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Robert D. Pike
College of William and Mary, rdpike@wm.edu

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Structure and Bonding in Copper(I) Carbonyl and Cyanide Complexes

Robert D. Pike*

Department of Chemistry, College of William and Mary, Williamsburg, VA 23187-8795.
rdpike@wm.edu

ABSTRACT The coordination chemistry of copper(I) carbonyls and cyanide complexes is reviewed. Primary attention is focused on structural chemistry, including coordination behavior, bridging modes, network formation, flexible coordination number, and reversible ligand binding. Additional coverage of infrared spectroscopy and orbital interactions in carbonyl and cyanide bonding, and photophysical behavior of metal cyanide complexes is also included.

BRIEF The coordination chemistry of copper(I) carbonyls and cyanide complexes is reviewed.

Introduction

The isoelectronic diatomics carbon monoxide and cyanide have rich histories as ligands for transition metals. Both ligands inevitably bond metal centers primarily through carbon, placing them amongst the simplest and most robust of carbon-bound ligands. However, despite the clear analogy between CO and CN⁻, carbonyl is regarded as one of the quintessential ligands in organometallic chemistry, whereas cyanide has traditionally been regarded a strictly inorganic ligand. There are some good arguments for
this designation, such as the analogy between CN\(^-\) and the halides, its stability as an aqueous anion, and its ability to form simple metal salts. Nevertheless, there are arguably better reasons for classifying metal-cyano complexes as organometallics. Foremost among these is the aforementioned M–CN linkage, but of equal importance is the bonding analogy of CN\(^-\) with CO, as well as with the isoelectronic N\(_2\) and NO\(^+\). Bonding in each of these ligands involves a combination of \(\sigma\)-donation by the HOMO (or NHOMO, in the case of N\(_2\)), and \(\pi\)-acceptance (\(\pi\)-backbonding) by the LUMO (see Fig. 1). The latter is, of course, instrumental in stabilizing the electron-rich d-subshell that is hallmark of low-valent transition metal organometallics. Because cyanide \(\sigma\)-donation is relatively strong and its \(\pi\)-acceptance relatively weak, CN\(^-\) can often support higher oxidation states that can the carbonyl ligand. Nevertheless, the fact that copper(I) cyanide is air-stable, and copper(II) cyanide does not normally exist is a tribute to the reducing power of cyanide, either through electron sharing or out-and-out electron transfer.

**Figure 1.** Bonding in metal-carbonyl and metal-cyano complexes.

Both carbonyl and cyanide are notable for their ability to act as either terminal or bridging ligands. Unlike the dianionic peroxo ligand, neither CO nor CN\(^-\) is known to chelate. As suggested in Fig. 2, all terminal carbonyls and cyanides are C-bound. Bonding distinctions between CO and CN\(^-\) become apparent in their bridging behavior. When the carbonyl ligand bridges metal centers, it shares its largely carbon-centered HOMO electrons with two, or even three, metal centers (\(\mu_2\)-C,C or \(\mu_3\)-C,C,C mode), Figs. 1 and 2. The bridging carbonyls are shown as triply bonded in Fig. 2 to avoid any implication that carbonyl is reduced to a dianion (i.e., deprotonated formaldehyde, O=C\(^2-\)) during bridging. It remains neutral C≡O, simply sharing the lone pair with two or three metal atoms. Bridging cyano ligands are very common. In contrast to the \(\mu_2\)-C,C behavior of bridging CO, secondary ligand connections for
cyanide involve N-bonding (μ₂-C,N mode, Fig. 2). In those cases for which cyanide links to three metal centers, the μ₃-C,C,N mode is invariably found. This latter mode is usually part of a dimeric arrangement that features a relatively close metal-metal interaction, as shown using a dashed line in Fig. 2.

**Figure 2.** Bridging modes in metal-carbonyl and metal-cyano complexes.

The history of metal carbonyls, starting with Mond’s Ni(CO)₄, is closely intertwined with the history of organometallics itself. This saga has been often told and does not need repeating here. However, it should be pointed out that structurally characterized copper carbonyls are relatively late additions to the catalog of metal carbonyls. While the study of Cu–CO complexes has only bloomed in the last several decades, cyanide complexes have a long history in inorganic chemistry. One of standouts in this story is the mixed valence iron cyanide called Prussian Blue, {Fe₄[Fe(CN)₆]₃}. Although originally used as a substitute pigment for expensive Lapis lazuli, cyanide-bridged cage structures related to Prussian Blue that feature redox active metal centers have recently been an active area of research in magnetochemistry, catalysis, and electron transfer studies. This work is summed up in some recent reviews. The current review will focus on the coordination chemistry of copper(I) carbonyl and cyanide complexes, paying special attention to the structural and network chemistry. Spectroscopic and photophysical behavior will also be touched upon. Copper(II) carbonyls are not known, and copper(II) cyano complexes, except for some mixed valence cyanocuprates, will not be covered.

**Copper(I) Carbonyls**
The reactivity of CuCl with CO has been recognized since the 19th century. Solutions of CuCl readily absorb carbon monoxide at CO pressures of under 1 atm. The adduct that is formed, CuCl(CO), has a sheet-like structure. It features a ν_C≡O of 2127 cm⁻¹, indicative of surprisingly little π-backbonding. CuCl(CO) releases CO at pressures of under 0.5 atm CO. The carbonylation of MCuCl₄ (M = Al, Ga) results in MCuCl₄(CO) phases, I. Due to the highly electron-deficient nature of the Cu(I) environment in I, these materials exhibit enhanced σ-donor behavior with essentially no π-backbonding, as indicated by the ν_C≡O of 2156 cm⁻¹, which is actually higher than the free CO value of 2143 cm⁻¹ (see Table 1). This unusual form of MCO bonding has been described as *non-classical*. Titration of sub-atmospheric pressures of CO into solid Cu(AsF₆) has led to the formation of the homoleptic, non-classical cations Cu(CO)ₙ⁺ (n = 1, 2, and 3). The unusual 3-coordinate copper dicarbonyl, II, also shows very high frequency carbonyl stretching bands at 2158 and 2184 cm⁻¹. The 18-electron Cu(CO)₄⁺ ion has been crystallographically characterized as part of a salt with a carborane anion (ν_C≡O = 2184 cm⁻¹). The same paper reports the Cu(CO)₂ fragment coordinated to an alkene bearing a pendant carborane anion. Neon-matrix-isolated CuCO⁺ shows the highest recorded stretching frequency of 2234 cm⁻¹.

