Inorg. Chem. **1996,** *35,* 3145−3153 **3145**

Crystal Structures of a Family of New Copper(I) Cyanide Complexes of Thiourea and Substituted Thioureas

Fred B. Stocker,* Melissa A. Troester,[†] and Doyle Britton[‡]

Departments of Chemistry, Macalester College, St. Paul, Minnesota 55105, and University of Minnesota, Minneapolis, Minnesota 55455

Received August 23, 1995[⊗]

The syntheses and crystal structures of the first cyanide, sulfur mixed ligand copper(I) complexes are reported. The first complex of the family was discovered when $(CuCN)_3(C_6H_{12}N_4)_2$ (**1**) ($C_6H_{12}N_4$ = hexamethylenetetramine) was treated with aqueous thiourea. The sulfur ligands include thiourea (tu), 1,3-dimethyl-2-thiourea (dmtu), 1,3-diethyl-2-thiourea (detu), 1,1,3,3-tetramethyl-2-thiourea (tmtu), and 2-imidazolidinethione (*N,N′*-ethylenethiourea, etu). Synthesis was effected by adding the ligand to a solution of CuCN in aqueous sodium thiosulfate. Complex **2**, $(CuCN)_2(tu)_3(H_2O)$, crystallizes in the triclinic space group $P\bar{1}$ with unit cell dimensions $a = 7.696(5)$ Å, $b = 9.346(2)$ Å, $c = 10.772(2)$ Å, $\alpha = 106.53(2)°$, $\beta = 91.11(4)°$, $\gamma = 98.42(3)°$, and $Z = 2$. Complex **3**, $(CuCN)_3(dmtu)_2$, crystallizes in the monoclinic space group *Cc* with unit cell dimensions $a = 10.082(3)$ Å, $b = 14.984(5)$ Å, $c = 11.413(3)$ Å, $\beta = 104.50(2)°$, and $Z = 4$. Complex **4**, $(CuCN)_2(detu)(H_2O)$, crystallizes in the monoclinic space group $P2_1/n$ with unit cell dimensions $a = 7.969(5)$ Å, $b = 11.559(4)$ Å, $c = 13.736(5)$ Å, $\beta = 100.48(4)°$, and $Z = 4$. Complex **5**, (CuCN)(tmtu) (polymorph a), crystallizes in the orthorhombic space group $P2_12_12_1$ with unit cell dimensions $a = 8.653(1)$ Å, $b = 9.426(1)$ Å, $c = 11.620(3)$ Å, and $Z = 4$. Complex **6**, (CuCN)(tmtu) (polymorph b), which has the same connectivity as **5**, crystallizes in the triclinic space group $P\bar{1}$ with unit cell dimensions $a = 9.660(4)$ Å, $b = 14.202(4)$ Å, $c = 16.03(1)$ Å, $\alpha = 101.68(5)°$, $\beta = 107.08(6)°$, $\gamma = 70.07(2)°$, and $Z = 8$. The difference between the polymorphs is that **5** has a zig-zag chain with a repeat unit of two while **6** has a 4-fold helix. Complex **7**, $(CuCN)_2(etu)$, crystallizes in the monoclinic space group $P2_1$ with unit cell dimensions $a = 3.994(2)$ Å, $b = 13.886(3)$ Å, $c = 7.556(1)$ Å, $\beta = 97.07(2)°$, and $Z = 2$.

Introduction

The parent compound, a complex of copper cyanide and thiourea, was discovered while we were exploring the chemistry of a new complex of copper cyanide with hexamethylenetetramine (HMTA), $(CuCN)_3(C_6H_{12}N_4)_2$ (**1**), which we characterized a few years ago.[1] During solubility studies, we found that solutions of **1** in aqueous thiourea (tu) deposited colorless crystals of the complex $(CuCN)_2(tu)_3(H_2O)$ (**2**) (Scheme 1). On the basis of the knowledge that the HMTA was a "spectator" during the reaction, we attempted a comparable preparation using copper cyanide and aqueous thiourea (Scheme 2). This reaction proceeded smoothly in comparable yield. Although samples of the hydrate were found to be unchanged after 6 months when stored in tightly closed containers, samples left open to a low-humidity atmosphere for extended periods gave analyses consistent with quantitative dehydration.

