

Crystal Structures of a Series of Complexes Produced by Reaction of Copper(I) Cyanide with Diamines

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A new synthetic procedure developed recently in our laboratories has made possible the synthesis of variety of new complexes of CuCN with diamines. Synthesis was effected by adding the ligand to a solution of CuCN in aqueous sodium thiosulfate. This procedure also provides an alternative pathway to a novel diamine complex reported by us previously, $(\text{CuCN})_3(\text{HMTA})_2$ (**1**) (where HMTA = hexamethylenetetramine). The other diamine ligands used were 1,4-diazabicyclo[2.2.2]octane (dabco), 1,4-dimethylpiperazine (dmpip), piperazine (pip), 1,4-butanediamine (butda), *N,N,N',N'*-tetramethylethylenediamine (tetmen), and *N*-phenylpiperazine (phpip). Complex **2**, $\text{Cu}_2(\text{CN})_3(\text{dabco-H})$, crystallizes in the hexagonal space group $P6_3$ with unit cell dimensions $a = 8.174(3)$ Å, $c = 8.083(4)$ Å, and $Z = 2$. Complex **3**, $(\text{CuCN})_2(\text{dmpip})$, crystallizes in the monoclinic space group $C2/m$ with unit cell dimensions $a = 8.812(3)$ Å, $b = 9.631(2)$ Å, $c = 7.266(3)$ Å, $\beta = 113.40(3)^\circ$, and $Z = 2$. Complex **4**, $(\text{CuCN})_2(\text{pip})$, crystallizes in the monoclinic space group $C2/c$ with unit cell dimensions $a = 9.439(3)$ Å, $b = 10.561(2)$ Å, $c = 8.870(3)$ Å, $\beta = 98.32(3)^\circ$, and $Z = 4$. Complex **5**, $\text{Cu}_2(\text{CN})_3(\text{pip-H})$, crystallizes in the monoclinic space group $C2/c$ with unit cell dimensions $a = 20.573(9)$ Å, $b = 8.354(2)$ Å, $c = 15.989(6)$ Å, $\beta = 133.70(3)^\circ$, and $Z = 8$. Complex **6**, $(\text{CuCN})_2(\text{butda})$, crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions $a = 10.456(2)$ Å, $b = 5.550(1)$ Å, $c = 8.669(3)$ Å, $\beta = 106.80(2)^\circ$, and $Z = 2$. Complex **7**, $(\text{CuCN})_2(\text{tetmen})$, crystallizes in the orthorhombic space group $\text{Cmc}2_1$ with unit cell dimensions $a = 11.889(4)$ Å, $b = 33.380(8)$ Å, $c = 9.012(3)$ Å, and $Z = 12$. Complex **8**, $(\text{CuCN})(\text{phpip})$, crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions $a = 17.8819(3)$ Å, $b = 6.9190(1)$ Å, $c = 8.6972(1)$ Å, $\beta = 96.720(1)^\circ$, and $Z = 4$.

Introduction

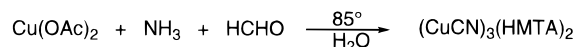
In 1991, we reported the synthesis and X-ray crystal structure of a new complex of copper(I) cyanide and hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$, HMTA).¹ The preparation of this complex, $(\text{CuCN})_3(\text{HMTA})_2$ (**1**), which was discovered by accident, came about during an attempt to prepare imidazoles by reacting sugars with Cu(II) salts, ammonia, and formaldehyde (Parrod synthesis). The formation of **1** occurred in the absence of sugars (Scheme 1).

It is noteworthy that none of the constituents (the Cu(I), the CN, or the HMTA) of the product was present in the starting materials. All attempts at synthesis of **1** by direct combinations of CuCN and HMTA in various solvents failed.

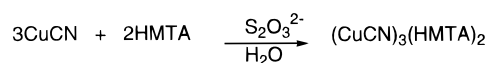
A synthetic method recently developed in our laboratories provided an alternative pathway to **1**. This method, which is widely applicable, consists of "thiosulfate-assisted" direct combinations of CuCN and water-soluble organic ligands. The weak complex of $\text{CuCN}/\text{S}_2\text{O}_3^{2-}$ has a strong tendency to release CuCN to virtually any water soluble ligand (L), thus producing a new complex of CuCN/L . Scheme 2 shows how this technique was used in the new preparation of **1**.

This method is appropriate for a variety of amines, but this paper will focus entirely on diamines. Only a few complexes

Scheme 1



Scheme 2



of CuCN and diamines have been reported. Two such complexes, based on the 1,10-phenanthroline (phen) system, are $\text{CuCN}(\text{phen})$ and $\text{CuCN}(\text{dmphen})$ (where dmphen = 2,9-dimethyl-1,10-phenanthroline).² Another involving hydrazine (the limiting diamine) is $\text{CuCN}(\text{N}_2\text{H}_4)$.³ Ethylenediamine (en) is present in a mixed Cu(II)/Cu(I) complex with the composition $\text{Cu}(\text{II})\text{Cu}(\text{I})_2(\text{CN})_4(\text{en})_2(\text{H}_2\text{O})$.⁴ The phen and hydrazine complexes were synthesized by direct combination of CuCN and the neat ligand, whereas the en complex was prepared by dissolving CuCN in 50% aqueous ethylenediamine. For prospective diamine ligands that are solids (e.g., HMTA) or that are liquids that fail to exhibit dissolving power for CuCN, the thiosulfate-assisted synthesis provides a powerful new synthetic approach. We, therefore, set out to use this method to prepare a variety of new diamine complexes of CuCN.

This study covered a variety of diamines, including bicyclic, cyclic, acyclic, primary, secondary, and tertiary types. Also, a

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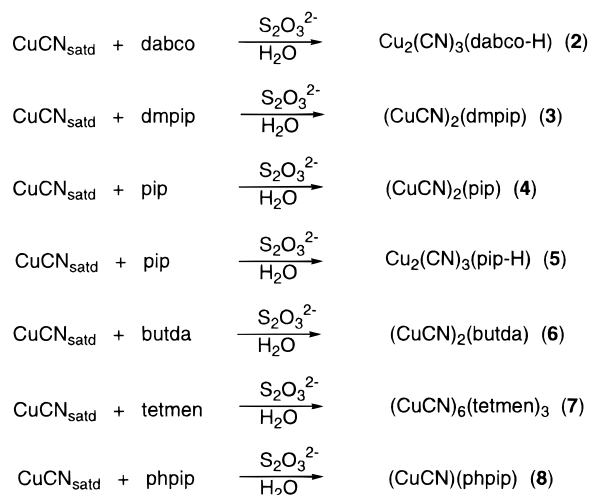
(1) Stocker, F. B. *Inorg. Chem.* **1991**, 30, 1472.

(2) Dyason, J. C.; Healy, P. C.; Engelhardt, L. M.; Pakawatchai, C.; Patrick, V. A.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1985**, 839.

(3) Cromer, D. T.; Larson, A. C.; Roof, R. B. *Acta Crystallogr., Sect. B* **1966**, 20, 279.

