Structure and luminescence of copper(I) cyanide–amine and –sulfide networks

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**Abstract**

Copper(I) cyanide reacts with various liquid amines and sulfides (L) under solvent-less conditions to form (CuCN)L\(_n\), \(n = 0.5, 0.57, 0.75, 0.8, 1, 1.25, 1.5, 2\). New X-ray structures are reported for \(L = \text{Py (pyridine), 2-MePy (2-methylpyridine), 3-EtPy (3-ethylpyridine), 3-CIPy (3-cyano-4-pyridyl), 3-MeOpy (3-methoxy-4-pyridyl), 4^\text{-}BuPy (4-tert-butylpyridine), piperidine, N-methylmorpholine (N-MeMor), \text{N,N-dimethylcyclohexylamine (N,N-DHCA), 1-methylimidazole (1-MeIm), Me}_2\text{S (dimethylsulfide), tetrahydrothiophene (THF), 1-methylmorpholine (N-MeMor).}\) The amine structures (except for the monomeric 1-methylimidazole complex) reveal 1D CuCN chains decorated with 0–2 L per metal atom. Chain structures observed include zigzag, helical and figure-8 helical. The CuCN-sulfide structures show sulfur-bridging of CuCN chains. In some cases (CuCN)L\(_{1.5}\) species are transformed to (CuCN)L under vacuum. Thermal analysis shows facile release of ligand, yielding CuCN. Most of the (CuCN)L\(_n\) products are photoluminescent, emitting in the visible region. In some cases, coordination of very similar amines results in remarkably different emission spectra.

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**1. Introduction**

Self-assembly reactions are currently a hot topic, and for good reason [1]. In contrast to “brute-force” synthetic methods, the self-assembly process exploits simple reactions that proceed spontaneously in order to effect desired transformations. Often, these reactions are reversible, opening up opportunities in gas storage, catalysis, separations, sensing and other applications [2]. We are particularly interested in the spontaneous reactions of volatile organic chemicals (VOCs) with inorganic substrates with an eye toward chemical detection systems [3,4]. The coupling of a reversible spontaneous reaction with an observable change can provide the foundation for a detector. A prototypical “sniffing” device for detection of VOCs via self-assembly and luminescence is shown in Fig. 1. During the course of our recent studies on copper(I)-diamine networks we noted the remarkable and facile reactions of amines with CuCN to form luminescent products [5,6]. A survey of the literature revealed that several CuCN–amine complexes were known, all of them being CuCN polymers decorated with 1–2 amine ligands per copper center. However, there were no reports of luminescence in these species. The monoamine CuCN–L complexes that have been reported to date are: (CuCN)L\(_n\), \(n = 0.5, 0.57, 0.75, 0.8, 1, 1.25, 1.5, 2\). Two related non-amine (CuCN)L structures (L = thioacetamide, dimethylsulfoxide) also show the decorated polymer motif [8]. In contrast, an older ammine structure, (CuCN)NH\(_3\) exhibits formation of 2D sheet structures through \(\mu_2\)-bridging cyano groups that produce Cu\(_2\)CN\(_2\)NH\(_3\)_2 units [9]. Finally, an unusual (CuCN)\(_3\)(thiomorpholine) also exhibits cyano bridging [10]. We have shown that luminescence emission of CuCN–amine addsucts occurs in the visible region, representing a bathochromic shift from the 392 nm emission of CuCN itself [5]. Our density field theory examination of [Cu\(_6\)(CN)]\(_{1+}\) polymeric chains (as models for the infinite chains found in CuCN) showed that favored excitations are \(\pi-\pi^*\) transitions between molecular orbitals roughly characterized as d\(_{xy}\) of CuCN and p\(_{x,y}\) of cyan [11]. Evidence was found for a low-energy triplet excited state with non-linear geometry at copper. Since bending is an outcome of ligand coordination at copper, this finding is consistent with the lower energy emission associated with CuCN–amine complexes compared to that of CuCN itself [5].
The observation that CuCN luminescence emission wavelength is modulated by various incoming ligands suggests that this system might provide the foundation for an amine vapor-sensing device [3,4]. Therefore, we set out to thoroughly investigate the CuCN-amine system with regard to its structural chemistry, self-assembly capabilities, and photophysics.

Herein we describe the interaction of a variety of amines and two sulfides (Chart 1) with CuCN. The structures and luminescence behavior of the resulting (CuCN)Ln products are reported. We also show that exposure of CuCN to amine liquid or vapor results in luminescence due to the reversible formation of small amounts of (CuCN)Ln phases identical to bulk (CuCN)L. The reversible formation of luminescent CuCN adducts provides a potential foundation for an amine detection system. Some of these results have recently been communicated [12].

2. Experimental

2.1. Materials and general methods

All reagents were purchased from Aldrich or Acros and used without purification. Analyses for C, H, and N were carried out by Atlantic Microlabs, Norcross, GA. IR measurements were made on pressed KBr discs using a Digilab FTS 7000 FTIR spectrophotometer. 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 300 °C under 60 mL/min N2 flow.

2.2. Synthesis of (CuCN)Py2, 1a

Copper(I) cyanide (0.150 g, 1.67 mmol) was suspended in about 2 mL toluene in a sealed tube under Ar. The mixture was heated to 70 °C in an oil bath overnight without stirring. After cooling, the suspended solid was collected by means of filtration, washed with diethyl ether, and then air dried for 15 min. A yellow powder was isolated (0.393 g, 1.59 mmol, 94.7%). IR (cm⁻¹) 2126, 2102. Anal. Calc. for C25H20N9Cu5: C, 54.4. Found: 55.2 (110–130 °C). Calcld for (CuCN)Py: 71.5. Found: 75.8 (85–110 °C). Calcld for CuCN: 39.1. Found: 40.3 (90–110 °C).

2.3. Synthesis of (CuCN)Py4, 1b

The procedure was identical to that used for 1a, except that the product was vacuum dried overnight. A white powder was isolated (95.3%). IR (cm⁻¹) 2126, 2101, 2086. Anal. Calc. for C25H20N9Cu5: C, 39.29; H, 2.64; N, 16.50. Found: C, 39.37; H, 2.61; N, 16.45%. TGA Calcld for (CuCN)Py4: 88.2. Found: 82.8 (55–85 °C). Calcld for (CuCN)Py: 71.5. Found: 75.8 (85–110 °C). Calcld for CuCN: 39.1. Found: 36.7 (110–125 °C).

2.4. Synthesis of (CuCN)(3MePy), 1c

Complex 1b (99.0 mg, 0.130 mmol) was suspended in toluene (10 mL) and heated to 70 °C in an oil bath overnight with stirring. A white powder was isolated (82.0 mg, 0.0869 mmol, 93.6%). IR (cm⁻¹) 2124, 2104, 2087. Anal. Calc. for C27H20N11Cu7: C, 58.6. Found: 59.7 (100–125 °C). Calcld for CuCN: 36.1. Found: 36.7 (110–125 °C).