![Diagram](image)

Table 1. Some representative Cu(I)-carbonyl stretching frequencies

<table>
<thead>
<tr>
<th>Material/Complex</th>
<th>ν_C≡O, cm⁻¹</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(CO)]⁺, Ne/CO matrix</td>
<td>2234</td>
<td>9</td>
</tr>
<tr>
<td>Cu<a href="CO">N(SO₂CF₃)₂</a>₂, II</td>
<td>2184, 2158</td>
<td>7</td>
</tr>
<tr>
<td>[Cu(CO)]⁺(AsF₆)⁻</td>
<td>2178</td>
<td>5</td>
</tr>
<tr>
<td>CuAlCl₄(CO), I</td>
<td>2156</td>
<td>4</td>
</tr>
<tr>
<td>Cu(O₂CCF₃)(CO), IV</td>
<td>2155</td>
<td>14d</td>
</tr>
<tr>
<td>Compound</td>
<td>Frequency</td>
<td>Note</td>
</tr>
<tr>
<td>----------</td>
<td>-----------</td>
<td>------</td>
</tr>
<tr>
<td>CO</td>
<td>2134 (g)</td>
<td>–</td>
</tr>
<tr>
<td>[(2,9′-Bu2Phen)Cu(CO)]+(SbF6)−, VI</td>
<td>2130 (CH2Cl2)</td>
<td>17k</td>
</tr>
<tr>
<td>CuCl(CO)</td>
<td>2127</td>
<td>4c</td>
</tr>
<tr>
<td>{[(2-PyCH2)3N]Cu(CO)}+[B(C6F5)4]−, VIII</td>
<td>2091b, 2074c (THF)</td>
<td>17i</td>
</tr>
<tr>
<td>[(bpen)Cu(CO)(CH3CN)+PF6]−, VII</td>
<td>2088</td>
<td>19a</td>
</tr>
<tr>
<td>[(Pipz)CuCl(CO)]−, IX</td>
<td>2084</td>
<td>30</td>
</tr>
<tr>
<td>TpCu(CO)</td>
<td>2083</td>
<td>24a</td>
</tr>
<tr>
<td>(en)CuCl(CO)</td>
<td>2080</td>
<td>28a</td>
</tr>
<tr>
<td>{[(en)Cu(CO)]2(μ2-en)}2+(BPh4)−2</td>
<td>2078</td>
<td>17b</td>
</tr>
<tr>
<td>{CpCo[(MeO)2PO]3}Cu(CO), V</td>
<td>2075 (hexane)</td>
<td>16</td>
</tr>
<tr>
<td>CuCl(CO), MeOH solution</td>
<td>2070</td>
<td>4b</td>
</tr>
<tr>
<td>[(2-Py)2NH]CuCl(CO)</td>
<td>2069</td>
<td>28e</td>
</tr>
<tr>
<td>[(′BuO)Cu(CO)]4, III</td>
<td>2063 (toluene)</td>
<td>11</td>
</tr>
<tr>
<td>[(en)2Cu(CO)]+I−</td>
<td>2060</td>
<td>17b</td>
</tr>
<tr>
<td>[(2-MeQuinO)Cu(CO)]4d</td>
<td>2050</td>
<td>10a</td>
</tr>
<tr>
<td>[Cu2(μ-CO)(μ-isonicotinoate)2], X</td>
<td>1950</td>
<td>32</td>
</tr>
<tr>
<td>{[(tmen)Cu]2(μ-O2CPh)(μ-CO)}+(BPh4)−</td>
<td>1926</td>
<td>31a</td>
</tr>
<tr>
<td>{Cu3[(μ2-CO)2(μ3-CO)MoCp]3}, XI</td>
<td>1969, 1899, 1863, 1820</td>
<td>33</td>
</tr>
</tbody>
</table>

*a*All values recorded in solid state, KBr, or Nujol mull, except as noted. *b*4-Coordinate Cu with pendant pyridyl arm. *c*5-Coordinate Cu. *d*2-MeQuinO = 2-methylquinolin-8-olato.

Uncharacteristically for the soft copper(I) ion, the CuCO unit is often found coordinated to the oxygen donor anions: alkoxide,10-13 carboxylate,14 sulfonate,15 and phosphonate.16 These complexes, which are usually formed under 1 atm of CO, form oligomers and polymers, such as III-V.11,16 The cubane
geometry reflected in **III** is very common for Cu(I), most commonly being encountered with $\mu_3$-halide corners.

![Diagram of Cu(I) complexes](image)

The most common coordination sphere for CuCO complexes involves amine ligands, usually chelating. A great many such monomers, amine-bridged dimers, and occasionally higher oligomers are known. A rare structurally-characterized non-chelate is (NH$_3$)$_3$Cu(CO)$^+$, which was crystallized as a Co(CO)$_4$ salt. An interesting CuCO complex of $\eta^6$-trans,trans,trans-1,5,9-cyclododecatriene has recently been reported. Remarkably, several five coordinate N$_4$Cu–CO complexes violate the usual rule that Cu(I) does not allow coordination numbers above four. Studies of Cu(I) carbonyl complexes bearing potentially tetradentate nitrogen ligands have revealed a four-to-five coordination number equilibrium, with the fourth nitrogen site alternately coordinated and “dangling”. Complexes VI–VIII are examples of 3-, 4-, and 5-coordinate amine CuCO cations. Complex VII is a unique example of a polymeric copper carbonyl cation. Generally, cationic CuCO complexes have modest stability at best, and are subject to CO dissociation in the absence of CO atmosphere. Copper(I) fragments that bind carbonyl can usually bind $\pi$-alkene or dioxygen in place of CO; substitution of oxygen for CO is more difficult since Cu–CO bonding is usually stronger than the Cu–O$_2$ bonding.

![Diagram of Cu(I) complexes](image)
Copper carbonyl stability is generally enhanced by the presence of chelating anionic ligands, including tris(pyrazolyl)borate (Tp⁻) and its analogs,²⁴,²⁵ among others.²²,²⁶ Some cationic tris(pyrazolyl)methane (Tpm) complexes of CuCO have also been prepared.²⁵,²⁷ Careful comparison of Tp⁻ and Tpm species by X-ray, DFT calculations, voltammetry, IR, and reactivity have confirmed expectations that the more electron-rich TpCuCO complexes exhibit greater stability due to higher degree of π-backbonding, as evidenced by stronger Cu−C and weaker C≡O bonding.²⁵ In fact, the first structurally characterized copper carbonyl complex, TpCuCO, reported in 1972,²⁴ is still among the most stable known.