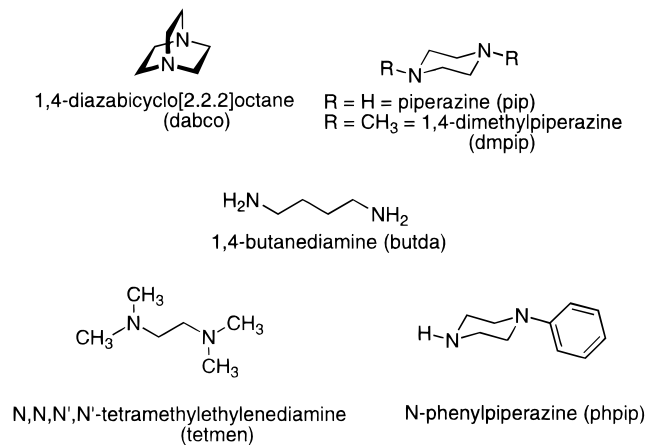
(4) Williams, R. J.; Larson, A. C.; Cromer, D. T. *Acta Crystallogr., Sect. B* **1972**, 28, 858.

Scheme 3



series of straight-chain diamines of the general structure $\text{H}_2\text{N}-(\text{CH}_2)_n\text{NH}_2$ were explored, where $n = 3-6$. In most cases, the diamines tested did produce insoluble solid complexes that gave positive chemical tests for Cu and IR spectral evidence for both CN and ligand. However, not all of these products were stoichiometric and not all produced crystals suitable for X-ray structure determinations. Scheme 3 shows the transformations that led to the complexes whose crystal structures are reported in this paper.

The structures of the ligands are as follows:



Experimental Section

General Methods. Commercial chemicals were used without further purification. Infrared spectra were recorded as KBr pellets with a Perkin-Elmer model 1430. Except where noted, all elemental analyses were determined by Galbraith Laboratories, Knoxville, TN. The crystal structures were determined by the X-ray Service Laboratory, Department of Chemistry, University of Minnesota, Minneapolis, MN.

General Methods of Preparation. To prepare crystals of sufficient size for X-ray structure determinations, the following standard procedure was used. Copper(I) cyanide (270 mg, 3 mmol) was added to a solution prepared by dissolving $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (2.482 g, 10 mmol) in 30 mL of distilled water (this is called the "standard solution"). After the CuCN dissolved, the ligand was added (1.0 mmol), and the mixture was heated and stirred until clear. The hot solution was filtered by gravity, and except where noted, the filtrate was poured into several small test tubes (13 mm $\times$ 100 mm) that were immersed in a hot water (400 mL) bath. The bath was either held at elevated temperatures for several hours on a steam cone or allowed to cool spontaneously on an insulated surface. After crystal growth appeared to be complete (rate of crystal growth dependent upon ligand), the crystals were collected by suction filtration

and washed with distilled water. All preparations were carried out in the presence of air, and all of the new compounds reported have proven to be stable in air for periods in excess of 1 year.

Preparation of $(\text{CuCN})_3(\text{HMTA})_2$ (1). In a variation of the usual preparation, hexamethylenetetramine (280 mg, 2 mmol) was dissolved at room temperature in the "standard solution". Within minutes, a white precipitate formed that was dissolved by swirling the flask over a steam bath. The hot, essentially clear solution was filtered, corked, and set aside on an insulated surface. Within a few hours, glistening micro-crystals were evident. After 1 day, the bottom of the flask was covered with colorless crystals, but the product was not isolated until the twelfth day. By then the solution had taken on a very faint blue tint. The white crystalline product (124 mg, 22.6%) gave an IR spectrum that was identical to the IR spectrum of an authentic sample.

Preparation of $\text{Cu}_2(\text{CN})_3(\text{dabco-H})$ (2). To the "standard solution" was added 1,4-diazabicyclo[2.2.2]octane (112 mg, 1 mmol), which dissolved with mild heating. After the colorless solution was heated to 88 °C and filtered, it was transferred to test tubes that were suspended in a 40 °C water bath that was allowed to cool spontaneously to room temperature. Crystals began to appear after the first few hours. The product (pale pink crystals, 108 mg, 33.9%) was collected by filtration after 2 days: IR 3420 br, w, 3020 s, 2955 w, 2770 w, 2608 w, 2130 w, 2075 s, 1620 br, w, 1465 w, 1450 m, 1392 s, 1372 w, 1312 m, 1236 w, 1173 w, 1047 s, 1020 w, 987 w, 830 m, 795 s, 603 m, 595 w, 405 cm^{-1} . Anal. Calcd for $\text{C}_9\text{H}_{13}\text{Cu}_2\text{N}_5$: C, 33.96; H, 4.12; Cu, 39.92; N, 22.00. Found: C, 33.21, 33.82; H, 4.06, 4.14; Cu, 42.67, 42.43; N, 21.30, 21.82.

Preparation of $(\text{CuCN})_2(\text{dmpip})$ (3). To 30 mL of the "standard solution" was added 1,4-dimethylpiperazine (114 mg, 1 mmol). Warming caused the ligand to dissolve, and after the temperature reached about 80 °C, the colorless solution was filtered and then placed in a 60 °C water bath. The water bath was allowed to cool slowly over a period of several hours to room temperature. Crystal growth was evident the next day, but the product was not collected for 5 days. The colorless prisms amounted to 33 mg (11%): IR 3450 br, m, 2973 m, 2950 w, 2890 w, 2815 m, 2760 w, 2705 w, 2140 s, 1670 br, w, 1630 br, w, 1455 s, 1422 w, 1377 w, 1297 m, 1158 m, 1128 w, 1100 w, 1057 w, 1017 s, 917 w, 825 m, 638 w, 433 w cm^{-1} . Anal. Calcd for $\text{C}_8\text{H}_{14}\text{Cu}_2\text{N}_4$: C, 32.76; H, 4.81; Cu, 43.33; N, 19.10. Found: C, 32.08; H, 4.88; Cu, 44.36; N, 18.83.

Preparation of $(\text{CuCN})_2(\text{pip})$ (4). Piperazine hexahydrate (194 mg, 1 mmol) dissolved readily in the "standard solution" to give a clear solution. After being heated on a hot plate to 85 °C, the solution took on a light tan color, and a fine, dusty tan precipitate appeared. Filtration produced a clear solution that was placed in an 80 °C water bath that was allowed to cool slowly to room temperature. Crystal growth was evident within 2 h. The following day, the first crop of product was collected by filtration (predominantly clear prisms, with a few brown present, 100 mg, 37.7%). The mother liquor later produced another batch of crystals, which turned out to be 5 (see next preparation): IR 3430 br, m, 3265 s, 2938 m, 2870 w, 2835 w, 2195 s, 2045 m, 1625 br, w, 1455 m, 1443 w, 1323 m, 1282 w, 1108 s, 1093 m, 997 m, 860 s, 627 m cm^{-1} . Anal. Calcd for $\text{C}_6\text{H}_{10}\text{Cu}_2\text{N}_4$: C, 27.17; H, 3.80; Cu, 47.91; N, 21.12. Found:⁵ C, 26.94; H, 3.88; Cu, 48.09; N, 21.36. Found: C, 27.26; H, 4.63; Cu, 45.51; N, 20.92.