2.5. Synthesis of (CuCN)2(2MePy)3, 2a

The procedure was identical to that used for 1a. A pale yellow powder was isolated (99.5%). IR (cm⁻¹) 2128. Anal. Calc. for C25H20N9Cu5: C, 54.7. Found: 56.6 (50–80 °C). TGA Calcld for (CuCN)2(2MePy): 74.5. Found: 70.3 (50–85 °C). Calcld for CuCN: 39.1. Found: 40.3 (85–110 °C).

2.6. Synthesis of (CuCN)(2MePy), 2b

The procedure was identical to that used for 1b. A white powder was isolated (82.2%). IR (cm⁻¹) 2128, 2102. Anal. Calc. for C25H20N9Cu5: C, 56.8. Found: 57.8 (110–125 °C). Calcld for CuCN: 39.1. Found: 40.3 (85–110 °C).

2.7. Synthesis of (CuCN)(3MePy), 3a


2.8. Synthesis of (CuCN)(2MePy), 2b

The procedure was identical to that used for 1b. An off-white powder was isolated (81.4%). IR (cm⁻¹) 2124, 2112, 2087. Anal. Calc. for C25H20N9Cu5: C, 46.02; H, 3.86; N, 15.33. Found: C, 45.25; H, 3.79; N, 15.20%. TGA Calcld for (CuCN)(2MePy): 74.5. Found: 76.0 (60–100 °C). Calcld for CuCN: 49.0. Found: 50.2 (100–140 °C).

Fig. 1. Design for a potential luminescent VOC “sniffing” detector.
2.12. Synthesis of \((\text{CuCN})_2(4\text{MePy})_3\), 6

The procedure was identical to that used for 1a. A white powder was isolated (100%). IR (cm\(^{-1}\)) 2119, 2106. Anal. Calc. for \(\text{C}_{13}\text{H}_{16}\text{N}_3\text{O}_2\text{Cu}\): C, 50.40; H, 5.21; N, 13.56. Found: C, 50.49; H, 5.44; N, 13.64. TGA Calc. for \((\text{CuCN})_2(3\text{MeOPy})_2\): 57.2. Found: 58.9 (45–105 °C). Calc. for \((\text{CuCN})_2(3\text{MeOPy})_2\): 46.5. Found: 48.7 (105–240°C). Calc. for CuCN: 53.8. Found: 57.7 (240–300°C).

2.13. Synthesis of \((\text{CuCN})_2(4\text{EtPy})_3\), 7

The procedure was identical to that used for 1b. A white powder was isolated (99.5%). IR (cm\(^{-1}\)) 2125, 2107. Anal. Calc. for \(\text{C}_{13}\text{H}_{16}\text{N}_3\text{Cu}\): C, 48.85; H, 4.61; N, 14.24. Found: C, 49.06; H, 4.66; N, 13.95. TGA Calc. for CuCN: 45.5. Found: 47.5 (90–125 °C).

2.14. Synthesis of \((\text{CuCN})(2\text{Chloro})_2\), 8

The procedure was identical to that used for 1a. In this case a solution was formed in the 4EtPy. Addition of EtOH was required to precipitate the product. A yellow powder was isolated (77.4%). IR (cm\(^{-1}\)) 2130, 2123. Anal. Calc. for \(\text{C}_{13}\text{H}_{16}\text{N}_3\text{CuCl}\): C, 48.85; H, 4.61; N, 14.24. Found: C, 48.03; H, 4.47; N, 14.08. TGA Calc. for \((\text{CuCN})(\text{4EtPy})_2\): 86.4. Found: 86.2 (60–110 °C). Calc. for \((\text{CuCN})(\text{4EtPy})_2\): 59.1. Found: 62.0 (110–150°C). Calc. for CuCN: 45.5. Found: 47.5 (150–300 °C).

2.15. Synthesis of \((\text{CuCN})(3\text{Py})_2\), 9

The procedure was identical to that used for 1a. An off-white powder was isolated (90.8%). IR (cm\(^{-1}\)) 2139, 2117, 2100, 2088. Anal. Calc. for \(\text{C}_{13}\text{H}_{16}\text{N}_3\text{ClCu}\): C, 35.48; H, 1.99; N, 13.79. Found: C, 35.27; H, 1.89; N, 13.92. TGA Calc. for CuCN: 44.1. Found: 46.6 (50–80 °C).

2.16. Synthesis of \((\text{CuCN})(2\text{BrPy})_2\), 10

The procedure was identical to that used for 1a. An off-white powder was isolated (91.1%). IR (cm\(^{-1}\)) 2128. Anal. Calc. for \(\text{C}_{17}\text{H}_{16}\text{N}_3\text{BrCu}\): C, 29.11; H, 1.63; N, 11.32. Found: C, 28.11; H, 1.44; N, 11.53. TGA Calc. for \((\text{CuCN})(2\text{BrPy})_2\): 84.0. Found: 84.7 (30–65°C). Calc. for CuCN: 36.2. Found: 38.7 (65–115°C).

2.17. Synthesis of \((\text{CuCN})(3\text{BrPy})_2\), 11

The procedure was identical to that used for 1a. A white powder was isolated (95.3%). IR (cm\(^{-1}\)) 2126, 2112, 2100. Anal. Calc. for \(\text{C}_{17}\text{H}_{16}\text{N}_3\text{BrCu}\): C, 29.11; H, 1.63; N, 11.32. Found: C, 29.18; H, 1.53; N, 11.36. TGA Calc. for \((\text{CuCN})(3\text{BrPy})_2\): 68.0. Found: 69.3 (85–105 °C). Calc. for CuCN: 36.2. Found: 37.4 (105–130 °C).

2.18. Synthesis of \((\text{CuCN})(3\text{MeOPy})_2\), 12

The procedure was identical to that used for 1a. An off-white powder was isolated (91.5%). IR (cm\(^{-1}\)) 2098, 2083. Anal. Calc. for \(\text{C}_{17}\text{H}_{16}\text{N}_3\text{O}_2\text{Cu}\): C, 50.40; H, 5.21; N, 13.56. Found: C, 50.49; H, 4.64; N, 13.64. TGA Calc. for \((\text{CuCN})(3\text{MeOPy})_2\): 64.5. Found: 66.8 (50–80 °C). Calc. for \((\text{CuCN})(3\text{MeOPy})_2\): 52.7. Found: 54.4 (80–105 °C). Calc. for CuCN: 29.1. Found: 30.3 (105–130 °C).