Copper carbonyl species with coordinated anions are common. These can take the form of simple monomers \( L_2Cu(CO)X \) (\( X = Cl, I, ClO_4, \) or OTf)¹⁸,²⁸ or anion-bridged dimers \( L_2Cu(CO)(\mu-X)Cu(CO)L_2^+ \) (\( X = Cl, Br, I, \) or \( ClO_4 \)).⁴,¹⁸ Copper(I) tends to form rhomboid dimers via the bridging of halide ions, \( Cu(\mu-X)_2Cu \). These dimers have been strung into linear polymers using bridging diamines in the presence of CO to form polymers, IX.³⁰ Although copper readily forms bridging arrangements with other metal carbonyls during cluster formation, only a few clusters containing homonuclear \( \mu_2-C,C \) \( Cu_2(\mu_2-CO) \) complexes are known. These include a few carboxylate scaffold-supported Cu(I) dimers (see X).³¹ This scaffolding of \( Cu_2(\mu_2-CO) \) by carboxylate has been used to produce a pair of interesting 5-coordinate 2-D polymers, \( [Cu_2(\mu_2-CO)(nic)_2] \), X (nic = isonicotinoate, nicotinoate).³² Homonuclear bridging Cu(I) carbonyls are also found in several clusters containing Fe³³ and Mo (XI).³⁴ The latter is quite interesting structurally, exhibiting a triangle of Cu atoms sharing cuprophilic interactions. The Cu⋯Cu bond distances in such interactions (in this case 2.6211(13), 2.6167(13), and 2.6594(13) Å) are near or less than the van der Waals radius sum (about 2.80 Å), and therefore represent significant overlap between the Cu 4s or 4p₂ orbitals. In this case the bond lengths are shorter even than the 2.65 Å Cu–Cu value in copper metal. Cuprophilic interactions are found extensively in cyano-bridged complexes. Most such interactions are supported by additional bonds, such as a bridging carbonyl or cyanide. Unsupported cuprophilic interactions are rare.
Copper(I) cyanide is a air-stable, nearly white solid that is essentially insoluble in all common solvents. It does dissolve in aqueous solutions of alkali cyanides, in which case soluble complex anions $\text{Cu}_x(\text{CN})_{y-x}^{-}$ are formed in equilibrium.\textsuperscript{35} CuCN has two known polymorphs (Fig. 3). The commercially available low-temperature phase contains rippled 1-D polymer chains in which 2-coordinate Cu(I) centers are bridged by site-disordered CN$^-$.\textsuperscript{36} The undulating chains are produced by five crystallographically independent Cu atoms with $\text{X–Cu–X} = 176.7–179.0^\circ$ and $\text{Cu–X–X} = 174.0–179.4^\circ$. The high temperature polymorph forms above 565 °C. It is crystallographically much simpler,\textsuperscript{37,38} having the same structure as AgCN,\textsuperscript{39} i.e. a single linear 2-coordinate unique Cu atom coordinated to a site-disordered CN. Significantly, in neither structure is there any evidence of cuprophilic interactions, cyano bridging, or coordination of copper to a third ligand.
Figure 3. X-ray structures of low temperature (left) and high temperature (right) forms of CuCN (copper orange, disordered nitrogen and carbon grey)\textsuperscript{36-38}.

Luminescence spectroscopy of copper(I) cyanide reveals a broad, intense absorption feature with peaks at 288, 307, and 345 nm and an intense emission band at 392 nm\textsuperscript{40}. This phosphorescence emission peak shows a slight thermochromic shift to 412 nm at 77 K. Recent work by Bayse using DFT to study model compounds of the infinite $\cdots$Cu–C≡N$\cdots$ system suggested that the origin of the excitation is associated with $\pi$-symmetry transitions from orbitals that are essentially Cu d$_{\pi}$/CN $\pi$ to Cu p/CN $\pi^*$.\textsuperscript{41} This effect is exemplified by the 7$\pi_g$ to 7$\pi_u$ excitation in K$_2$Cu(CN)$_2^+$ (Fig. 4). Although this transition is alternately referred to as being either MLCT or Cu-centered in nature, in fact it is really a combination of the two. The resulting triplet state undergoes a Jahn-Teller type symmetry distortion, leading to removal of the excited state degeneracy (Fig. 4).
Figure 4. Walsh diagram of the distortion of the $\pi$ MOs of the triplet state of $K_2Cu(CN)_2^+$ in $C_{2v}$ symmetry, Cu atom located at center and K atoms at the ends.$^{41}$

The finding accords well with the observation of excimer and halide exciplex formation of $Cu(CN)_2^-$ in aqueous solution.$^{42}$ Formation of a trigonal exciplex with halide, which is illustrated in reaction (1), leads to characteristic blue-green luminescence emission a centered at 476, 482, and 486 nm for $X = Cl^-$, $Br^-$, and $I^-$, respectively, upon excitation around 280 nm.

$$Cu(CN)_2^* + X^- \rightarrow Cu(CN)_2X^{2-}$$  (1)

The lowering of the $Cu(CN)_2^-$ emission energy upon trigonal deformation is consonant with the results shown in Fig. 4. The lowering of excited state emission energy via bending at copper explains the observation that amine substituted CuCN-L polymers (see below) emit at longer wavelengths than does CuCN, moving well into the visible region.$^{40,43}$ Addition of ammonia to $Cu(CN)_2^-$ has been shown to produce $Cu(CN)_2(NH_3)^-$, as well as $Cu_3(CN)_2(NH_3)_3^+$ and $Cu_3(CN)_4(NH_3)_3^-$.$^{44}$ All of the $Cu(CN)_2^-$ adducts: $Cu(CN)_3^{2-}$, $Cu(CN)_2X^{2-}$, and $Cu(CN)_2(NH_3)^-$, when photo-excited, can also form long-lived excited states that photo-eject an electron to the solvent with high quantum efficiency.$^{42c,44}$

**Infrared and Raman Analysis of Copper(I) Cyanides**

Cyanide $C≡N$ exhibits a strong band in the IR in the range of 2050–2200 cm$^{-1}$ (Fig 5A). In pure CuCN, this band is found at 2170 cm$^{-1}$. In cyano-bridged compounds, such as CuCN itself, a single Cu–C/N band is invariably observed, representing the average energy of the Cu–C and Cu–N bonds. The $C≡N$ stretching frequency in CuCN complexes correlates well with the crystallographically determined Cu–C/N distance.$^{45-47}$ A decrease of about 35 cm$^{-1}$ in $\nu_{C≡N}$ corresponds to an elongation of about 0.1 Å. Solid state spectra of CuCN should not be collected as KBr pellets due to a reversible reaction between CuCN and Br$^-$ in the solid state. Like CO ligands, CN groups might be expected to show IR frequencies corresponding to weaker stretching when bridging. However, IR indicates that $\mu$-C,N bridging $C≡N$ is usually slightly stronger. This effect appears to be the outcome of the relatively strong CN $\sigma$ bonding.$^{39,48}$ In bridged cyanides, $\nu_{C≡N}$ decreases as the Cu coordination number increases.
Again, these data correlate to Cu–C/N bond lengths: 1.80 to 1.86 Å in the nearly linear 2-coordinate systems, 1.92-1.96 Å in the planar 3-coordinate complexes, and 1.94-2.00 Å for 4-coordinate cyanocuprates. In the far IR (and Raman), bands have been identified for the other normal vibrational modes of pure CuCN (Fig. 5): B = 591 cm$^{-1}$, C = 326 cm$^{-1}$, and D = 168 cm$^{-1}$. These values are nicely supported by DFT results.$^{41b}$ Upon addition of ligands to the copper(I) centers in the CuCN chain, bands A–C show a decrease in frequency. Band D becomes non-degenerate, splitting into a higher and lower frequency pair of features.$^{47}$

![Diagram](image)