Preparation of $\text{Cu}_2(\text{CN})_3(\text{pip-H})$ (5). The mother liquor from the previous experiment produced a second crop of crystals over a 3 day period at room temperature (thick brown diamond shaped plates, 20 mg, 6.8%). Anal. Calcd for $\text{C}_7\text{H}_{11}\text{Cu}_2\text{N}_5$: C, 28.77; H, 3.79; Cu, 43.48; N, 23.96. Found: C, 28.64; H, 3.75; Cu, 43.84; N, 23.99. We have found in other preparations using the same procedure with piperazine that a delay in collection of the product increases the proportion of 5 produced relative to 4. For example, filtration after 11 days produced a product mixture consisting of 80 mg of large brown diamond-shaped crystals (5), easily separated from 40 mg of small white crystals (4): IR 3250 m, 3165 w, 3110 w, 3040 s, 2810 w, 2625 w, 2440 w, 2110 s, 1670 br, w, 1580 s, 1460 m, 1447 m, 1410 m, 1387 m, 1298 w, 1200 w, 1110 m, 1060 w, 1027 w, 995 m, 973 s, 880 w, 867 m, 815 w, 600 w, 466 m, 425 w cm^{-1} .

(5) This analysis was performed by M-H-W Laboratories, Phoenix, AZ.

Table 1. Crystallographic Data^a

complex no.	2	3	4	5	6	7	8
formula	C ₉ H ₁₃ Cu ₂ N ₅	C ₈ H ₁₄ Cu ₂ N ₄	C ₆ H ₁₀ Cu ₂ N ₄	C ₇ H ₁₁ Cu ₂ N ₅	C ₆ H ₁₂ Cu ₂ N ₄	C ₈ H ₁₆ Cu ₂ N ₄	C ₁₁ H ₁₃ CuN ₃
fw	318.33	293.32	265.26	292.29	267.28	295.34	250.78
space group	P6 ₃ (No. 173)	C2/m (No. 12)	C2/c (No. 15)	C2/c (No. 15)	P2 ₁ /c (No. 14)	Cmc2 ₁ (No. 36)	P2 ₁ /c (No. 14)
a, Å	8.714(3)	8.812(3)	9.439(3)	20.573(9)	10.456(2)	11.889(4)	17.8819(3)
b, Å		9.631(2)	10.561(2)	8.354(2)	5.550(1)	33.380(8)	6.9190(1)
c, Å	8.083(4)	7.266(3)	8.870(3)	15.989(6)	8.669(3)	9.012(3)	8.6972(1)
α, deg	90.0	90.0	90.0	90.0	90.0	90.0	90
β, deg	90.0	113.40(3)	98.32(3)	133.70(3)	106.80(2)	90.0	96.720(1)
γ, deg	120.0	90.0	90.0	90.0	90.0	90.0	90
V, Å ³	531.5(6)	566.0(7)	874.9(8)	1987(3)	481.6(4)	3576(3)	1068.67(3)
Z	2	2	4	8	2	12	4
ρ _{calcd} (g cm ⁻³)	1.989	1.721	2.014	1.954	1.843	1.645	1.559
μ, cm ⁻¹	39.91	37.38	48.26	42.62	43.84	35.50	20.11
T, °C	24	24	24	24	25	24	25
R ^b	0.030	0.033	0.029	0.043	0.028	0.068	0.0321
R _w ^c	0.038	0.039	0.032	0.039	0.031	0.057	0.0927

^a Radiation: Mo Kα (graphite monochromated, λ = 0.710 73). ^b R = Σ||F_o| - |F_c||/Σ|F_o|. ^c R_w = [(Σw(|F_o| - |F_c||)²/ΣwF_o²)]^{1/2}.

Preparation of (CuCN)₂(butda) (6). Upon dissolving 1,4-diaminobutane (88 mg, 1 mmol) in 30 mL of the "standard solution", a blue color appeared. After the solution was heated to 70 °C, the color faded, changing from blue to pale green and eventually a faint yellow color. The hot solution was filtered and placed in a 70 °C water bath that was allowed to cool to room temperature. The following day, the crystals (colorless prisms, 133 mg, 50%) were collected by filtration: IR 3420 br, m, 3115 s, 3275 s, 2915 s, 2855 m, 2080 s, 1598 m, 1463 w, 1370 w, 1250 w, 1095 m, 1053 s, 955 m, 532 w, 455 w cm⁻¹. Anal. Calcd for C₆H₁₂Cu₂N₄: C, 26.96; H, 4.53; Cu, 47.55; N, 20.96. Found: C, 26.91; H, 4.65; Cu, 48.83; N, 20.71.

Preparation of (CuCN)₆(tetmen)₃ (7). A blue color developed when N,N,N',N'-tetramethylethylenediamine (174 mg, 1 mmol) was dissolved in 30 mL of the "standard solution". When heated to 95 °C, the solution became colorless. After the hot solution was filtered, it was placed in a 95 °C water bath that was allowed to cool to 80 °C over a 90 min period. At that point (crystal formation was evident), the water bath was placed on an insulated surface and allowed to cool to room temperature. The next day the crystals (predominantly colorless, but with a scattering of pale-blue green present, 99 mg, 33%) were collected by filtration: IR 3420 br, m, 2975 w, 2950 w, 2865 m, 2830 m, 2790 w, 2107 s, 2060 m, 1628 br, w, 1458 s, 1350 w, 1283 m, 1245 w, 1183 w, 1158 w, 1127 w, 1098 w, 1043 w, 1030 m, 1007 w, 950 m, 797 m, 768 w, 580 br, w, 480 br, w cm⁻¹. Anal. Calcd for C₂₄H₄₈Cu₆N₁₂: C, 32.54; H, 5.46; Cu, 43.03; N, 18.97. Found: C, 32.36; H, 5.60; Cu, 45.57; N, 18.72.

Preparation of (CuCN)(phpip) (8). N-Phenylpiperazine (81 mg, 0.5 mmol) was added to 30 mL of the "standard solution". Stirring with a magnetic mixer produced a very pale yellow solution with a small amount of a white precipitate. By warming to 85 °C on the steam bath, nearly all of the precipitate dissolved. After the hot solution was filtered, the flask was stoppered and placed on an insulated surface. Within a few hours nearly colorless crystals were visible. The next day the product (large needles, 176 mg, 65%) was collected by filtration: IR 3420 br, m, 3205 m, 3045 w, 3025 w, 2965 w, 2940 w, 2915 w, 2805 m, 2108 m, 2060 s, 1592 s, 1585 w, 1483 s, 1440 s, 1377 m, 1324 doublet m, 1285 w, 1250 m, 1222 s, 1187 m, 1145 m, 1105 m, 1075 w, 1030 w, 1018 m, 983 m, 908 s, 885 w, 850 m, 750 s, 690 s, 635 w, 520 m, 415 br, w, 515 br, w. Anal. Calcd for C₁₁H₁₃CuN₃: C, 52.68; H, 5.22; Cu, 25.34; N, 16.75. Found: C, 51.79, 52.48; H, 5.60, 5.57; Cu, 25.90, 27.12; N, 16.52, 16.56.