2.19. Synthesis of \((\text{CuCN})(4\text{BuPy})_2\), 13

The procedure was identical to that used for 1a. A yellow crystalline solid was isolated (94.7%). IR (cm\(^{-1}\)) 2124. Anal. Calc. for \(\text{C}_{17}\text{H}_{16}\text{N}_3\text{BrCu}\): C, 55.19; H, 5.44; N, 13.99. Found: C, 55.08; H, 5.44; N, 13.97. TGA Calc. for \((\text{CuCN})(4\text{BuPy})_2\): 57.2. Found: 58.9 (45–105 °C). Calc. for \((\text{CuCN})(4\text{BuPy})_2\): 46.5. Found: 48.7 (105–240°C). Calc. for CuCN: 35.8. Found: 34.5 (240–315 °C).

2.20. Synthesis of \((\text{CuCN})(26\text{Lut})_1\), 14

The procedure was identical to that used for 1a. A white powder was isolated (98.8%). IR (cm\(^{-1}\)) 2128. Anal. Calc. for \(\text{C}_{17}\text{H}_{16}\text{N}_3\text{Cu}\): C, 48.85; H, 4.61; N, 14.21. Found: C, 48.56; H, 4.41; N, 14.03. TGA Calc. for CuCN: 45.5. Found: 45.7 (85–125 °C).

2.21. Synthesis of \((\text{CuCN})(26\text{Coll})_1\), 15

The procedure used for 1a did not effect complete conversion. Exchange reaction: 247 mg (0.323 mmol) 1b was suspended in about 5 mL 26Coll in a sealed tube under Ar. The mixture was heated to 70 °C in an oil bath overnight without stirring. After cooling, the suspended solid was collected by means of filtration, washed with diethyl ether, and then air dried. A white powder was isolated (0.318 g, 2.86 mmol, 88.4%). IR (cm\(^{-1}\)) 2162, 2125. Anal. Calc. for \(\text{C}_{17}\text{H}_{16}\text{N}_3\text{Cu}\): C, 51.29; H, 5.26; N, 13.29. Found: C, 51.02; H, 5.24; N, 13.36. TGA Calc. for CuCN: 42.5. Found: 42.9 (85–145 °C).

2.22. Synthesis of \((\text{CuCN})(\text{Quin})_1\), 16

The exchange procedure was identical to that used for 1a. A white powder was isolated (90.0%). IR (cm\(^{-1}\)) 2123. Anal. Calc. for \(\text{C}_{17}\text{H}_{16}\text{N}_3\text{Cu}\): C, 54.91; H, 3.23; N, 12.81. Found: C, 54.61; H, 3.07; N, 12.81. TGA Calc. for CuCN: 40.9. Found: 41.4 (135–175 °C).

2.23. Synthesis of \((\text{CuCN})(\text{NET}_3)_2\), 17

The procedure was identical to that used for 1a. A white powder was isolated (92.6%). IR (cm\(^{-1}\)) 2129. Anal. Calc. for \(\text{C}_{17}\text{H}_{16}\text{N}_3\text{Cu}\): C,
The procedure was identical to that used for 1a. An off-white powder was isolated (92.3%). IR (cm$^{-1}$) 2120, 2116. Anal. Calc. for C$_{16}$H$_{18}$N$_{2}$Cu: C, 45.34; H, 7.28; N, 16.09. Found: C, 44.61; H, 7.16; N, 15.97%. TGA Calc. for (CuCN)$_3$(Pipd)$_2$: 72.0. Found 75.0 (35–90 °C). Calcld for (CuCN)$_3$(Pipd)$_2$: 58.1. Found 58.8 (90–215 °C). Calcld for CuCN: 44.1. Found 44.5 (215–270 °C).

2.27. Synthesis of (CuCN)$_4$(MePipd)$_2$

The procedure was identical to that used for 1a. A pale yellow powder was isolated (99.3%). IR (cm$^{-1}$) 2139, 2132. Anal. Calc. for C$_{10}$H$_{15}$N$_{2}$Cu: C, 36.91; H, 6.81; N, 17.22. Found: C, 36.62; H, 6.73; N, 17.09%. TGA Calcld for CuCN: 54.8 (50–75 °C).

2.28. Synthesis of (CuCN)$_4$(EtPipd)$_2$

The procedure was identical to that used for 1a. An off-white powder was isolated (97.6%). IR (cm$^{-1}$) 2130. Synthesis of (CuCN)$_2$(NEt$_3$)$_3$, Calcld for CuCN: 63.9. Found 63.6 (40–85 °C). Calcld for (CuCN)$_2$(NEt$_3$)$_3$: 73.5. Found 65.9 (35–55 °C). Calcld for CuCN: 46.9. Found 48.3 (55–75 °C).

2.29. Synthesis of (CuCN)$_2$(Morph)$_3$

The procedure was identical to that used for 1a. A white crystalline solid was isolated (93.7%). IR (cm$^{-1}$) 2120. Anal. Calcld for C$_{14}$H$_{27}$N$_5$O$_3$-Cu: 18.18; N, 12.70. Found: C, 18.08; H, 1.65; N, 12.71%. TGA Calcld for (CuCN)$_3$(Me$_2$NCy)$_2$: 87.5. Found 87.6 (30–55 °C). Calcld for CuCN: 81.2. Found 80.5 (55–105 °C).

2.30. Synthesis of (CuCN)$_2$(Morph)$_3$

The procedure was identical to that used for 1a. A white powder was isolated (93.3%). IR (cm$^{-1}$) 2120. Anal. Calcld for C$_{20}$H$_{28}$N$_6$Cu$_2$: C, 41.25; H, 6.35; N, 16.03. Found: C, 40.38; H, 6.20; N, 15.91%. TGA Calcld for (CuCN)$_2$(Morph)$_3$: 75.6. Found 72.0 (35–75 °C). Calcld for CuCN: 51.3. Found 50.3 (90–105 °C).

2.31. Synthesis of (CuCN)(Morph)$_3$

The procedure was identical to that used for 1a. A pale yellow powder was isolated (100%). IR (cm$^{-1}$) 2126. Anal. Calcld for C$_{26}$H$_{37}$N$_6$O$_2$Cu: C, 38.17; H, 6.18; N, 15.90. Found: C, 37.45; H, 6.10; N, 15.81%. TGA Calcld for (CuCN)(Morph)$_3$: 80.2. Found 78.4 (50–70 °C). Calcld for (CuCN)(Morph)$_3$: 53.9. Found 52.8 (70–105 °C). Calcld for CuCN: 40.7. Found 40.1 (105–135 °C).

2.32. Synthesis of (CuCN)(Me$_2$NCy)$_2$

The procedure was identical to that used for 1a. A white crystalline solid was isolated (93.0%). IR (cm$^{-1}$) 2137. Anal. Calcld for CuCN: 46.9; N, 5.40; N, 29.19. Found: C, 46.72; H, 5.33; N, 29.34%. TGA Calcld for (CuCN)$_3$(Me$_2$NCy)$_2$: 63.3. Found 59.0 (55–90 °C). Calcld for (CuCN)$_3$(Me$_2$NCy)$_2$: 38.9. Found 36.9 (90–205 °C). Calcld for CuCN: 26.7. Found 26.5 (205–285 °C).