**Figure 5.** Normal vibrational modes in CuCN.$^{39}$

**Non-networked CuCN Complexes**

Copper(I) complexes containing cyano ligands that do not bridge are relatively few in number. They can be divided into four main subgroups: (1) L$_2$CuCN$^1$,$^{43,49}$ (2) L$_2$Cu(CN)$_2^-$,$^{50}$ (3) simple cyanocuprates Cu(CN)$_2^-$, Cu(CN)$_3^{2-}$ and Cu(CN)$_4^{3-}$,$^{42,51-53}$ and various metal clusters incorporating CuCN.$^{54}$ Examples of the former groups include [((LL)Cu(PPh$_3$)(CN)], [((LL)Cu(CN)$_2$]$^-$ (LL = 2,2'-Bpy, Phen, and related ligands). Only one compound of this type is constructed solely from monodentate ligands: (1-MeIm)$_3$CuCN.$^{43}$ Species **XII** and **XIII** are unique examples of neutral 3- and 2-coordinate CuCN complexes.$^{51b,55}$ In **XII** the trigonal angle sum is a nearly planar value of 359.5°, and in **XIII** the C–Cu–C bond angle is a nearly linear 177.5(3)°. Given the tendency of cyanide to bridge copper(I) centers, these coordinatively unsaturated cyano complexes are remarkable for not completing the Cu
coordination sphere in this way. Species XIV exhibits a cuprophilic interaction supported by the bridging diphosphine with a Cu⋯Cu distance of 2.940(1) Å.\textsuperscript{56} The Mo-Cu cation XV is another example of a Cu(I) cubane.\textsuperscript{53k} Several instances of simple cyano-bridged mixed valence Cu(I)-Cu(II) complexes with terminal cyanides are known.\textsuperscript{57} An example is XVI, which is essentially a collapsed ion pair between Cu\textsuperscript{II}(CN)\textsubscript{2}\textsuperscript{−} and Cu\textsuperscript{II}(1,3-propanediamine)\textsubscript{2}\textsuperscript{2+}.\textsuperscript{57d} In all such mixed valence complexes, cyanide C always bonds to Cu(I) and N to Cu(II). Finally, there are a handful of known complexes which feature a simple Cu\textsuperscript{I}=C≡N–Cu\textsuperscript{I} bridge.\textsuperscript{47b,50b,50c,58} These generally involve large and/or chelating ligands. One example is XVII.\textsuperscript{58b}

Cyanocuprate networks

It has been noted that monomeric cyanocuprates of formulas Cu(CN)\textsubscript{2}\textsuperscript{−}, Cu(CN)\textsubscript{3}\textsuperscript{2−}, and Cu(CN)\textsubscript{4}\textsuperscript{3−} exist in aqueous solution and in certain solid state structures. Cyanocuprates more commonly occur as anionic networks (Fig. 6). Like simple cyanocuprate monomers, many of these anionic networks are highly photoluminescent. In the vast majority of cyanocuprate networks, cyanide atom positions are disordered. The simplest of these is a polymeric version of Cu(CN)\textsubscript{2}\textsuperscript{−} (XVIII), which is encountered as its K\textsuperscript{+}, [Na(H\textsubscript{2}O)\textsubscript{2}]\textsuperscript{+}, or \textsuperscript{4}Bu\textsubscript{4}N\textsuperscript{+} salt.\textsuperscript{51a,59} In this polymer, zigzag (CuCN)\textsubscript{x} chains are decorated with a terminal ordered cyano at each roughly planar Cu atom. The cation is associated with the nitrogen atom of the pendant cyanide, bridging the chains. In the related mixed anion cyanocuprates Cu(CN)X\textsuperscript{−}, (X = Br, I), the basic chain structure is retained, with the halide ions replacing the pendant CN groups.\textsuperscript{45} The
commonly-encountered cyanocuprate \( \text{Cu}_2\text{(CN)}_3^- \) allows all copper atoms to be 3-coordinate. This usually leads to a (6,3) hexagonally tiled sheet consisting of \((\text{CuCN})_6 \) rings, **XIX**. In addition to two polymorphs of \( \text{KCu}_2\text{(CN)}_3 \),\(^6\) \( \text{Cu}_2\text{(CN)}_3^- \) salts of other alkali metals, ammonium, tetraalkylammonium, \( \text{PPh}_4^+ \), and other cations,\(^6\) or copper(II) complex ions (see below) have been reported. As is the case with all networked cyanocuprates, the cations tend to be found inside the large network pores. In one case, a mixture of \((\text{CuCN})_6 \) and \((\text{CuCN})_5 \) rings was observed.\(^6\) Most of these 2-D \( \text{Cu}_2\text{(CN)}_3^- \) sheets are flat, however, increased rippling is seen with larger cations.

![Diagram of cyanocuprate network structures](image)

**Figure 6.** Some cyanocuprate network structures.

Three-dimensional cyanocuprate networks can arise either through \( \mu_3\text{-C}_6\text{N}_5 \) cyano bridging or 4-coordinate Cu centers. The former is rare, but has been encountered.\(^6\) The resulting 3-D framework anionic materials contain organic cations which act as templating agents within the pores. The \( \text{Cu}_2\text{(CN)}_4^2^- \) network, **XX**, contains 4-coordinate Cu and forms a diamond-like network (Fig. 6).\(^6\)\(^4\)\(^5\) The \( \text{Cu}_3\text{(CN)}_4^- \) ion (**XXI**) in the \( \text{nBu}_4\text{N}^- \) salt shows a tiled hexagonal pattern similar to that of \( \text{Cu}_2\text{(CN)}_3^- \), but with the replacement of a two CN units in each \((\text{CuCN})_6 \) ring by \( \text{CN}^-\text{Cu}^-\text{CN}^- \), expanding the rings in one trigonal direction (Fig. 6).\(^5\)\(^5\) These same 2-coordinate copper units, \( \text{CN}^-\text{Cu}^-\text{CN}^- \), are found along all six edges of the giant 36-atom macrocycle \((\text{CuCN})_{12} \) that occurs in the Cu(I)-Cu(I) salt \[ \text{Cu}_2\text{(CN)}(\text{Bpy})_2]^{+}[\text{Cu}_5\text{(CN)}_6]^-, \] and the mixed valence Cu(I)-Cu(II) compound \( \text{Cu}_5\text{(CN)}_6\text{(DMF)}_4 \).\(^6\)\(^7\)
Several unusual variations on the known cyanocuprate network themes have appeared. Hydrothermal reactions are notorious for producing unexpected products. Hydrothermal treatment of a mixture of CuCl₂, tetrazole, and MeCN at 160 °C produced a solution which yielded two polymorphs of [H₂O₂][Cu₂(CN)₃]⁻. The source of the cyanide ion presumably was the acetonitrile solvent. Although both of these networks show the standard (6,3) Cu₂(CN)₃⁻ network, one of them exhibits a 2.86 Å cuprophilic interaction between adjacent layers link the rippled sheets into a diamondoid network. The hydrogen-bonded, protonated water dimers sit within anion lattice pores. In the other polymorph, Cu⋯Cu interactions are much more tenuous (>3 Å) and the (6,3) honeycomb is more like that seen for other Cu₂(CN)₃⁻ lattices. The Cu₀(CN)₁₅⁶⁻ ion found in a benzylviologen salt has nine crystallographically independent Cu centers, three of which are 4-coordinate. In this anion (CuCN)₈ and (CuCN)₃ helices are linked together.