Preparation of (CuCN)₂(propda) (9). The addition of 1,3-propanediamine (74 mg, 1 mmol) to the "standard solution" produced an immediate purple-blue solution. While the solution was heated on the steam bath, the color lightened briefly and then became dark blue with a tinge of purple. After the temperature reached 85 °C, the solution was filtered to remove a small amount of mauve precipitate. The flask was placed in a 70 °C water bath that was allowed to cool slowly to room temperature. The following day the product (red-wine rhomboid microcrystals, 49 mg, 19%) was collected by filtration: IR 3420 br, m, 3285 s, 3235 m, 2920 w, 2880 w, 2095 s, 1583 s, 1467 w, 1430 w,

1398 w, 1310 w, 1280 w, 1175 m, 1093 w, 1053 w, 1023 m, 953 w, 900 m, 883 w, 665 m, 625 w, 495 w, 360 w. Anal. Calcd for C₅H₁₀Cu₂N₄: C, 23.71; H, 3.98; Cu, 50.18; N, 22.12. Found: C, 23.14; H, 3.53; Cu, 50.12; N, 22.05.

X-ray Structure Determinations

The crystals were mounted on glass fibers, and measurements were made at 24 ± 2 °C. Data for 2–7 were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The intensities of three representative reflections were measured after every 50–80 min of X-ray exposure time; in each of the seven data sets these intensities remained constant throughout data collection, indicating crystal and electronic stability (no decay corrections were applied). Data for 8 were collected on a Siemens SMART system using the same radiation. Again no decay corrections were necessary. Crystallographic data for 2–8 are presented in Table 1. The structures were solved by direct methods using the programs MITHRIL⁶ and DIRDIF.⁷ The neutral atom scattering factors used include correction for the real and imaginary components of the effect of anomalous dispersion.⁸ All calculations were performed using the TEXSAN⁹ crystallographic software package. The non-hydrogen atoms were refined anisotropically except for the cyanide atoms in 7, which is discussed later. There is a tendency for the bridging CN groups to have end-for-end disorder in these compounds. In 3 and 4, the space group symmetry required this disorder to be complete. In the remaining compounds, each such group was refined with the degree of disorder as a variable. The atoms in all the bridging groups are labeled C1N, etc., as a reminder of the possible disorder. Except for H11 in 8, which was refined with isotropic displacement parameters, H atoms were included in the structure factor calculations in idealized positions and were assigned isotropic displacement parameters that were 20% greater than the B_{eq} value of the atom to which they were bonded.

Cu₂(CN)₃(dabco-H) (2) occurs in a chiral space group. Both enantiomers were refined, and the enantiomer with the lower R value is reported. The opposite enantiomer refined with R =

(6) MITHRIL: Gilmore, C. J. *J. Appl. Crystallogr.* **1984** *17*, 42.

(7) DIRDIF: Beurskens, P. T. Technical Report 1984/1 Crystallography Laboratory, Toernooiveld, 6525 Ed Nijmegen, Netherlands.

(8) (a) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A. (b) Cromer, D. T. *Ibid.* Table 2.3.1.

(9) TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corp., 1985.

0.032, $R_w = 0.043$. The CN groups, which might have been ordered, appear to be completely disordered within experimental error.

(CuCN)₂(dmpip) (3) and (CuCN)₂(pip) (4) were straightforward.

Cu₂(CN)₃(pip-H) (5) has an arrangement similar to that of (2), and again the CN groups might have been ordered but appear to be disordered within experimental error.

(CuCN)₂(butda) (6) was straightforward.

(CuCN)₂(tetmen) (7) occurred as colorless and pale blue green crystals. Both kinds of crystals had identical unit cell dimensions and were presumed to be the same. The crystals are acentric, which leads to a lower value for the ratio of the number of observations to the number of parameters. There are 1567 observed reflections plus another 1416 Friedel opposites, which cannot be regarded as independent with respect to refining positional and displacement parameters. These were not enough data to allow all the atoms to be refined as anisotropic. It was decided to refine the CN atoms isotropically, despite their possible disorder, as soon as it became apparent that the tetmen atoms were even more disordered. Five-membered metal-ethylenediamine rings are usually slightly puckered. In this structure, where the rings lie across a mirror plane, this puckering leads to disorder, which shows up as very anisotropic displacement ellipsoids. The presence of the disorder leads to a lowering of the diffraction intensities and contributes to the shortage of data. The CN atoms were treated as possibly disordered, but the uncertainties in the occupancies are large, and nothing certain can be said about the degree of order or disorder. Since this structure is in a polar space group, refinement was carried out in both polarities. The two refinements converged to identical R and R_w values, and the one reported was chosen arbitrarily. It is possible that the crystal was actually a racemic twin.

In (CuCN)(phpip) (8) the CN group might be expected to be completely disordered, but it appears to be partially ordered with occupancy 0.81(2) for the major component.

Selected bond angles and bond distances for 2–8 are provided in Table 2. The bond distances are in the normal range. The bond angles around the Cu show large distortions from 120° for the three-coordinate Cu and from 109.5° for the four-coordinate Cu, but the distortions are no larger than those found in other Cu(I) structures. The most interesting localized structural features are the Cu₂(CN)₂ fragments found in several of the structures. These are discussed at the end of the Solid State Structures section of the Discussion. The anisotropic displacement ellipsoids for the seven structures are available in the Supporting Information. The packing is shown in Figures 1–8.

Discussion

Solid-State Structures. There is more variety than similarity in the seven structures reported here. The CN groups are involved in bridging in every case, but even here the usual Cu–CN–Cu bridge is replaced by a Cu₂–CN–Cu₂ arrangement for one of the CN groups in 4 and by Cu₂–CN–Cu bridges in 6–8. In the complexes with dabco-H (2) and pip-H (5), one of the amine nitrogens is protonated. In the complex with phpip (8) the nitrogen bearing the phenyl group is active as a H-bond acceptor to the hydrogen atom on the other nitrogen in an adjacent piperazine. In every other case the amine nitrogens are bonded to copper. In the complexes with dmpip (3), pip (4), and butda (6) the diamine forms an ambidentate bridge; in the complex with tetmen (7) the diamine chelates with the copper.