2.33. Synthesis of (CuCN)(Me$_2$NCy)$_3$

The procedure was identical to that used for 1a. A white crystalline solid was isolated (84.1%). IR (cm$^{-1}$) 2145, 2125. Anal. Calcld for C$_{25}$H$_{61}$N$_9$Cu: C, 18.15; H, 1.83; N, 12.70. Found: C, 18.08; H, 1.65; N, 12.71%. TGA Calcld for (CuCN)$_3$(Me$_2$NCy)$_2$: 87.5. Found 87.6 (30–55 °C). Calcld for CuCN: 81.2. Found 80.5 (55–105 °C).

2.34. Synthesis of (CuCN)(Me$_2$S)$_2$

The procedure was identical to that used for 1a. A white crystalline solid was isolated (70.4%). IR (cm$^{-1}$) 2122. Anal. Calcld for C$_{20}$H$_{33}$N$_6$Cu: C, 18.37; H, 4.54; N, 7.88. Found: C, 33.32; H, 4.31; N, 7.88%. TGA Calcld for CuCN: 50.4. Found 50.7 (65–125 °C).

2.37. X-ray crystallographic analyses

In some cases X-ray quality crystals were produced in the tube reactions described above. Single crystal determinations were carried out on these crystals using a Bruker SMART Apex II diffractometer using graphite-monochromated Cu Kα radiation [13]. The data were corrected for Lorentz and polarization [14] effects and absorption using SADABS [15]. The structures were solved by use of direct methods or Patterson map. Least squares refinement on the exchange procedure was identical to that used for 15. A white crystalline solid was isolated (70.4%). IR (cm$^{-1}$) 2122. Anal. Calcld for C$_{25}$H$_{61}$N$_9$Cu: C, 18.15; H, 1.83; N, 12.70. Found: C, 18.08; H, 1.65; N, 12.71%. TGA Calcld for (CuCN)$_3$(Me$_2$NCy)$_2$: 87.5. Found 87.6 (30–55 °C). Calcld for CuCN: 81.2. Found 80.5 (55–105 °C).

The procedure was identical to that used for 1a. A white crystalline solid was isolated (93.7%). IR (cm$^{-1}$) 2120. Anal. Calcld for C$_{14}$H$_{27}$N$_5$O$_3$-Cu: 18.18; N, 12.70. Found: C, 18.08; H, 1.65; N, 12.71%. TGA Calcld for (CuCN)$_3$(Me$_2$NCy)$_2$: 87.5. Found 87.6 (30–55 °C). Calcld for CuCN: 81.2. Found 80.5 (55–105 °C).

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2.38. Theoretical Methods

Models of selected decorated copper(I) cyanide chains were optimized using Gaussian03 [17] at the DFT level using the BLYP [18,19] exchange–correlation (xc) functional. Copper atoms were represented by the Ermel–Christiansen relativistic effective core potential (RECP) basis set [20] modified to include the 4p contractions of Couty and Hall [21]. Basis sets for the carbon and nitrogen atoms were the split-valence triple-ζ plus polarization functions (TZVP) representations of Dunning [22]. The Dunning double-ζ basis set was used for hydrogen atoms. The potassium atoms were represented by the Hay–Wadt RECP basis set. The excitation spectrum of selected model chains were obtained using time-dependent DFT (TD-DFT) to generate all transitions to singlet states less than 5.2 eV.

2.39. Luminescence spectroscopy

Steady-state photoluminescence spectra were recorded with a Model QuantaMaster-1046 photoluminescence spectrophotometer from Photon Technology International. The instrument is equipped with two excitation monochromators and a single emission monochromator with a 75 W xenon lamp. Low temperature steady-state photoluminescence measurements were achieved by using a Janis ST-100 optical cryostat equipped with a Honeywell temperature controller. Liquid nitrogen or liquid helium was used as coolant.

3. Results and Discussion

3.1. Synthesis and Analysis

Complexation of amines to CuCN was readily accomplished by heating CuCN suspensions to 70 °C in neat liquid amine. In many cases changes in crystal size and habit were observable during the reaction as the CuCN powder converted to the more crystalline (CuCN)N adducts. In a few cases, the CuCN actually dissolved in the warm amine, crystallizing upon cooling. In several instances, X-ray quality crystals directly resulted from these reactions. However, even when crystals large enough for single crystal diffraction were not present, the products were found to have high crystallinity, showing sharp X-ray powder diffraction patterns. Attempts to prepare several of the products from 10% solutions of amine in cyclohexane at 70 °C were unsuccessful, yielding only unconverted CuCN. Bowmaker et al. have reported that (CuCN)Py2 can be used in exchange reactions with other amine bases [7c]. This approach was found to be successful in the current study, producing good yields of (CuCN)N. In fact in the cases of L = 246Coll, Quin and THF, direct reaction of CuCN with ligand resulted in mixtures of (CuCN)N and unreacted CuCN, while exchange reactions yielded pure products. The various complexes produced in the study are listed in Table 1.

For those amines listed in Table 1 as producing two or more bulk products (Py, 2MePy, 3MePy, 3EtPy, Morph), the more amine-rich product (1b, 2b, 3b, 6b, and 24b) was always produced in the direct reaction. In each case the less amine-rich product (1b, 2b, 3b, 6b, and 24b) was formed upon vacuum drying. Three particular cases bear further comment. Pyridine forms three (CuCN)Py2 species: (CuCN)Py2(1a), (CuCN)Py2(1b), (CuCN)Py2(1c). The conversion 1a → 1b has previously been reported and is readily accomplished by air or vacuum drying [7c]. Complex 1c, which is now in this contribution, has been previously conveniently produced by refluxing a suspension of 1a or 1b in hydrocarbon solvent. The other two cases of interest involve 3CIPy and Me2S. Reaction of 3CIPy with CuCN produces (CuCN)(3CIPy) almost exclusively, as confirmed by elemental analysis. However, a few larger crystals were present in the otherwise microcrystalline product. These proved to be (CuCN)(3CIPy)2 upon X-ray structural determination. Similar results were obtained with Me2S, which yielded (CuCN)(Me2S) product containing a few X-ray quality crystals of (CuCN)(Me2S).