Chippindale and Hibble have reported several interesting cyanocuprates using K⁺ and Cs⁺ counterions produced under hydrothermal conditions. The complex K₂[Cu₃(CN)₅] forms an unusual planar sheet of (CuCN)₈ rings. One of the 2.5 independent cyano groups is terminal (C-bound) and points into the tiled ring (Fig 7A). A very different sort of [Cu₃(CN)₅]²⁻ network is found in the mixed valence complex Cu₄(CN)₅(NH₃)₄(H₂O)₂ (Fig. 7D). In this case, μ₃-C,C,N dimers bridge (CuCN)₄ rings into a 3-D network. A very short cuprophilic interaction (Cu1⋯Cu2 = 2.4885(7) Å) is present within the dimers. The cyanocuprate networks, Cu₃(CN)₄⁻, found for alkali salts differ greatly from that of XXI. In Cs[Cu₃(CN)₄], (CuCN)₈ rings form buckled sheets that enable two identical networks to interpenetrate (Fig. 7B). The K⁺ salt of Cu₃(CN)₄⁻ is more complex, containing 2-, 3-, and 4-coordinate Cu(I) centers in a quadruply-interpenetrated 3-D net (Fig. 7C) that is analogous to that of Ag₂Cu(CN)₄⁻.
Figure 7. (A) (6,3) (CuCN)$_8$ sheet in K$_2$Cu$_3$(CN)$_5$.$^{59b}$ (B) Interpenetrating (6,3) (CuCN)$_8$ sheets in CsCu$_3$(CN)$_4$. $^{60b}$ (C) top: (4,4) Anion net in KCu$_3$(CN)$_4$. Bottom: Interpenetration of four nets.$^{60b}$ (D) [Cu$_3$(CN)$_3$]$^{2-}$ Anion net in Cu$_4$(CN)$_5$(NH$_3$)$_4$(H$_2$O)$_2$. $^{70}$ (E) Anion net in [Me$_4$N]$_2$[Cu$_4$(CN)$_3$I]. $^{73}$ (F) Interpenetrating sub-lattices (color and greyscale) in Cs[Cs$_3$(CN)$_3$Br] (Br green spheres). $^{72}$

The use of solventothermal conditions has led to the formation of interesting halo-cyano networks, including K[Cu$_2$(CN)$_2$Br]$\cdot$H$_2$O, K$_3$[Cu$_6$(CN)$_6$I$_3$]$\cdot$2H$_2$O, Cs[Cs$_3$(CN)$_3$X] (X = Cl, Br, Fig. 7F), Cs$_2$[Cu$_4$(CN)$_4$I$_2$]$\cdot$H$_2$O,$^{72}$ and [Me$_4$N][Cu$_3$(CN)$_2$Br$_2$] and [Me$_4$N]$_2$[Cu$_4$(CN)$_3$I] (Fig. 7E).$^{73}$ All of the alkali-containing 3-D networks contain infinite CuCN chains with various forms of halide cross-linking. In the case of [Cu$_4$(CN)$_3$I]$^{2-}$ the 3-D network is produced via cross-linking of the CuCN/CuCl chains by $\mu_3$-C,C,N cyano dimers. In contrast, the [Cu$_3$(CN)$_2$Br$_2$]$^-$ anion is composed of a fused ring (CuBr)$_2$ ladder motif that is cross-linked by NC–Cu–CN units.

Thus far, we have focused almost exclusively on cyanocuprate(I) networks, but mixed valence cyanocuprates are also widely recognized. There are two general types: those in which isolated
copper(II) ions are guests within a cyanocuprate(I) lattice, and those for which cyanide bridging produces a single network. The Cu(II) guest molecules that have been identified in cyanocuprate(I) nets include Cu(H$_2$O)$_4^{2+}$, Cu(NH$_3$)$_4$(H$_2$O)$_2^{2+}$, Cu(en)$_2$(H$_2$O)$_2^{2+}$, and Cu(NN)$_2^{2+}$ (NN = en or 1,3-propanediamine). There exists a wide range of integrated Cu(I)-Cu(II) cyanocuprate networks. These vary from 1D to 3D, higher dimensionality networks being extended through μ$_3$-C,C,N bridging or the occurrence of 4-coordinate Cu atoms. Several examples are shown in Fig. 8. The many known mixed metal cyanocuprates are considered beyond the scope of this review.

**Figure 8.** (A) Ribbon of fused Cu$_5$(CN)$_3$(NH$_3$)$_3$ rings in Cu$^{II}$Cu$^{II}_2$(CN)$_4$(NH$_3$)$_3$. (B) Sheet of tiled Cu$_{12}$$(CN)_{12}$(cyclam)$_6$ with 4-coordinate Cu centers and pendant cyano units in Cu$^{II}_3$Cu$_2$(CN)$_8$(cyclam)$_3$(H$_2$O)$_5$. (C) Rippled sheet of tiled Cu$_6$(CN)$_6$(dmen)$_3$ rings in [Cu$^{II}$_3Cu$^{I}$(CN)$_3$(dmen)]. (D) μ$_3$-C,C,N-bridged 3-D structure of Cu$^{II}_5$Cu$^{II}_4$(CN)$_6$(DMF)$_4$. In Figures 8, 11, 13-15, except as noted: copper atoms are shown as orange spheres, cyano nitrogen and carbon (although often disordered) as blue and grey spheres, respectively, and non-cyano ligands as wireframe; hydrogens are omitted.

**CuCN-L Networks**

Copper(I) cyanide itself features unusually low-coordinate metal centers. As a result, it has a strong tendency to acquire additional ligands. This usually results in simple decoration of the CuCN zigzag chain, as shown in Fig. 9. A list of polymeric CuCN-monodentate ligand complexes is provided in Table
2. Although the most commonly found $m/n$ value for $(\text{CuCN})_m\text{L}_n$, is 1 (XXIII), both more and less ligand-rich cases are well established. An $m/n$ ratio of 1 usually means 3-coordinate copper centers, while values $>1$ suggest the presence of 2-coordinate centers, and values $<1$ suggest the addition of 4-coordinate centers. It is not at all unusual for a particular ligand to give rise to multiple $(\text{CuCN})_m\text{L}_n$ stoichiometries depending on the availability of L, e.g. $(\text{CuCN})_7\text{Py}_4$, $(\text{CuCN})_3\text{Py}_4$, $(\text{CuCN})_2\text{Py}$. The many simple zigzag $(\text{CuCN})\text{L}$ complexes show large cyano–Cu–cyano angles ($130.3^\circ – 148.9^\circ$) indicative of weak ligand binding. A plot of these angles versus Cu–N bond lengths (2.044–2.205 Å) shows a rough correlation. Both metrics confirm that bonding is weaker for aliphatic than for aromatic amines.

