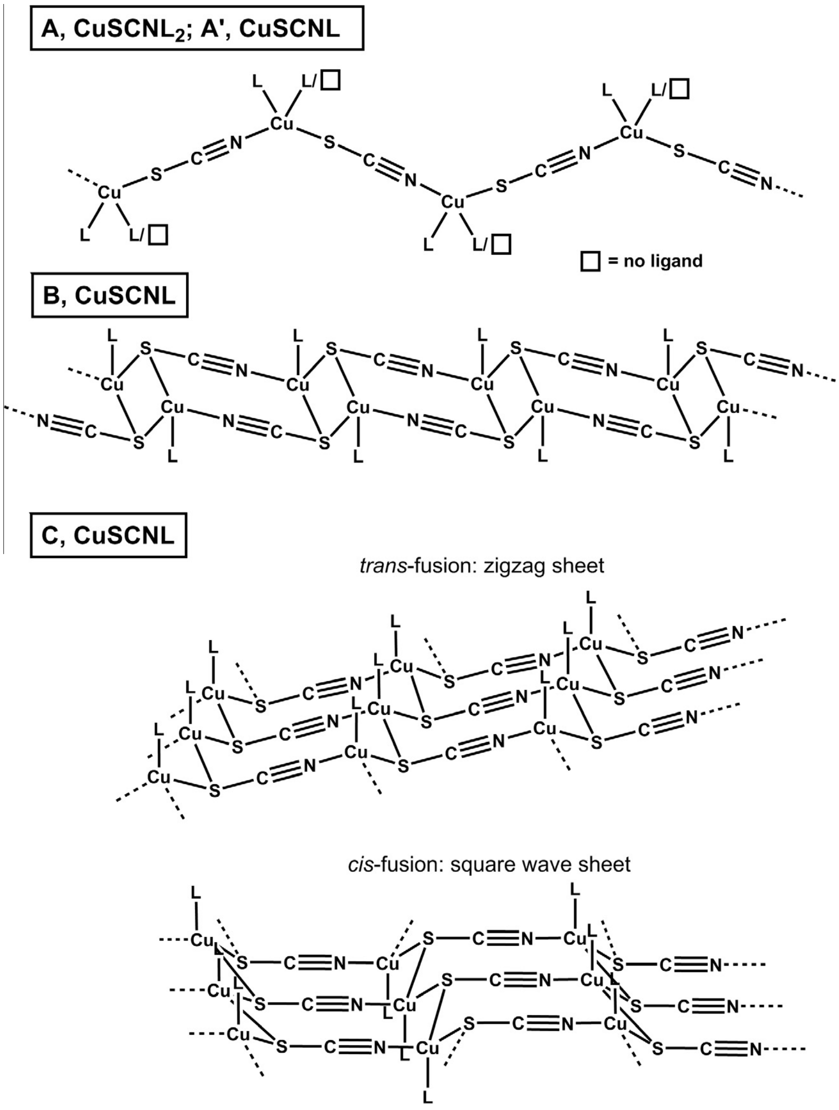


Chart 1. CuSCN network motifs.

(see Chart 1). Type C decorated sheets are recognized for L = 3-ClPy (*trans*), 3-BrPy (*trans*), and N-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 (CuSCN)(LL). Type B ladders can be linked together to form 2-D sheets of stoichiometry $(CuSCN)_2(LL)$. 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, LL = Pyz, 2-MePyz [7,8], (2) 2-D sheets of crosslinked Type B ladders, LL = 2-MePyz [5,6], (3) 3-D crosslinked *trans*-fused Type C networks, LL = Pyz and 2,5-Me_2Pyz [9–11], and (4) a 3-D crosslinked *cis*-fused Type C network, LL = 2-Me-3-EtPyz [12]. Two additional bridging Pyz networks are based upon the simple rhomboid Cu_2S_2 building unit. In both $(CuSCN)_2$(3-IPyz) and $(CuSCN)_2$(2,3-Me_2Pyz), 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 $Cu_2(SCN)_2$ 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 (CuSCN)(2-NCPyz)$_2$, a 1-D Type A chain (2-NCPyz bonds through a ring N) [5], and (CuSCN)(2-Me-3-EtPyz), a 1-D Type B ladder [12].

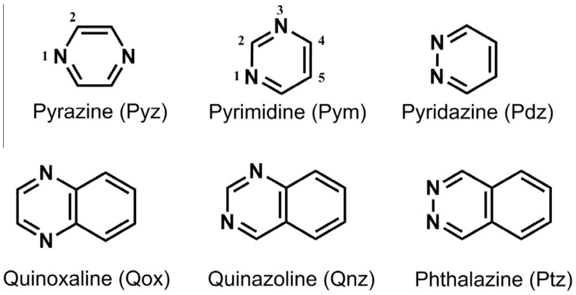


Chart 2. Ligands (with numbering where needed).