The stoichiometries of the (CuCN)N adducts were established by means of elemental analysis; however, thermogravimetric analysis (TGA) proved to be particularly convenient for determination of n. All of the products smoothly lose amine at temperatures under ca. 300 °C, ultimately leaving recoverable CuCN powder. Amine-loss temperatures, predictably, are roughly correlated with amine boiling point. In many cases, copper-rich phases are evident as plateaus during amine loss. Although the chemical identity of the intermediates represented by the plateaus tends to be speculative, interpretations are provided in the Experimental Section. The TGA traces for 1a, 1b, and 1c (Fig. 2) suggest the reaction sequences represented in equations (1–3). Although the first plateaus of reaction (1) analyzes better for (CuCN)Py, the fact that 1a air dries directly to 1b suggests the latter as the likely first step product in this TGA experiment.

\[(\text{CuCN})\text{Py}_2(1a) \rightarrow (\text{CuCN})\text{Py} + 1b \rightarrow (\text{CuCN})\text{Py}_4(1c) \rightarrow (\text{CuCN})\text{Py} \rightarrow \text{CuCN} \]

Product stoichiometry has proved highly variable and difficult to predict. The results shown in Table 1 reveal that CuCN:L = 1:1 is a commonly encountered ratio, occurring with 21/29 ligands (2b, 3b, 5b, 6b, 7, 8, 9b, 10, 11, 14–18, 21, 23, 24b, 25, 26, 28a, and 29). The 1:1 ratio corresponds to attachment of L at each copper atom in the CuCN chain, forming 3-coord. Cu centers. Ligand-rich ratios, CuCN:L ≤ 1:1 (1a, 2a, 3a, 4a, 6a, 9a, 12, 13, 20, 24a, and 27), are suggestive of the presence of 4-coord. Cu centers (although the structure of complex 13 represents an exception, as noted below). On the other hand, ligand-deficient ratios, CuCN:L > 1:1 (1b, 1c, 19, 22, 28b), require the presence of some at least some 2-coord. Cu centers. This has been confirmed in the structure of 1c (see below).

3.2. X-ray crystallography

3.2.1. Amine complexes

X-ray structures of 13 new compounds have been determined: (CuCN)Py (1c), (CuCN)(2MePy) (2b), (CuCN)(3EtPy) (6a), (CuCN)(3CIPy) (8), (CuCN)(3CIPy)2 (9a), (CuCN)(3MeOPy) (12), (CuCN)(4BuPy) (13), (CuCN)(4MePy) (20), (CuCN)(Me2S) (25), (CuCN)(Me2NCy) (26), (CuCN)(1MeIm) (27), (CuCN)(Me2S) (28a), and (CuCN)(THT) (29). Crystallographic parameters are listed in Table 2 and selected structural parameters for new and literature (CuCN)N adducts are compiled in Table 3. As has been noted previously for copper(I) cyanide complexes [5–8], cyano nitrogen and carbon atoms usually show positional disordering. This is so in all cases here except for 8, 12, and 27. Therefore cyano nitrogen and carbon atoms are labeled herein as “X.” All of these structures (except for 27) are further variations on the theme of amine-decorated CuCN chains, which has previously been noted for the known CuCN-L complexes 1a, 2a, 4, 24b, 25, and 26 and for the more ligand-rich amine chain complexes 6a, 9a, 12, 13, and 27.
Cu–N (2.254(2) Å) and Cu gen atom in MeMorph. Due to the 4-coord. nature of Cu in (CuCN)L since there is a fourth Cu coordination by the oxy- and X–Cu–X bond angles of 130.3–148.0° complexes (see Table 3) show C–N distances of 2.044–2.205 Å

The piperidine complex shows figure-8 helicity. Aside from the 4’BuPy “solvate” complex 13, only three 2:3 CuCN amines complexes have been structurally characterized to date. Each of these (CuCN)3L3 species shows alternating 3- and 4- coord. metal centers. Complex 6a is a new helical example (Fig. 6), joining helical 2a and zigzag 4 [7a,c]. As is evident from the ligand torsion angles (N–Cu–Cu–N, Table 3), the MePy ligands in 4 are located in three orientations at roughly 0, 90 and 180°, respectively; the fourth position (270°) lie in the plane of the zigzag chain. Nevertheless, acetylpyridine complexes 30 and 31 form helices and 18 shows figure-8 helicity.

New structures 2b, 8, and 26 are straightforward examples of 1:1 CuCN–amine species, having 3-coord. copper centers. These complexes (see Table 3) show C–N distances of 2.044–2.205 Å and X–Cu–X bond angles of 130.3–148.0°. New complex 25 is an atypical [CuCN] since there is a fourth Cu coordination by the oxygen atom in MeMorph. Due to the 4-coord. nature of Cu in 25, the Cu–N (2.254(2) Å) and Cu–O (2.537(3) Å) bonds are relatively long and the X–Cu–X angle (154.19(9)°) is very open. In this complex, the normal 1D decorated CuCN chain is crosslinked to form a 2D sheet. Since the copper lies in axial orientation to the piperidine ring, when viewed along the CuCN chain, the ligands are seen to assume alternating positions above and below the plane of the chain. Ligand bridging has previously been observed with CuCN complexes of diamine ligands [5,6], and in [CuCN]3(thiomorpholine)– [10]. Another complex that belongs in the (CuCN)L category is 13, which has 2:3 stoichiometry, but is actually (CuCN)(4’BuPy)1/2(4’BuPy). In this case the excess ligand is not coordinated to copper, but is trapped in the lattice in the manner of a solvent molecule. The long-range chains in most of the 1:1 complexes form zigzag arrangements with 180° Cu–Cu–Cu–Cu torsion angles along the chain (Fig. 6). The coordinated amines (except those of 25) lie in the plane of the zigzag chain. Nevertheless, acetylpyridine complexes 30 and 31 form helices and 18 shows figure-8 helicity.

Aside from the 4’BuPy “solvate” complex 13, only three 2:3 CuCN amines complexes have been structurally characterized to date. Each of these (CuCN)3L3 species shows alternating 3- and 4- coord. metal centers. Complex 6a is a new helical example (Fig. 6), joining helical 2a and zigzag 4 [7a,c]. As is evident from the ligand torsion angles (N–Cu–Cu–N, Table 3), the MePy ligands in 4 are located in three orientations at roughly 0, 90 and 180°, respectively; the fourth position (270°) is unoccupied (Fig. 6).

Complex 6a is a new helical example (Fig. 6), joining helical 2a and zigzag 4 [7a,c]. As is evident from the ligand torsion angles (N–Cu–Cu–N, Table 3), the MePy ligands in 4 are located in three orientations at roughly 0, 90 and 180°, respectively; the fourth position (270°) is unoccupied (Fig. 6). The piperdine complex 20 shows a heretofore unknown (CuCN)3L4 stoichiometry, with two 3-coord. copper centers for every 4-coord. center. It adopts a figure-8 style helical chain (Fig. 6).

Table 1

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*a* Excitation λ = 365 nm, except as noted.

*b* Excitation λ = 354 nm.

*c* Trace formation of this product, see text.

*d* Compound has 1:1/2L stoichiometry.

*e* Compound produced via exchange reaction, see text.

Fig. 2. TGA traces for 1a, 1b, and 1c.
Interestingly, these two compounds are among the few herein that do not luminesce at room temp. In the current contribution, we add two new (CuCN)\textsubscript{2} structures, \textbf{9a} and \textbf{12}. These products show helical chains with more even distribution of amine ligands around the chains.