CuCN-L stoichiometry is usually easily determined through thermogravimetry, see Fig. 10, wherein sequential loss of 2-MePy in traces A and B suggests transformations (1) – (3):

\[
\begin{align*}
(C\text{CN})_2(2\text{-MePy})_3 \hspace{1em} \rightarrow \hspace{1em} & 2 (C\text{CN})(2\text{-MePy}) \hspace{1em} (s) \hspace{1em} + \hspace{1em} 2\text{-MePy} \hspace{1em} (g) \hspace{1em} \uparrow \\
2 (C\text{CN})(2\text{-MePy}) \hspace{1em} (s) \hspace{1em} \rightarrow \hspace{1em} & (C\text{CN})_2(2\text{-MePy}) \hspace{1em} (s) \hspace{1em} + \hspace{1em} 2\text{-MePy} \hspace{1em} (g) \hspace{1em} \uparrow \\
(C\text{CN})_2(2\text{-MePy}) \hspace{1em} (s) \hspace{1em} \rightarrow \hspace{1em} & 2 \text{CuCN} \hspace{1em} (s) \hspace{1em} + \hspace{1em} 2\text{-MePy} \hspace{1em} (g) \hspace{1em} \uparrow 
\end{align*}
\]

Figure 9. Nucleophile-decorated CuCN chain arrangements.
Figure 10. Thermogravimetric traces of (A) (CuCN)$_3$(2-MePy)$_2$, (B) (CuCN)(2-MePy), and (C) CuCN exposed to saturated atmosphere of 2-MePy at room temperature.\textsuperscript{77}

Table 1. (CuCN)$_m$(L)$_n$ complexes (L = monodentate ligand).

<table>
<thead>
<tr>
<th>$m/n$</th>
<th>Lattice Type</th>
<th>L</th>
<th>Cu Coord.$^a$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:1</td>
<td>$\mu_3$-C,C,N 2-D sheets with –CN–Cu–CN– links, and terminal Cu(OH$_2$) units</td>
<td>H$_2$O</td>
<td>2, 3</td>
<td>78</td>
</tr>
<tr>
<td>2:1</td>
<td>$\mu_2$-C,N 1-D chains</td>
<td>3-MePy, NH$_3$Pr$_2$, PPh$_3$</td>
<td>2, 3</td>
<td>43,79</td>
</tr>
<tr>
<td>7:4</td>
<td>$\mu_2$-C,N 1-D chains with threaded CuCN chains</td>
<td>Py</td>
<td>2, 3</td>
<td>43,80,81</td>
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<tr>
<td>3:2</td>
<td>$\mu_2$-C,N 1-D chains</td>
<td>PhCN, $o$-MeC$_6$H$_4$CN</td>
<td>2, 3</td>
<td>47c</td>
</tr>
<tr>
<td>4:3</td>
<td>[no structure]</td>
<td>N-EtPipd</td>
<td>–</td>
<td>43,77</td>
</tr>
<tr>
<td>5:4</td>
<td>[no structure]</td>
<td>Py</td>
<td>–</td>
<td>43,47a,77</td>
</tr>
<tr>
<td>1:1</td>
<td>$\mu_3$-C,C,N 2-D sheets</td>
<td>NH$_3$, CH$_3$CN</td>
<td>3</td>
<td>82,47c</td>
</tr>
<tr>
<td>1:1</td>
<td>$\mu_2$-C,N 1-D chains</td>
<td>DMSO, CN$^\prime$Bu, (CH$_3$CN•0.5 18-crown-6), EtCN, S=C(NMe$_2$)$_2$, S=C(NH$_2$)CH$_3$, $^b$ 2-MePy, 3-MePy, 2-EtPy, 3-EtPy, 4-EtPy, 2-ClPy, 3-ClPy, 2-BrPy, 3-BrPy, 2,4-Me$_2$Py, 2,4,6-Me$_3$Py, 3-AcOPy, 4-AcOPy, 4-EtO$_2$C-Py, Quin, NHEt$_2$, NEt$_3$, N-MePipd, Me$_2$NCy, N-MeMorph, $^b$ MBIA, $^c$</td>
<td>3</td>
<td>43,47a,47c,5, 5,77,80,81,8, 3-85</td>
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<tr>
<td>1:1</td>
<td>μ₂-C,N cyclic oligomers</td>
<td>DMPz(^d)</td>
<td>PCy(_3), TMTHT(^c)</td>
<td>3</td>
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<td>-----</td>
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<td>-------------</td>
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<tr>
<td>3:4</td>
<td>μ₂-C,N 1-D chains</td>
<td>Pipd, PyBIIm(^f)</td>
<td>3, 4</td>
<td>43,77,85,86</td>
</tr>
<tr>
<td>2:3</td>
<td>μ₂-C,N 1-D chains</td>
<td>2-MePy, 3-MePy, 4-MePy, 3-EtPy, NH(_2)Cy</td>
<td>3, 4</td>
<td>43,47a,77,84,87</td>
</tr>
<tr>
<td>2:3</td>
<td>μ₂-C,N 1-D chains plus (\frac{1}{2}) molecule of free ligand</td>
<td>4'-BuPy</td>
<td>3</td>
<td>43,77</td>
</tr>
<tr>
<td>1:2</td>
<td>μ₂-C,N 1-D chains</td>
<td>Py, (3:1 Py:PPh(_3)), 3-ClPy, 3-MeOPy, P(OPh)(_3)</td>
<td>4</td>
<td>43,47a,47b,7,89,90</td>
</tr>
<tr>
<td>1:2</td>
<td>μ₂-C,N cyclic hexamers</td>
<td>PPh(_3)</td>
<td>4</td>
<td>61b</td>
</tr>
</tbody>
</table>

\(^a\)C,C-cyanide bridges assigned as ligand to only one Cu. \(^b\)Long range Cu−S of 2.708(4) Å in (CuCN)\([SÇ(C(NH\(_2\))CH\(_3\))]^{85b}\) and Cu−O of 2.537(3) Å in (CuCN)(N-MeMorph)\(^{43,77}\) weakly cross-link CuCN chains. \(^c\)MBIA = 2-(2-methyl-1H-benzo[\(d\)]imidazol-1-yl)acetonitrile. \(^d\)DMPz = 3,5-dimethyl-1H-pyrazole \(^e\)TMTHT = 3,3,6,6-tetramethyl-2,3,6,7-tetrahydrothiepine (\(\eta^2\)-alkene-bonded). \(^f\)PyBIIm = 2-(pyridin-4-yl)-1H-benzo[\(d\)]imidazole.