Scheme 1

$$2(CuCN)_3(HMTA)_2 + tu_{satd\ aq} \rightarrow 3(CuCN)_2(tu)_3(H_2O) + 4HMTA$$

Scheme 2

$$6CuCN + tu_{satd\ aq} \rightarrow 3(CuCN)_2(tu)_3(H_2O)$$

A review of the literature of copper(I) complexes of thiourea and substituted thioureas[2] revealed that several substituted thioureas are also effective ligands. These include 1,3-dimethyl-2-thiourea (dmtu), 1,3-diethyl-2-thiourea (detu), 1,1,3,3-tetramethyl-2-thiourea (tmtu) and 2-imidazolidinethione (*N,N′*-ethylenethiourea, etu). We set out to determine whether copper cyanide could complex with these substances, as well. Unfortunately, the synthetic approach shown in Scheme 2, when applied to these ligands, failed to provide satisfactory complexes

In another research project, we had learned that aqueous sodium thiosulfate solutions would dissolve and retain substantial concentrations of CuCN without separation of an insoluble $CuCN/Na_2S_2O_3$ complex.[3] We have been able to show that these solutions of "available CuCN" readily form crystalline complexes with a wide variety of water soluble ligands. As can be seen in Scheme 3, this new preparative procedure gave stoichiometric complexes with each of the thiourea derivatives attempted. The procedures for the preparations of the poly-

Scheme 3

$$CuCN_{satd} + dmtu \xrightarrow{Na_2S_2O_3/H_2O} (CuCN)_3(dmtu)_2\ (\mathbf{3})$$

$$CuCN_{satd} + detu \xrightarrow{Na_2S_2O_3/H_2O} (CuCN)_2(detu)(H_2O)\ (\mathbf{4})$$

$$CuCN_{satd} + tmtu \xrightarrow{Na_2S_2O_3/H_2O} (CnCN)(tmtu)(polymorph\ a)\ (\mathbf{5})$$

$$CuCN_{satd} + tmtu \xrightarrow{Na_2S_2O_3/H_2O} (CuCN)(tmtu)(polymorph\ b)\ (\mathbf{6})$$

$$CuCN_{satd} + etu \xrightarrow{Na_2S_2O_3/H_2O} (CuCN)_2(etu)\ (\mathbf{7})$$

---

* To whom correspondence should be addressed.

[†] Currently a graduate student in the Department of Chemistry, University of Chicago.

[‡] University of Minnesota.

[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1996.

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

S0020-1669(95)01102-5 CCC: $12.00

morphs **5** and **6** differed primarily in the relative amounts of sodium thiosulfate and tmtu utilized in the reaction. The preparation of **5** used a 34% higher concentration of sodium thiosulfate along with a 3:1 ratio of CuCN to tmtu, whereas the preparation of **6** used the standard concentration of sodium thiosulfate along with a 3:2 ratio of CuCN to tmtu. All of the new colorless complexes **3-7** exhibit stability under ordinary conditions. In fact, several of these new compounds appear to be unchanged after over a year in storage.

Experimental Section

General Information. Commercial chemicals were used without further purification. $(CuCN)_3(HMTA)_2$ was prepared as previously reported.[1] Infrared spectra were recorded as KBr pellets with either a Perkin-Elmer Model 283 or Model 1430 spectrometer. Except where noted, all elemental analyses were determined by M-H-W Laboratories, Phoenix, AZ, and the percent copper was calculated from ash. The presence of copper has been known to interfere with the analysis for sulfur,[4] and with two or three of the new complexes the "found" analytical values for copper and sulfur did depart significantly from the theoretical values. The crystal structures were determined by the X-Ray Service Laboratory, Department of Chemistry, University of Minnesota, Minneapolis, MN.