Table 2. Selected Bond Distances (Å) and Angles (deg)

bond distances		bond angles	
Cu ₂ (CN) ₃ (dabco-H) (2)			
Cu1–C1N	1.957(4)	N2C–Cu2–N11	102.1(2)
Cu2–N2C	1.984(4)	N2C–Cu2–N2C'	115.7(1)
Cu2–N11	2.238(6)	C1N–Cu1–C1N'	119.9(2)
(CuCN) ₂ (dmpip) (3)			
Cu1–N1C	1.878(3)	N1C–Cu1–N1C'	156.7(2)
Cu1–N11	2.244(3)	N1C–Cu1–N11	101.4(1)
(CuCN) ₂ (pip) (4),			
Cu1–Cu1'	2.581(1)	N1C–Cu1–N1C'	105.0(1)
Cu1–N1C	2.011(3)	N1C–Cu1–N2C	116.8(1)
Cu1–N1C'	2.221(3)	N1C–Cu1–N11	112.9(1)
Cu1–N2C	1.933(3)	N1C'–Cu1–N2C	114.7(1)
Cu1–N11	2.107(2)	N1C'–Cu1–N11	92.4(1)
		N2C–Cu1–N11	112.3(1)
Cu ₂ (CN) ₃ (pip-H) (5)			
Cu1–C1N	1.941(5)	C3N'–Cu1–N5C'	125.5(2)
Cu1–C3N'	1.909(5)	C1N–Cu1–N5C	115.7(2)
Cu1–N5C'	1.918(5)	C1N–Cu1–C3N'	117.4(2)
Cu2–N2C	1.956(5)	N4C–Cu2–C6N	110.9(2)
Cu2–N4C	2.012(4)	N2C–Cu2–C6N	122.2(2)
Cu2–C6N	1.952(5)	N2C–Cu2–N4C	109.5(2)
Cu2–N11	2.153(3)	N2C–Cu2–N11	106.2(2)
		N4C–Cu2–N11	101.7(1)
		C6N–Cu2–N11	104.0(1)
(CuCN) ₂ (butda) (6)			
Cu1–Cu1'	2.672(1)		
Cu1–N1C	1.969(2)	N1C–Cu1–C2N'	123.3(1)
Cu1–C2N'	1.890(3)	N1C–Cu1–N11	105.5(1)
Cu1–N11	2.060(2)	C2N–Cu1–N11	124.1(1)
(CuCN) ₂ (tetmen) (7)			
Cu1–C1N'	1.90(2)	N2C–Cu1–N4C	103.8(6)
Cu1–N2C	1.98(2)	C1N'–Cu1–N4C	127.4(6)
Cu1–N4C	1.95(1)	C1N'–Cu1–N2C	128.8(6)
Cu2–Cu3	2.307(2)	N21–Cu2–N21'	88.5(5)
Cu2–C3N	2.15(2)	C5N–Cu2–N21	115.9(4)
Cu2–C5N	1.97(2)	C3N–Cu2–N21	110.0(4)
Cu2–N21	2.08(1)	C3N–Cu2–C5N	113.8(7)
Cu3–C3N	2.02(2)	C5N–Cu3–N31	111.4(4)
Cu3–C5N	2.16(2)	C3N–Cu3–N31	117.1(4)
Cu3–N31	2.09(1)	C3N–Cu3–C5N	111.3(7)
		N31–Cu3–N31'	86.5(5)
Cu4–N6C	1.99(1)	C8N–Cu4–N10C	126.3(5)
Cu4–C8N	1.84(2)	N6C–Cu4–N10C	106.2(6)
Cu4–N10C	1.97(1)	N6C–Cu4–C8N	127.5(6)
Cu5–N7C	1.93(2)	C9N'–Cu5–N11C	115.5(7)
Cu5–C9N'	1.85(2)	N7C–Cu5–N11C	114.5(7)
Cu5–N11C	1.93(1)	N7C–Cu5–C9N'	130.0(5)
Cu6–C12N	1.84(1)	N61–Cu6–N61'	86.6(5)
Cu6–N61	2.06(1)	C12N–Cu6–N61	136.7(3)
(CuCN)(phpip) (8)			
Cu1–Cu1'	2.534(1)		
Cu1–N1C	1.946(2)	C2N'–Cu1–N11	104.6(1)
Cu1–C2N'	2.013(3)	N1C–Cu1–N11	116.1(1)
Cu1–N11	2.148(2)	N1C–Cu1–C2N'	121.8(1)
N11–H11	0.84(2)	N11–H11...N14'	166.2(7)
H11...N14'	2.55(3)		
N11...N14'	3.271(3)		

In Cu₂(CN)₃(dabco-H) (2) (see Figure 1), there are hexagonal sheets, [Cu₂(CN)₃]_n, similar to those found in KCu₂(CN)₃·H₂O.¹⁰ The difference is that in KCu₂(CN)₃·H₂O the large hexagonal holes were filled by potassium ions and water molecules that were not covalently bonded to the sheets, whereas in our compound there is a dabco-H⁺ group bonded to alternate Cu atoms making the entire two-dimensional sheet neutral. These dabco-H⁺ groups all point in the same direction, both in a single sheet and in adjacent sheets, the groups from one sheet filling the holes in the next sheet. The H atom on N14 points directly

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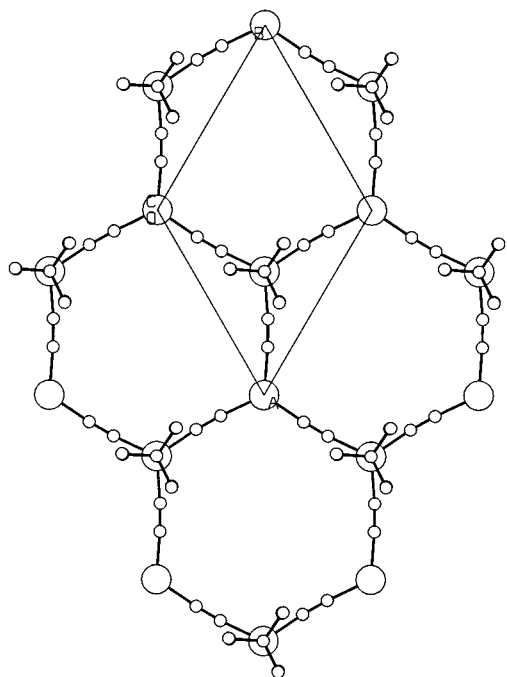


Figure 1. Extended structure of $\text{Cu}_2(\text{CN})_3(\text{dabco-H})$ (2). The view is along the c axis. In this and the following figures showing extended structures the Cu atoms have been shown larger than the rest. H atoms have been omitted for clarity.

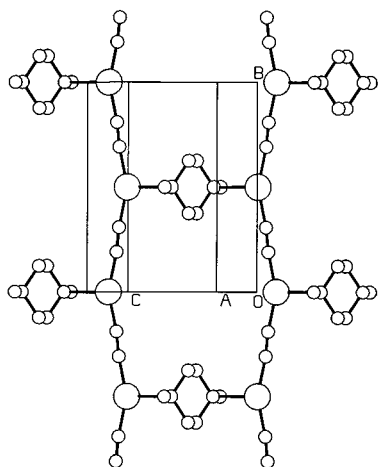


Figure 2. Extended structure of $(\text{CuCN})_2(\text{dmpip})$ (3). The view is normal to the (201) plane. H atoms have been omitted for clarity. The bonds from the piperazine ring to the Cu atoms are in axial positions, leading to a highly puckered two-dimensional sheet.

at the Cu2 atom two layers away (that is, $\text{N-H}\cdots\text{Cu}$) with a surprisingly short $\text{N}\cdots\text{Cu}$ distance of 3.296(4) Å.