The new Py complex \textbf{1c} reported herein is unique among CuCN–monoaamine species. With a 7:4 CuCN:Py ratio, it is highly ligand deficient. It is composed of two separate sublattices, (CuCN)\textsubscript{Py} and CuCN, in 4:3 ratio. The former is a fairly straightforward zigzag chain running in the crystallographic $b$-direction. The free CuCN chains propagate in the $c$-direction and are quite remarkable. One independent metal atom (Cu1) has a (symmetry-imposed) linear $X$–Cu–$X$ angle, while the other (Cu2) is severely bent (127.3(4)$^\circ$) and has a very close Cu–Cu interaction (2.454(2) Å) with Cu3, which is part of the Py-bearing sublattice. Similarly threaded CuCN chains (or chain segments) have been seen in CuCN–diimine networks [5,6g,6h,6k]. However, in the fourteen previous cases, both the 2-coord. $X$–Cu–$X$ angles (minimum = 146.3$^\circ$, commonly > 160$^\circ$) and the Cu–Cu distances (minimum = 2.541 Å, commonly > 2.7 Å) are significantly more modest. This combination of small bond angle and short Cu–Cu distance suggests a relatively strong cuprophilic interaction [23].

An interesting aspect of the various (CuCN)\textsubscript{m} structures listed in Table 3 is the consistently large $X$–Cu–$X$ angle. The range of angles for 3-coord. copper amine complexes (excluding \textbf{1c}) is 128.6–148.9$^\circ$, with an average value of 138.0$^\circ$ and the range for 4-coord. copper amine complexes (excluding \textbf{25}) is 120.7–139.5$^\circ$, with an average value of 131.7$^\circ$. These angles are much larger than the nominal sp$^2$ and sp$^3$ values of 120$^\circ$ and 109.5$^\circ$. Corollary to these obtuse $X$–Cu–$X$ angles are relatively small $N$–Cu–$N$ angles noted at 4-coord. copper centers (91.6–98.5$^\circ$). Limited bending of the linear $X$–Cu–$X$ angle by incoming ligands is probably indicative of relatively weak Cu–N bonding, a behavior that is relevant to the ready loss of amine ligands that has been noted with these compounds.

Fig. 7 shows a plot of Cu–N bond lengths vs. $X$–Cu–$X$ bond angles. Correlations exist between Cu–N and $X$–Cu–X for 3-coord. Cu (alkaline amine $r^2 = 0.893$, aromatic amine, excluding \textbf{1c}, $r^2 = 0.475$). Average bond lengths favor 3-coord. Cu and unsaturated amine: Cu$_3$-coord–N aromatic (avg = 2.081 Å) < Cu$_4$-coord–N aromatic (avg = 2.165 Å) < Cu$_3$-coord–N aliphatic (avg = 2.165 Å). There is only one known example of Cu$_4$-coord–N aliphatic bonding (in \textbf{20}, 2.180(1) Å). Presumably, such interactions are usually too weak to result in permanent bonding. Correlations between Cu–N lengths and $X$–N IR frequencies were not readily discernible.

In light of the many known CuCN–$L$ chain structures, the nature of the 1-MelM product, \textbf{27}, was surprising. Consistent with the 1:3 CuCN:1Melm ratio suggested by TGA and elemental analysis data, this compound was found to be a molecular species with 4-coord. copper(I) and a terminal (and fully ordered) cyanide ligand. There are no close interactions between the molecules. The angles around copper are close to the nominal tetrahedral values. This unique, non-polymeric species is not luminescent at ambient temperature.

### 3.2.2. Sulfide complexes

Two 1:1 sulfide structures \textbf{28a} and \textbf{29} were solved; these are shown in Fig. 8. As with their amine analogs, sulfide ligands decorate the Cu sites on CuCN chains. However, 3D networks are formed as a result of sulfide bridging of the 4-coord. copper centers. The Me$_2$S complex, \textbf{28a}, features zigzag CuCN chains running in the [1 1 0] and [−1 1 0] directions. The chains are crosslinked at Cu by S, forming helical CuS chains parallel to the $a$-axis. The methyl groups occupy channels between the crosslinked CuCN chains. In contrast to those in \textbf{28a}, the CuCN chains in THT complex, \textbf{29}, are nearly linear; nevertheless, they too are crosslinked by bridging sulfur atoms. Instead of forming (CuS)$_n$ polymers, the...
Table 3
(CuCN)L\_n Structural Comparison.a

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<th>Cu(^{2+})-N (Å)</th>
<th>X–Cu(^{2+}}-X angle (°)</th>
<th>X–Cu(^{2+}}-X angle (°)</th>
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a X indicates cyanide C/N, N indicates L ligand.
b 3-Coord. copper.
c 4-Coord. copper.
d (CuCN)Py sublattice.
e CuCN sublattice.
f Cu–Cu bonded center, Cu–Cu = 2.454 Å; there is also a 2-coord. Cu center with X–Cu–X = 180°.
g Ref. [7e].
h Ref. [7c].
i Ref. [7a].
j There is an additional Cu–O bond of 2.537 Å.
k Ref. [7d].
l Ref. [7b,c]; there are two crystal modifications of 1a with similar structural parameters.
m Cu–S.

Fig. 3. X-ray structures of 2b, 8, 25, and 26. Key to Figs. 3–6 and 8: copper and cyano atoms shown as spheres. Amine (and sulfide) ligands shown as wireframe. Color scheme for all X-ray figures: orange = Cu, grey = C, blue = N, red = O, green = Cl, yellow = S. Hydrogen atoms omitted. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 4. X-ray structures of 6a, 9a, 12, 13, and 20.
crosslinks form 6-membered Cu₃S₃ rings. These half-independent rings are nearly planar (max. atom deviation = 0.0959(3) Å). The rings are stacked in alternating fashion with two sulfur atoms in adjacent rings vertically aligned. The THT rings extend into channels in the structure.

Only two other CuCN‒S structures have been reported to date: [CuCN]₃(thiomorpholine) the ligand bridges Cu through S and also coordinates through N [10]. In contrast, only monodentate sulfur coordination is seen in (CuCN)(thioacetamide), which forms a simple 1D CuCN helix [8b]. Sulfide complexes of copper(I) halides are well-known. The polymeric structures of (CuY)(Me₂S) (Y = Cl, Br, I) contain rhomboid Cu₂(μ-Y)₂ units bridged by Me₂S ligands to form 1D (Cu₃Y)(μ-Me₂S)₅ or (Cu₂Y₂(μ-Me₂S³Me₂S)₂ chains [24]. The THT complexes of CuY are particularly diverse, including the molecular dimer (Cu₁)₂(THT)₄, polymeric (CuBr)₂(μ-THT)(THT)₂, and five different CuCl–THT species that feature CuCl dimers, zigzag chains and ladder polymers [24b,25]. One of these CuCl complexes shows Cu₃S₃ rings akin to those seen in 29.