Preparation of $(CuCN)_2(tu)_3(H_2O)$ (2). a. From $(CuCN)_3(HMTA)_2$ (1). To 20 mL of a saturated solution (filtered) of tu (est. 30 mmol) was added 549 mg (1 mmol) of **1**. After stirring the slurry for 8−10 min the solid appeared to be completely dissolved. Following a filtration, the clear colorless solution was stoppered and set aside. Within 2 days tiny clear crystals had appeared. Crystal growth continued so that after 10 days a considerable amount was present. Although there did not appear to be appreciable crystal growth after the 10 day mark, the product was not actually isolated until a total of 63 days had passed. The clear white crystalline product was filtered with suction and washed with distilled water (yield 265 mg, 41.5%): IR: 3600 w, 3533 w, 3485 w, 3385 s, 3312 w, 3165 w, 2113 w, 2087s, 1602 s, 1480 m, 1435 w, 1402 s, 1383 w, 1090 w, 770 w, 715 m, 552 m, 471 s cm^{-1}. Anal. Calcd for $C_5H_{14}Cu_2N_8OS_3$: C, 14.11; H, 3.32; Cu, 29.87; N, 26.34; S, 22.61. Found: C, 14.30; H, 3.11; Cu, 30.15; N, 26.68; S, 22.93. Another portion of this sample which had been ground to a powder became dehydrated after storage for approximately 5 months in a desiccator. Anal. Calcd for $C_5H_{12}Cu_2N_8S_3$: C, 14.72; H, 2.97; Cu, 31.15; N, 27.58; S, 23.58. Found: C, 15.16; H, 2.88; Cu, 32.04; N, 27.23; S, 23.03.

b. From CuCN. To 160 mL of a saturated solution (filtered) of tu (contains approximately 16 g, 210 mmol) was added 1792 mg (20 mmol) of CuCN. The slurry was stirred and heated to simmering on a hot plate. Within a few minutes the solid appeared to be fully dissolved. The colorless solution was filtered while hot, cooled to room temperature, stoppered, and allowed to stand. Within 24 h the first clear tiny crystals had appeared, and crystal growth continued thereafter for another 10−15 days. After a total of 38 days the clear white crystalline product was isolated by suction filtration and washed with distilled water (yield 1746 mg, 41.0%). Anal. Calcd for $C_5H_{14}Cu_2N_8OS_3$: C, 14.11; H, 3.32; Cu, 29.87; N, 26.34; S, 22.61. Found: C, 14.36; H, 3.43; Cu, 30.43; N, 26.67; S, 23.01. Another portion of this sample spontaneously dehydrated when stored on an uncovered watch glass in a dust-free cabinet for several weeks. Anal. Calcd for $C_5H_{12}Cu_2N_8S_3$: C, 14.72; H, 2.97; Cu, 31.15; N, 27.58; S, 23.58. Found: C, 15.27; H, 3.20; Cu, 31.43; N, 27.36; S, 23.28.[5]

General Methods of Preparation of Substituted Thiourea Complexes. 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 $Na_2S_2O_3{\cdot}5H_2O$ (2.482 g, 10 mmol) in 30 mL distilled water (this is called the "standard solution"). After the CuCN dissolved, the solution was heated to 75−80 °C on a steam bath, ligand was added (1.0−2.0 mmol), and while maintaining that temperature, the mixture was stirred until clear. This hot solution was filtered by gravity, and the filtrate was poured into several small test tubes (13 mm × 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 cooled slowly 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.

Preparation of $(CuCN)_3(dmtu)_2$ (3). To the warm standard solution of sodium thiosulfate and copper(I) cyanide was added dmtu (104.2 mg, 1.0 mmol). Using a steam cone, the temperature of the water bath was held at 75−80 °C. The presence of crystals was observed after approximately 1 h. After 3.5 h the hot solution was filtered, yielding clear crystals (26.3 mg, 13.58%) that varied in color from white to light tan and took on various shapes (feathery needles, irregular spheres, and rhombic prisms). Only the rhombic prisms were of adequate size and quality for X-ray studies. IR (KBr): 3425 w, 3331 s, 3300 sh, 3029 w, 2940 w, 2120 w, 2115 m, 2105 m, 1585 s, 1518 s, 1480 w, 1454 w, 1442 w, 1420 w, 1369 w, 1287 m, 1195 w, 1148 w, 1034 m, 1010 m, 719 w, 600 w, 540 w, 448 w cm^{-1}. Anal. Calcd for $C_4H_8CuN_3S$: C, 24.80; H, 4.16; Cu, 32.80; N, 21.69; S, 16.55. Found: C, 24.81, 25.28; H, 4.34, 4.59; Cu, 30.73, 31.03; N, 21.54, 21.88; S, 20.19, 17.14.