In $(\text{CuCN})_2(\text{dmpip})$ (3) (see Figure 2), there are two-dimensional sheets. Cu-CN-Cu-CN chains are held together by bridging dmpip molecules. Somewhat similar arrangements occur in $(\text{CuCN})_2\cdot\text{etu}$ (etu = 2-imidazolidinethione or N,N' -ethylenethiourea)¹¹ and $(\text{CuCN})_2\cdot\text{detu}\cdot\text{H}_2\text{O}$ (detu = 1,3-dimethyl-2-thiourea),¹² although in both cases the arrangement of the bridging groups between chains is different from that in $(\text{CuCN})_2(\text{dmpip})$.

$(\text{CuCN})_2(\text{pip})$ (4) (see Figure 3) has a three-dimensional network. This structure contains $\text{Cu}_2(\text{CN})_2$ fragments. This type

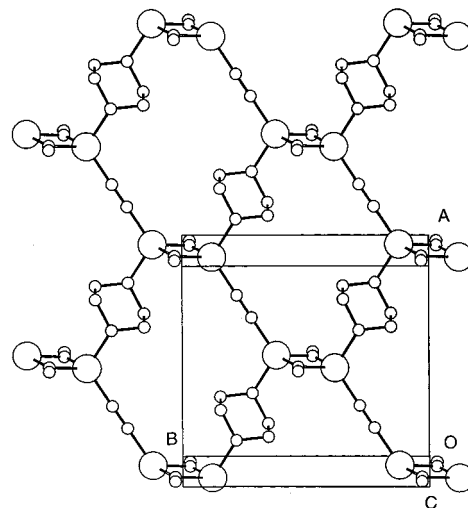


Figure 3. View perpendicular to the (001) plane of a two-dimensional sheet out of the extended structure of $(\text{CuCN})_2(\text{pip})$ (4). The overall three-dimensional structure is completed with $\text{Cu}_2\text{-CN-Cu}_2\text{-CN}$ chains parallel to the c axis. $\text{CN-Cu}_2\text{-CN}$ fragments from these chains are shown. The next layer above or below is related to the one shown by a c glide. H atoms are omitted for clarity.

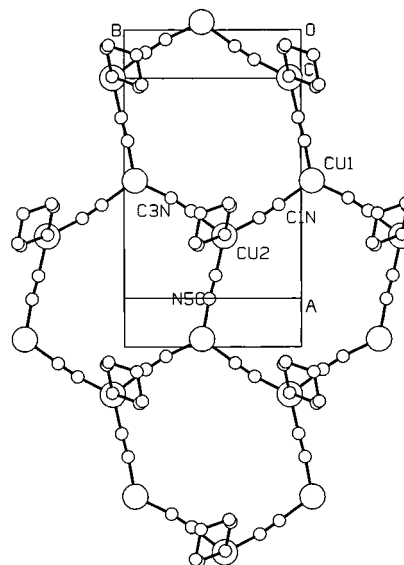


Figure 4. Extended structure of $\text{Cu}_2(\text{CN})_3(\text{pip-H})$ (5). View normal to the (101) plane. H atoms are omitted for clarity.

of group will be discussed at greater length after the discussion of 8. This structure can be thought of as Cu-Cu-CN-Cu-Cu chains held together by bridging pip molecules in a fashion similar to that in 3 to form two-dimensional sheets. These sheets are then held together by $\text{Cu}_2\text{-CN-Cu}_2$ bridges to the layer above. The Cu-Cu-CN-Cu-Cu chains in alternate layers are more or less orthogonal to each other.

$\text{Cu}_2(\text{CN})_3(\text{pip-H})$ (5) (see Figure 4) has an arrangement that is similar to that in $\text{Cu}_2(\text{CN})_3(\text{dabco-H})$ (2). Hexagonal sheets, $\text{Cu}_2(\text{CN})_3^-$, are neutralized by pip-H^+ ions bonded to alternate Cu atoms. In this structure, however, alternate layers point in opposite directions, and the pip-H^+ from one layer fill the hexagonal holes in the adjacent layer; this leads to a centric structure in this case. As was the case in 2 the H atom on N14 points directly at the Cu2 atom in an adjacent layer with another short $\text{N}\cdots\text{Cu}$ distance, 3.304(4) Å; in this case the arrangement is not required to be linear but the $\text{N-H}\cdots\text{Cu}$ angle is found to be 176°.

(11) Stocker, F. B.; Troester, M. A.; Britton, D. *Inorg. Chem.* **1996**, 35, 5, 3145.

(12) See ref 11.

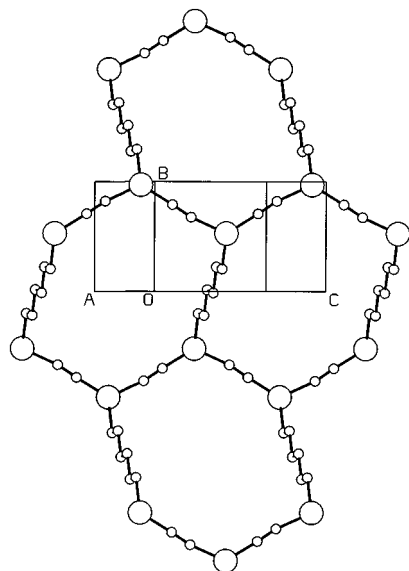


Figure 5. Extended structure of one two-dimensional sheet of $(\text{CuCN})_2(\text{butda})$ (**6**). View normal to the (100) plane. These sheets are highly puckered (see Figure 6). H atoms are omitted for clarity.

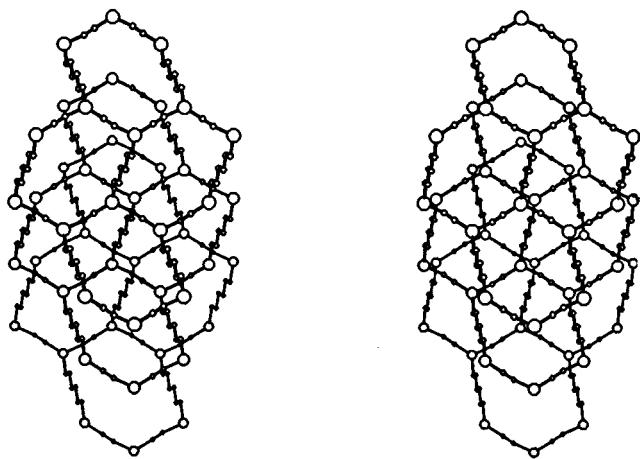


Figure 6. Stereoview of $(\text{CuCN})_2(\text{butda})$ (**6**) from the same direction as Figure 5, showing the interweaving of three of the two-dimensional sheets.