Several CuCN chains decorated with small ligands (H\(_2\)O, NH\(_3\), MeCN) are further cross-linked to form 2-D sheets via μ\(_3\)-C,C,N bridging. The resulting bimetallic nodes typically show cuprophilic interactions, and usually link according to XXVI. Other, less-commonly encountered, μ\(_3\)-C,C,N bridging variants include XXVII and XXVIII.\(^{91}\) The aqua compound (CuCN)\(_3\)(H\(_2\)O) is a very unusual species for two reasons: (a) it shows rare cyano−Cu(I)−O bonding, and (b) it features XXVI dimer units that are bridged in one direction by pendant 2-coordinate −CN−Cu−CN− units and are capped by −Cu−OH\(_2\) units in another direction (Figure 11A).\(^{78}\) Another interesting network is (CuCN)\(_2\)Py\(_4\), which consists of both (CuCN)Py and CuCN chain sub-lattices. These interact together through remarkably short, unsupported Cu−Cu interactions of 2.4537(17) Å (Figure 11B).\(^{43}\) 2,3-Dihydroxyquinoxaline forms a self-hydrogen-bonded network that is shot through with CuCN chains, which are only very
weakly associated with lattice oxygen atoms ($\text{Cu} \cdots \text{O} = 2.728(5)$ and $2.697(5)$ Å, cyano–Cu–cyano = 169.9(2)°), Fig. 11C.92

![Chemical structures and images](image)

**Figure 11.** (A) ($\text{CuCN})_3(\text{H}_2\text{O})$ structure featuring $\mu_3$-$\text{C},\text{C},\text{N}$ bridging units bearing terminal $\text{Cu(OH}_2)$ groups.78 (B) ($\text{CuCN})_7\text{Py}_4$ structure featuring ($\text{CuCN}$)Py and $\text{CuCN}$ sublattices.43 (C) Structure of ($\text{CuCN})(2,3$-dihydroxyquinoxaline) showing weak coordination of $\text{CuCN}$ to H-bonded ligand network (dashed lines).92 Hydrogens shown.

Our group has shown that reversible adsorption of amine or sulfide nucleophiles by bulk CuCN produces a shift of photoluminescent emission into the visible range.43,77 This reaction occurs spontaneously upon exposure of CuCN to liquid or vapor, providing the foundation for possible vapor-detection systems. The amount of nucleophile taken up by CuCN particles upon vapor exposure is quite small as revealed by TGA (see Fig. 10, trace C), nevertheless, a remarkable diversity of luminescence colors is produced, even for very similar amines (Fig. 12). The origin of the red shift appears to be
associated with bending at the Cu centers along the chain (see above), and the range of emission wavelengths appears to be tied to the stoichiometric and structural diversity of the surface product phases. Alternative stoichiometries for a particular nucleophile tend to produce different emission colors. For example, (CuCN)(2-Mepy) emits at 452 nm (blue) and (CuCN)$_2$(2-Mepy)$_3$ emits at both 452 and 525 nm (yellow-green). Both colors are visible in Fig. 12K.


Bidentate chelating nitrogen and phosphorus ligands, such as 2,2'-bpy and Phen, bind to CuCN chains, forming 4-coordinate Cu centers. Stoichiometries of fewer than one chelate ligand per copper contain both 4-coordinate and ligand-free 2-coordinate Cu centers within the chains. In some cases, −CNCu-L or −CNCuCNCu-L branches pendant to the main CuCN chain bear some or all of the ligands at their termini. In an unusual variation on the chain decoration theme, a long ligand (2,5-bis(3-pyridyl)-1,3,4-oxadiazole) bridges pairs of Cu atoms lying along CuCN chains.

Copper(I) cyanide networks that are cross-linked by bridging ligands are legion. Although they are generally prepared directly from CuCN, desulfurization of CuSCN by dppe has been reported. The simplest networks utilize 3-coordinate Cu centers, and are formed via simple bidentate ligand cross-linking of pairs of CuCN chains into 1-D ladders or series of CuCN chains into 2-D sheets. Only a very few ladders are known, one example uses the phthalazine ligand, Fig. 13A. Cross-linked sheets
usually feature (6,3) networks with tiled 3-coordinate Cu\textsubscript{6} rings.\textsuperscript{91,93,96,98,99} Long ligands can form (4,4) tiled networks with 4-coordinate Cu centers (Fig. 13B),\textsuperscript{95,100} and larger rings occasionally incorporate 2-coordinate Cu spacers.\textsuperscript{88} A few of these sheet networks additionally incorporate independent CuCN chains as a second sub-lattice threaded through the macrocyclic rings of the sheet structure. The known examples include [(CuCN)\textsubscript{2}(Pyz)]\textsuperscript{+}\textsuperscript{-}CuCN (Fig. 13C), 2[(CuCN)\textsubscript{2}(4,4′-Bpy)]\textsuperscript{+}3CuCN, [(CuCN)\textsubscript{2}(4,4′-Bpy)]\textsuperscript{+}2CuCN, 2[(CuCN)\textsubscript{2}(RPip)]\textsuperscript{+}3CuCN (RPip = N-methyl- or N-ethylpiperazine), and [(CuCN)\textsubscript{2}(R\textsubscript{2}Pip)]\textsuperscript{+}2CuCN (R = N,N′-dimethyl- or N,N′-diethylpiperazine).\textsuperscript{40,99,101} Cuprophilic interactions between sub-lattices are the rule in these structures. A unique binary network, (CuCN)\textsubscript{20}(Pip)\textsubscript{7} = 6[(CuCN)\textsubscript{2}(Pip)]\textsuperscript{+}[(CuCN)\textsubscript{8}(Pip)] incorporates two interpenetrating tiled sheet sub-lattices: a simple (6,3) planar network of stoichiometry (CuCN)\textsubscript{2}(Pip), and an unusual (CuCN)\textsubscript{8}(Pip) which contains seven 2-coordinate Cu atoms.\textsuperscript{40,102} All twenty copper atoms in (CuCN)\textsubscript{20}(Pip)\textsubscript{7} are crystallographically independent. An alternative to sheet formation in 3-coordinate networks involves bridging between CuCN chains that propagate in perpendicular directions.\textsuperscript{103} The resulting 3-D networks sometimes contain helical CuCN chains.