3.3. Computational studies

Short, amine-decorated CuCN chains capped with potassium ions, K₂[Cu₃(CN)₄(L)]⁺ (L = NH₃, Py), were optimized at the DFT(BLYP) level under the constraint of a planar zigzag geometry (C₃v symmetry). The calculated Cu–C and Cu–N bond distances along the CuCN backbone are slightly longer than the undecorated model (Table 4) and are comparable to those reported in the X-ray structure of 17. The X–Cu–X angles of ~150° and the relatively long bond distances described above can be attributed to a change in hybridization of the Cu(I) center from sp to sp². The smaller angle (~130°) observed in CuCN–L complexes of substituted pyridines may be due to the stronger basicity or a change in bonding due to the coordination of the ligand. In the Py-substituted model chains, the ligands prefer to be coplanar with the CuCN backbone. Varying the dihedral angle to simulate rotation about the Cu–NPy bond axis resulted in only a slight increase in energy (∆E = 1.0 kcal/mol at 90°) and little change in the structural parameters of the chain. When the C₃ constraint is removed, the CuCN chain twists into a helix with bond distances and angles similar to the planar zigzag models (Table 4). Based on the relative AG of the zigzag and helical chains (~5 kcal/mol), the driving force for twisting the chains results from an increase in entropy since the relative ∆H is roughly zero. These results confirm that the actual configurations of the chain are determined by packing of the chains in the lattice (dependent on ligand).

Geometry was also optimized for the 1:2 CuCN:Py chain model K₂[Cu₃(CN)₄(Py)]⁺. The dihedral angles of the CuCN backbone and the Py ligands with respect to the CuCN backbone were constrained to the values in the 1a X-ray structure [7b]. In the structure there are two distinct types of Py ligands: one nearly in the plane of the zigzag CuCN chain and another, having longer Cu–NPy bond distances, oriented perpendicular to the CuCN plane (Fig. 6). With release of these constraints, the model chain optimizes to a lower-energy helical conformation (∆AG = -2.4 kcal/mol) with roughly equivalent Py ligands. This structure shows an arrangement of Py ligands similar to that of 12, with the ligands evenly distributed about the helix. Models with substituted Py are being examined to further explore the preferences of ligands for various CuCN chain conformations.

Relative energies for coordination of the first and second amine to the model chains were compared. Addition of the first amine was found to be more favorable (average ∆H of ~5 kcal/mol) than addition of a second amine (average ∆H of ~2 to ~3 kcal/mol). The weaker coordination of the second amine is consistent with the lower temperatures required in the TGA experiments for loss of amine ligands for materials with stoichiometry greater than 1:1.

3.4. Luminescence

3.4.1. Room temperature luminescence and amine detection

Most of the [CuCN]₄⁺ products are luminescent at room temperature under 254 nm irradiation, see Fig. 9 and Table 1. Aromatic amines and sulfides are also emissive under 365 nm excitation.
Nevertheless, inspection of Fig. 9 reveals that a wide variety of emission colors is evident. For some chemically similar amines (e.g., the various substituted pyridines or piperidines), striking color differences are notable. This observation is of importance with respect to potential use of CuCN as a detector for VOCs. Copper(I) cyanide shows a luminescence emission shift into the visible range upon exposure to small amounts of liquid or gaseous amine (or sulfide) [12]. The emission colors of the authentic (CuCN)$_n$ complexes match those that are seen when CuCN is exposed to amine (or sulfide). TGA results show that CuCN powder or pressed pellet samples, made luminescent from ambient temp. exposure to nucleophile, contain only a few weigh percent of amine or sulfide [12]. Powder diffraction studies reveal evidence of (CuCN)$_n$ phases in exposed samples, accounting for the visible luminescence emission. For example, Fig. 10 shows the X-ray powder diffraction pattern of a sample of CuCN powder sample that was exposed to Py vapor for a period of 5 min. (trace A). This result is compared to the powder patterns of CuCN (trace B) and (CuCN)$_5$Py$_4$ (1b, trace C). It is evident that the vapor-exposed sample remains largely CuCN, but evidences a small amount of 1b phase.

### 3.4.2. Variable temperature luminescence

Variable temperature luminescence spectroscopy was carried out on a number of the authentic (CuCN)$_n$ phases produced in the neat reactions. Several spectra are shown in Fig. 11. Previously, we have reported that CuCN exhibits a broad excitation feature in the 250–375 nm region and a relatively sharp high energy (HE) emission band centered at 392 nm [5d]. At 77 K CuCN emission intensifies and moves to $\lambda_{\text{max}}$ of 412 nm. Earlier results in our lab have demonstrated that the excitation band is relatively unaffected upon conversion of 2-coord. CuCN polymer to the 3-coord. copper(I) centers present in (CuCN)$_2$(diamine) sheets. However, the relatively sharp HE CuCN emission band is usually red-shifted and broadened when CuCN is ligated by diamines. Previous DFT results for CuCN model networks have suggested a possible reason for this red shift [11]. It was shown in these studies that a bent X–Cu–X structure lowers the energy of the first triplet excited state due to loss of degeneracy of the frontier MOs. Thus, bending of the linear chain associated with an incoming ligand would be expected to stabilize the triplet state, lowering the emission energy. Finally, there are numerous cases in which coordination of diamine to CuCN results in the appearance of an additional low-energy (LE) band in the range of 500–600 nm. Instead of the usual blue emission for linear CuCN chains, green, yellow or orange color was noted in these compounds. This LE emission band has shown significant thermochromism, diminishing or disappearing completely at 77 K. The appearance of the LE band is very difficult to predict.

![Fig. 8. Views of the X-ray structures of 28a and 29.](image)