$(\text{CuCN})_2(\text{butda})$ (**6**) (see Figures 5 and 6) contains two-dimensional networks similar to those in **3** as can be seen in Figure 5. These networks have an hexagonal connectivity with large empty spaces in the centers of the hexagons. To fill space efficiently, three of these hexagonal networks interweave with successive networks related by translation along the *b* direction. A similar sort of interweaving occurs in the structure of $\text{AgC}(\text{CN})_3$,¹³ except that the interweaving only involves two layers rather than three. These triply interwoven networks form thick layers in which the faces of the layers are the Cu—CN—Cu—CN chains. Short Cu—Cu distances are found between layers as part of $\text{Cu}_2(\text{CN})_2$ fragments similar to those found in **4**. These are discussed after the discussion of structure **8**.

$(\text{CuCN})_2(\text{tetmen})$ (**7**) (see Figure 7) forms a ribbon that translates in the *c* direction. As one traverses the ribbon from side to side, in as direct a manner as possible, 12 Cu atoms are passed in the traverse. The two halves of the ribbon are related by a *c* glide relation so that six Cu atoms occur in the asymmetric unit. The ribbon can be thought of as three Cu—CN—Cu—CN chains parallel to the ribbon direction. The Cu1

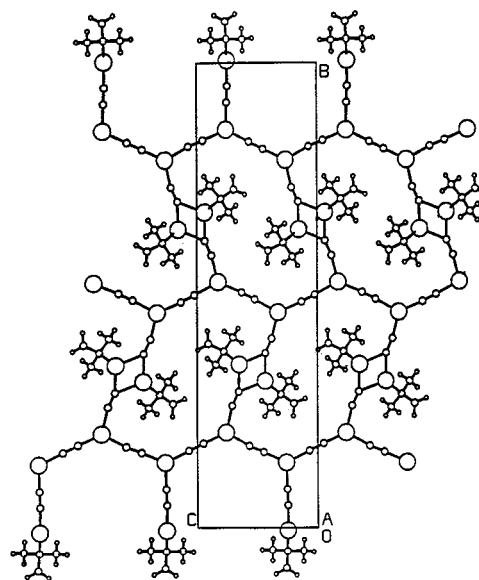


Figure 7. Extended structure of $(\text{CuCN})_2(\text{tetmen})$ (**7**). View along the *a* axis. This is a two-dimensional ribbon, with a width roughly equal to *b*, repeating along *c*. Except for the tetmen ligands, the ribbon is planar, lying in a mirror plane, and again only half of each tetmen molecule can be seen.

atoms are the basis of the central chain while Cu4 and Cu5 are the basis of the outer chains. The central and outer chains are connected by $\text{Cu}_2(\text{CN})_2$ groups similar to those found in **4** and **6**. The Cu in these bridges, Cu2 and Cu3, have their coordination completed by being part of a chelate ring with the tetmen. The last Cu, Cu6, is also part of such a chelate ring, and is attached, through a cyanide bridge to the outer chain. One can imagine two simpler arrangements. The first is a one-dimensional Cu—CN—Cu—CN chain similar to the outer chain with groups similar to the CN—Cu—tetmen groups attached at every Cu in the chain; there would be only two kinds of Cu in the arrangement. The second is a two-dimensional sheet where the motif between the two outer chains is continued indefinitely in both directions; there would only be two kinds of Cu atom in this arrangement. Presumably the observed form has a lower free energy than either of the two simpler, hypothetical phases. It is not obvious why this should be so.

$(\text{CuCN})(\text{phpip})$ (**8**) (see Figure 8) forms chains Cu—CN—Cu—CN with phpip groups attached to each Cu atom. This is an arrangement that is well-known, occurring in the $\text{Cu}(\text{CN})_2^-$ polymer in $\text{KCu}(\text{CN})_2$ ¹⁴ and $\text{NaCu}(\text{CN})_2 \cdot \text{H}_2\text{O}$,¹⁵ as well as in $\text{CuCN} \cdot \text{DMSO}$,¹⁶ $\text{CuCN} \cdot \text{Et}_2\text{NH}$ and $\text{CuCN} \cdot \text{Et}_3\text{N}$,¹⁷ $\text{CuCN} \cdot \text{ta}$ (ta = thioacetamide),¹⁸ and in both polymorphs of $\text{CuCN} \cdot \text{tmtu}$ (tmtu = tetramethylthiourea).¹⁹ The unique feature of this compound is that the H11 atom on N11 forms a hydrogen bond to an N14 atom from an adjacent chain (N11...N14, 3.371(5) Å; N11—H11...N14, 166(1)°; arrangement at N14, close to tetrahedral). These hydrogen bonds bind the chains into two-dimensional sheets. The N11...N14 distance is at the high end of the range for N—H...N hydrogen bonds, but each piperazine is involved in two such bonds, once as a donor and once as an acceptor and the H-bond lengths are not independent of the repeat

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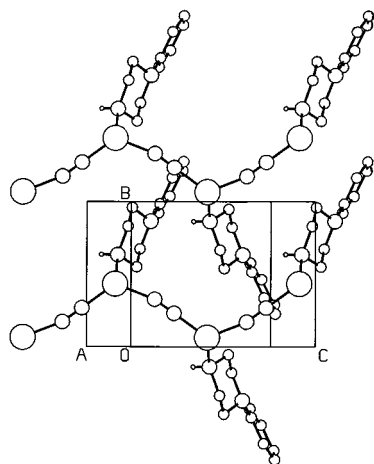
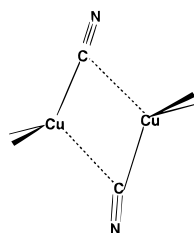


Figure 8. Extended structure of $(\text{CuCN})(\text{phpip})$ (**8**). View normal to the (100) plane. The N atoms are shown slightly larger than the C atoms. H atoms have been omitted for clarity, except for H11. One-dimensional chains occur parallel to the c axis. Adjacent chains are held together by hydrogen bonds. The H11 atom from one chain can be seen pointing toward an N14 atom from an adjacent chain.

Table 3. $\text{Cu}_2(\text{CN})_2$ Group Geometry



Cu—Cu (Å)	Cu—C (Å)	Cu...C (Å)	Cu—C—N (deg)	compound	ref
2.307	1.967	2.151	155.8	7	this
2.307	2.016	2.164	155.8	7	this
2.417	2.090	2.129	146.7	$\text{CuCN}\cdot\text{NH}_3$	20
2.534	2.013	2.347	160.7	8	this
2.581	2.011	2.221	151.2	4	this
2.636	1.931	2.418	158.9	$[\text{CuCN}]_3\cdot\text{H}_2\text{O}$	21
2.672	1.890	2.571	174.5	6	this

distance along the chain, which is largely fixed by the Cu—CN bonding. The Cu and CN groups from adjacent chains lie in planes, as can be seen in Figure 8. The packing is such that pairs of these planes are parallel to each other and near to each other so that there are short Cu—Cu distances as part of $\text{Cu}_2(\text{CN})_2$ groups, as was the case also in **4**, **6**, and **7**.