Figure 13. (A) (CuCN)\textsubscript{2}(phthalazine) structure showing ladder motif.\textsuperscript{91} (B) (CuCN)(1,4-bis(2-pyrimidinesulfanyl)methyl)benzene) structure showing 4-coordinate Cu\textsubscript{4}(CN)\textsubscript{2}L\textsubscript{2} rings.\textsuperscript{100b} (C) Structure of [(CuCN)\textsubscript{2}(Pyz)]\textsuperscript{+}CuCN threading of CuCN through a (6,3) network.\textsuperscript{99}

The addition of chelation\textsuperscript{96,104} or sulfur atom bridging\textsuperscript{85a,105} by the ligands into the 2-D networks described above increases the variety of possible motifs. A particularly interesting example is provided using a triply-bridging chelate hexaazatryptophane ligand which produces a tethering node for the
CuCN chains. The structure shown in Fig. 14A contains widely separated chains tethered together to form a nanoporous hexagonal network that entrains solvent molecules (THF, Pyz, 1,4-dioxane). A common way in which 3-D networks are formed from the 2-D sheets described above is through the formation of $\mu_3$-C,C,N-bridged dimer units with cuprophilic interactions, XXVI (see Fig. 14B). The formation of these networks is rather difficult to anticipate, since closely related or even identical ligands can produce both 2-D and $\mu_3$-bridged 3-D arrangements. This is clearly illustrated in Zubieta’s extensive structural study of pyrazine-based ligands. He found simple 2-D sheets for (CuCN)$_3$(Pyz), (CuCN)$_2$(2-EtPyz), (CuCN)$_2$(2,3,5,6-Me$_4$Pyz), (CuCN)$_2$(quinoxaline), and (CuCN)$_2$(phenazine), but observed 3-D $\mu_3$-C,C,N-bridged dimer-linked networks for (CuCN)$_2$(2-MePyz), (CuCN)$_2$(2,3-Me$_2$Pyz), (CuCN)$_2$(2,5-Me$_2$Pyz), and (CuCN)$_2$(2,6-Me$_2$Pyz).

**Figure 14.** (A) (CuCN)$_3$(3,7,11-triethoxy-2,6,10-tricyanoheaxaazatriphenylene)•THF structure. Position of disordered THF molecule indicated by large green sphere. (B) (CuCN)$_2$(1,4-butanediamine) structure, showing $\mu_3$-C,C,N cyano bridges. (C) (CuCN)Pyz structure, showing 4-coordinate diamondoid arrangement.

Another important 3-D motif for CuCN complexes with bridging bidentate ligands is the diamondoid network (see Fig. 14C). In this case copper centers are 4-coordinate and are linked by cyano units and bridging ligands in orthogonal directions. In addition to the 2-D and $\mu_3$-bridged 3-D pyrazine networks described above, both Pyz and 2-MePyz also form diamondoid networks, and Pyz itself also forms yet another diamondoid network, (CuCN)$_3$(Pyz)$_2$ which contains both 2- and 4-coordinate copper.
centers. Since the diamondoid net tends to be a porous nature, especially with relatively long ligand bridges, interpenetration of multiple sub-lattices is common. Instead of self-interpenetrating, the diamondoid [(CuCN)(4,4'-Bpy)]•2(4,4'-Bpy) incorporates two free ligand molecules within its channels.

Multidentate ligands produce a range of stoichiometries and network structures that is too large to tackle here. As an example, let us consider the complexes of CuCN with the potentially tetradentate, adamantane-like HTMA ligand. Three phases are known: (CuCN)$_3$(HMTA)$_2$, (CuCN)$_5$(HMTA)$_2$, and (CuCN)$_5$(HMTA), see Fig. 15. These correspond to bi-, tri-, and tetradentate bridging modes of the HMTA. They also reflect some of the variety of CuCN network formation. The 3:2 complex contains only 3-coordinate Cu atoms forming chains that are bridged by μ$_2$-HMTA, giving rise to 2-D sheets consisting of Cu$_4$ and Cu$_6$ rings. In contrast, both the 5:2 and 5:1 complexes are 3-D networks as the result of both μ$_3$-C,C,N bridges and polydentate ligand behavior. The 5:2 complex also contains a 4-coordinate Cu center, while the 5:1 complex features a 2-coordinate Cu center. Nevertheless, and presumably as a result of the steric constraints resulting from the crowding three or four copper atoms around each HMTA, all the other Cu centers in the 5:2 and 5:1 complexes are part of μ$_3$-C,C,N dimers.
Figure 15. (A) (CuCN)$_3$(HMTA)$_2$ structure, showing sheet structure.\textsuperscript{98b} (B) and (C) (CuCN)$_5$(HMTA)$_2$ and (CuCN)$_3$(HMTA) structures, showing $\mu_3$-C$_2$N cyanide bridges and increased network crowding around the higher-coordinate ligand.\textsuperscript{40} Only a single layer of 3-D structure is shown in (B) and (C).

Conclusions

Although the reaction of copper with CO has been known for a very long time, the number of isolated copper carbonyl complexes is still fairly modest, at least in part due to the relative lability of the Cu–CO bond. Terminal and bridged species are recognized. Carbonyl is most commonly attached to amine-bearing copper(I) centers, sometimes allowing unusual five-coordination. The bonding in Cu–CO complexes, as evaluated through IR spectroscopy, spans a range from strongly $\pi$-backbonding to virtually $\sigma$-donor-only behavior. This latter bonding mode for CO is poorly studied, and could be of interest in biological and/or environmental chemistry. The ability of aqueous Cu(I) solutions to scrub CO efficiently is an interesting and long-recognized phenomenon that might yet have technological applications.

Cyanide is almost the ideal network-forming ligand for copper(I). The simple, nearly linear chain structure of CuCN is elaborated into an astounding array of 1-D, 2-D, and 3-D networks through variable coordination number of Cu(I), variable modes of cyanide bridging, and the addition of various organic ligands. Nitrogen, phosphorus, and sulfur donors react readily with CuCN, and even coordination of oxygen donors, although rare, is known. Monodentate donors readily and reversibly decorate CuCN chains, while bidentate bridging ligands produce tiled sheets or diamondoid networks. Additional network cross-linking often results from the $\mu_3$-C$_2$N cyano bridge, which is usually accompanied by cuprophilic interaction. Copper(I) compounds, including a great many cyano complexes, tend to be photoluminescent through excitation of a 3d-electron into the 4s or a ligand $\pi^*$ orbital. Given the current intense interest in network chemistry in separations, molecular storage,
electronics, and sensing, the ability to modulate emission response in copper(I) cyanide networks will continue to make them very attractive topics for research.

Abbreviation List: bpen = trans-1,2-bis(2-pyridyl)ethylene, Bpy = dipyridyl, Cy = cyclohexyl, cyclam = 1,4,8,11-tetraazacyclotetradecane, DFT = density functional theory, dmen = N,N-dimethylethlenediamine, dppe = 1,2-bis(diphenylphosphino)ethane, DMF = N,N-dimethylformamide, DMSO = Dimethyl sulfoxide, en = ethylenediamine, HMTA = hexamethylenetetramine, IR = infrared, Melm = methylimidazole, Morph = morpholine, Phen = o-phenanthroline, Pipd = piperidine, Pipz = piperazine, Py = pyridine, Pyz = pyrazine, Quin = quinoline, THF = tetrahydrofuran, tmen = N,N,N,N'-tetramethylethlenediamine, Tp = tris(pyrazolyl)borate.

ACKNOWLEDGMENT We thank the National Science Foundation (CHE-0848109) for support of this work.

REFERENCES


81) In reference 78, the reported compound (CuCN)$_2$Py is probably (CuCN)$_7$Py$_4$. In addition, the compounds (CuCN)(2-MePy) and (CuCN)(2,4,6-Me$_3$Py) are misreported as 2:1 species in this reference.


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