### Table 4

<table>
<thead>
<tr>
<th></th>
<th>Cu–CN (Å)</th>
<th>Cu–N$_{\text{max}}$ (Å)</th>
<th>C–N (Å)</th>
<th>Cu–NC</th>
<th>Cu–N$_{\text{max}}$ (Å)</th>
<th>Cu–CN (Å)</th>
<th>C–N (Å)</th>
<th>N–K (Å)</th>
<th>C–Cu A–C ($^\circ$)</th>
<th>C–Cu A–N ($^\circ$)</th>
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<tr>
<td>Unsubstituted</td>
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<td>-</td>
<td>1.171</td>
<td>1.856</td>
<td>-</td>
<td>1.855</td>
<td>1.172</td>
<td>2.640</td>
<td>180.0</td>
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<td>2.275</td>
<td>1.175</td>
<td>1.917</td>
<td>2.275</td>
<td>1.872</td>
<td>1.177</td>
<td>2.611</td>
<td>151.5</td>
<td>152.1</td>
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<td>2.270</td>
<td>1.175</td>
<td>1.919</td>
<td>2.262</td>
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<td>1.177</td>
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<td>150.8</td>
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<td>1.175</td>
<td>1.915</td>
<td>2.243</td>
<td>1.878</td>
<td>1.177</td>
<td>2.605</td>
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<tr>
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<td>2.238</td>
<td>1.175</td>
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<td>2.230</td>
<td>1.873</td>
<td>1.177</td>
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<td>148.8</td>
<td>148.5</td>
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<td>1.180</td>
<td>2.588</td>
<td>141.5</td>
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The new luminescence data, examples of which are shown in Fig. 11, reveal excitation and emission behavior for the CuCN–amine complexes which is similar to that previously seen for the CuCN–diamine species. For example, the spectrum in Fig. 11A reveals only a HE emission band for 1:1 complex 2b; no thermochromism is seen for 2b. However, both HE and LE features are seen for 2a (Fig. 11B and C). The LE band is thermochromic, diminishing in relative intensity at 77 K. The CuCN–aliphatic amine compounds generally yielded more complex spectra than did their aromatic amine counterparts. Fig. 11D and E demonstrate the presence of multiple excitation and emission bands and a very strong thermochromic effect for 21. At room temperature, the emission spectrum is dominated by the LE band while higher energy emission peaks are seen at 77 K. As in the diamine study, there was no clear trend as to the appearance of the LE band. Of the samples examined, the LE band is seen in 2a, 3b, 6a, 6b, 11, 13, 20, 21, 22 and 23, but not in

2b, 5, 14, 17, 18, 25 and 26. Unlike in previous results, luminescence emission intensity was found to be generally similar between the aromatic and aliphatic amine adduct compounds. Although a few species (1b, 4, 7, 12 and 23) did not produce measureable emission, those that did generally showed good intensities. It should be pointed out that 4, which is non-emissive at ambient temp., became emissive at 77 K.

A noticeable difference between pure CuCN, and its aliphatic and aromatic amine adduct compounds is seen in the excitation spectra. Our theoretical study of copper(l) cyanide has show how the experimentally-observed transitions arises from the Laporte-allowed excitation of an electron from a π-type MO with anti-bonding character between the Cu 3d_{xy/yz} and the CN π bond to an unoccupied π-type MO with bonding character between the CN π orbital and the Cu 4p, [11]. Luminescence of CuCN exhibits a single emission (~400 nm) with excitation around 350 nm. For CuCN chains decorated with saturated amines, the excitation bands occur at relatively high energies (~315 nm) and all aromatic amine adducts exhibit excitation bands at lower energy (~325–390 nm). TD-DFT calculations of one-copper CuCN–L models, $K_{3}[Cu(CN)_{5}L]$ ($L = NH_{3}$, Py), demonstrate that, whereas the principle excitation in the aliphatic amine complex is similar to that of the undecorated chain (excitations between π-type MOs on the CuCN backbone), Fig. 12A, the excitation for the Py-substituted model is from a π-type MO on the CuCN chain to an empty π of the aromatic amine ligand (Fig. 12B). [Note: A full discussion of the transitions in these and larger models will appear separately.] TD-DFT calculations were also performed from the optimized structures of the Py-substituted model with the angle constrained between 0 and 90° (C3 symmetry). The conformation in which the Py is coplanar with the chain is 1 kcal/mol lower than that in which the ligand is perpendicular. As the angle increases, the intensity of the 3d_{xy/yz}→π*(Py) transition decreases in intensity as measured by the oscillator strength and a transition to π*(Py) from a delocalized CuCN MO related to the π MOs important for the undecorated chain increases in intensity. The former transition could be assigned as a traditional MLCT band (d(Cu) → π*(Py)) since the donor MO is highly localized on a single Cu. This assignment is in contrast with transitions between highly delocalized MOs in undecorated and NH_{3}-substituted CuCN. Since the acceptor MOs are centered on the ligand, tuning of the photoluminescent properties through modulation of the Py π MO with electron-withdrawing/donating groups may be possible. Additional analysis of the larger models is being performed to ensure that the interpretations of these transitions are not an artifact of the small model and to determine the nature of the triplet state.

The emission of aromatic amine complexes tends to occur at lower energy than that of saturated amine complexes. The former complexes’ emission exhibits a relatively large Stokes shift of approximately 9000 cm⁻¹ on average. In some cases, saturated amine compounds exhibit multiple emission peaks with specific excitation for each of them. Strangely, emission at lowest energy doesn’t necessarily result from the lowest excitation energy. Corresponding Stokes shift for amine adduct emission bands varies and ranges from 3000 cm⁻¹ (similar to that of pure CuCN) up to 17 000 cm⁻¹. The low energy emission bands (LE) mentioned above correspond to large Stokes shifts and therefore, result from large excited state reorganization. No systematic geometry-to-luminescence behavior relationship has been seen, except to note that extremely large and extremely low Stokes shifts are seen only in saturated amine compounds. We suppose that this phenomena arises from the excited states of the CuCN polymeric chains. It has been shown that delocalization and bending angle can affect the excited state energy of this type of chain [11].
4. Conclusions

We have shown that CuCN reacts with neat liquid amines and sulfides to form a series of \((\text{CuCN})_n\) phases. The observed values of \(n\) vary between 0.5 and 2.0, tending toward more ligand-rich values for aromatic amines. Multiple phases are accessible in some cases. These have proved to be inter-convertible, via vacuum treatment and re-exposure to ligand. The structures of \((\text{CuCN})_n\) are usually based on zigzag or helical CuCN chains, decorated with amine ligands. However, for MeMorph and the sulfides, ligand bridging occurs, in the case of 4\(^{t}\)BuPy, a half molecule (per Cu) of non-coordinated ligand is present, and in the case of 1MeIm, a molecular complex with monodentate cyanide forms. Computational results suggest that coordination of the first amine ligand is more energetically favorable than that of the second amine.

Most of the new phases produce visible luminescence upon UV irradiation. A remarkable variety of emission colors are noted, especially for chemically similar ligands. Higher excitation energies are found for aliphatic amines. High energy (blue) emission is seen for all amine complexes, and additional low energy emissions are observed for aromatic amines.

Fig. 11. Luminescence spectra: (A) 2b, \((\text{CuCN})(2\text{MePy})\) at 298 K. (B) 2a, \((\text{CuCN})_2(2\text{MePy})_3\) at 298 K. (C) 2a, \((\text{CuCN})_2(2\text{MePy})_3\) at 77 K. (D) 21, \((\text{CuCN})(\text{MePipd})\) at 298 K. (E) 21, \((\text{CuCN})(\text{MePipd})\) at 77 K.
thermochromic emission bands are noted for about half of the complexes. Exposure of CuCN powder to amine liquid or vapor reversibly produces traces of (CuCN)$_2$ phases, as confirmed by X-ray diffraction. This behavior provides the foundation for potential VOC-sensing devices.

Acknowledgments

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