In **4** and **6–8** above, $\text{Cu}_2(\text{CN})_2$ groups were found as part of the structures. These groups can be thought of as forming by the sideways approach of two antiparallel CuCN groups involving three-valent Cu in the original group. (See the drawing in Table 3.) At the start, before the groups approach each other, each group contains a trigonal Cu atom, approximately coplanar with its three ligands, and a CN group with a linear Cu—CN geometry. As the groups approach, the CN bends away from the incoming Cu, and the original Cu—C bond lengthens as a new, additional Cu...C bond is forming. In Table 3, data are tabulated for the four such groups found in this study, along with those from similar groups in $\text{CuCN}\cdot\text{NH}_3$ ²⁰ and $[\text{CuCN}]_3\cdot\text{H}_2\text{O}$.²¹ Table 3 is ordered from shortest to longest Cu—Cu

distance. It can be seen the changes described above occur, but not with complete regularity. The limit of a symmetric arrangement with both Cu—C distances the same is most nearly reached in $\text{CuCN}\cdot\text{NH}_3$. In the limit of the symmetric arrangement, we would regard the bonding as two three-center Cu—C—Cu bonds, reminiscent of the bonding in diborane.

The infrared stretch frequencies for the cyanide groups in **2–8** appeared in the normal range, from 2040 to 2195 cm^{-1} . In simple aqueous complexes of $\text{Cu}(\text{CN})_n^{n-1}$ (where $n = 2–4$) the stretch frequency of the cyanide group decreases with increasing coordination of the copper atom.²² Three-coordinate copper sites predominate in the new complexes, appearing as $\text{Cu}(\text{CN})_3$, $\text{Cu}(\text{CN})_2\text{L}$, or $\text{Cu}(\text{CN})(>\text{L})$. Complexes **2** and **5** show four-coordinate copper sites as $\text{Cu}(\text{CN})_3\text{L}$. No relationship between coordination number and frequency was evident in these compounds.

Synthesis. Piperazine, *N*-phenylpiperazine, and 1,4-dimethylpiperazine were not the only members of the piperazine family to form complexes with CuCN. Both 2-methyl- and *N*-methylpiperazine gave amorphous solids that were shown by their IR spectra to contain cyanide and ligand. The presence of copper was established by means of a simple test tube experiment. After a number of synthesis efforts failed to produce these solids in crystalline form, they were not examined further.

Our investigation of the complexing ability of aromatic diamines with CuCN was limited to reaction attempts with *o*-, *m*-, and *p*-phenylenediamine. In each of these cases, a decomposition outcome was indicated by the formation of black amorphous residues.

Variable results were obtained in the study of the reactivity of CuCN toward the straight-chain diamines, $\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$, where $n = 2–6$. In 1966, Cooper and Plane²³ treated CuCN with aqueous ethylenediamine (en), producing a mixed valence purple copper complex, $\text{Cu}(\text{II})\text{Cu}(\text{I})_2(\text{CN})_4(\text{en})_2(\text{H}_2\text{O})$. Our synthetic method, although differing substantially from theirs, produced the same complex. This was established by comparing the IR spectrum of our product with the published spectrum of Cooper and Plane's product. Cromer and co-workers²⁴ determined its crystal structure in 1972. We did produce the novel complex **7** from CuCN and the en derivative, *N,N,N',N'*-tetramethylethylenediamine. The reaction of 1,3-propanediamine with CuCN produced $(\text{CuCN})_2(\text{propda})$ **9**, a red-violet microcrystalline complex. Although a number of synthesis variations of **9** were attempted, we were unable to produce crystals large enough for X-ray determination. Complexation of 1,4-butanediamine with CuCN proceeded smoothly, giving an excellent yield of the crystalline complex **6**. Reaction attempts with 1,5-pentanediamine and 1,6-hexanediamine with $\text{CuCN}/\text{S}_2\text{O}_3^{2-}$ produced only traces of amorphous precipitates. These materials were not considered pure enough to warrant further examination.

General Methods. The original intent behind this work was to show that the synthetic method was more generally useful—that the thioureas previously used as ligands or bridges could be replaced by amines. To this end, the amines were chosen to represent a variety of types. The results were generally satisfactory in regard to the syntheses, although it should be noted that there are still synthetic questions. In particular, the compositions of the various products do not follow, in any easily understood way, from the compositions of the original reaction mixtures.

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The structural results, although they were not the primary goal, are of interest in their own right. The cyanide or nitrile group is a popular one for the construction of solid-state structures as the following recent examples show. Iwamoto and co-workers²⁵ have used $\text{Ni}(\text{CN})_4^{2-}$ as a bridging group to form a large series of clathrate complexes $[\text{Cd}(\text{diamine})_2\text{Ni}(\text{CN})_4] \cdot x\text{guest}$. Fischer and co-workers²⁶ have shown that $\text{Co}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{3-}$ anions bridge $\text{Sn}(\text{CH}_3)_3^+$ and $\text{Pb}(\text{CH}_3)_3^+$ cations in much the same fashion that CN^- anions do,²⁷ except that the greater complexity of the $\text{M}(\text{CN})_6^{3-}$ ions leads to three-dimensional polymers. Robson and co-workers²⁸ have developed variations on the Zn and Cd cyanide structures that lead to three-dimensional structures with variable properties, including one structure where $\text{C}(\text{C}_6\text{H}_4\text{CN})_4$ (plus appropriate ions to correct the charges) has replaced $\text{Zn}(\text{CN})_4^{2-}$ as a four-coordinate ambidentate group. They have also shown²⁹ that replacement of CN^- in $\text{Zn}(\text{CN})_2$ by $\text{C}(\text{CN})_3^-$ to form $\text{Zn}[\text{C}(\text{CN})_3]_2$ replaces the three-dimensional polymer of the cyanide (with four-coordinate Zn) with a three-dimensional polymer with six-coordinate Zn. Mao and Mayr³⁰ have used *p*-cyanoisocyanobenzene as a bridging group between metal ions to form one-, two-, and three-dimensional solid-state polymers.

The structures reported here and previously show that copper cyanide/ligand complexes usually form polymeric $(\text{CuCN})_n$

chains with the ligands involved in various ways. Sometimes, one-dimensional chains form with the ligands attached as side groups or two or three of the one-dimensional chains are cross-linked to form ribbons that are still one-dimensional polymers. Other times, the ligands, or additional cyanides, cross-connect the CuCN chains completely to form two-dimensional polymers. Finally, the CuCN chains can be cross-linked in two directions to give a three-dimensional polymer. The wide range of structural types means that copper cyanide/ligand complexes have possibilities for the design of solid-state materials with particular types of structures. Again, it should be noted that the particular structure formed is not readily predictable from the ligand used. A number of these complexes have been prepared since the original work of Cromer and co-workers³¹ but there has been, as yet, no systematic exploration of the structural possibilities.

Acknowledgment. We are indebted to Professor Wayne C. Wolsey of Macalester College for encouragement and helpful discussions and to Victor G. Young, Jr., of the X-ray Crystallographic Laboratory of the University of Minnesota for determining the structure of **8**. Financial support from the Howard Hughes Medical Institute is gratefully acknowledged.

Supporting Information Available: Figures showing the anisotropic displacement ellipsoids of **2–8** and X-ray crystallographic files for the structures of **2–8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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