Preparation of $(CuCN)_2(detu)(H_2O)$ (4). To the warm standard solution of sodium thiosulfate and copper(I) cyanide solution was added

---

(2) (a) Okaya, Y.; Knobler, C. B. *Acta Crystallogr.* **1964**, *B17*, 928 (preparation and structure of $Cu(tu)_3Cl$). (b) Vranka, R. G.; Amma, E. L. *J. Am. Chem. Soc.* **1966**, *88*, 4270 (preparation and structure of $Cu_4(tu)_9(NO_3)_4$). (c) Hanic, F.; Durcanska, E. *Inorg. Chim. Acta* **1969**, *3*, 293 (preparation and structure of $Cu_2(tu)_6(ClO_4)_2$). (d) Spofford, W. A., III; Amma, E. L. *Acta Crystallogr.* **1970**, *B26*, 1474 (preparation and structure of $Cu(tu)_2Cl$). (e) Girling, R. L.; Amma, E. L. *Inorg. Chem.* **1971**, *10*, 335 (preparation and structure of $Cu(dmtu)_3Cl$). (f) Weininger, M. S.; Hunt, G. W.; Amma, E. L. *J. Chem. Soc., Chem. Commun.* **1972**, 1140 (preparation and structure of $Cu(tmtu)_3BF_4$ and $Cu(etu)_3(SO_4)_{0.5}$). (g) Gash, A. G.; Griffith, E. H.; Spofford, W. A., III; Amma, E. L. *J. Chem. Soc., Chem. Commun.* **1973**, 256 (preparation and structure of $Cu_4(tu)_{10}(SiF_6)_2{\cdot}H_2O$). (h) Taylor, I. F.; Weininger, M. S.; Amma, E. L. *Inorg. Chem.* **1974**, *13*, 2835 (preparation and structure of $Cu_2(tu)_6(BF_4)_2$ and $Cu_2(dmtu)_6(BF_4)_2$). (i) Crumbliss, A. L.; Gestaut, L. J.; Rickard, R. C.; McPhail, A. T. *J. Chem. Soc., Chem. Commun.* **1974**, 545 (preparation and structure of $Cu_4(etu)_9(NO_3)_4{\cdot}6H_2O$). (j) Hunt, G. W.; Terry, N. W., III; Amma, E. L. *Cryst. Struct. Commun.* **1974**, *3*, 523 (preparation and structure of $Cu(tu)_4(SiF_6)_{0.5}$). (k) Taylor, I. F., Jr.; Weininger, M. S.; Amma, E. L. *Inorg. Chem.* **1974**, *13*, 2835 (preparation and structure of $Cu_2(tu)_6(BF_4)_2$ and $Cu_2(dmtu)_6(BF_4)_2$). (l) Jain, A. K.; Smith, A. J. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 707 (preparation and structure of Cu(tu)(*o*-phen)I). (m) Ferrari, M. B.; Gasparri, G. F. *Cryst. Struct. Commun.* **1976**, *5*, 935 (preparation and structure of $Cu_2(tu)_5SO_4{\cdot}3H_2O$). (n) Griffith, E. H.; Hunt, G. W.; Amma, E. L. *J. Chem. Soc., Chem. Commun.* **1976**, 432 (preparation and structure of $Cu_4(tu)_6(NO_3)_4{\cdot}4H_2O$ and $Cu_4(tu)_9(NO_3)_4{\cdot}4H_2O$). (o) Battaglia, L. P.; Corradi, A. B.; Nardelli, M.; Tani, M. E. V. *J. Chem. Soc., Dalton Trans.* **1976**, 143 (preparation and structure of $Cu(etu)_4NO_3$). (p) Cingi, M. B.; Lanfredi, A. M. M.; Tiripicchio, A.; Camellini, M. T. *Acta Crystallogr.* **1977**, *B33*, 3772 (preparation and structure of $Cu(tu)_3(C_8H_5O_4)$). (q) Hunt, G. W.; Terry, N. W., III; Amma, E. L. *Acta Crystallogr.* **1979**, *B35*, 1235 (preparation and structure of $Cu(tu)_4(SiF_6)_{0.5}$). (r) Eller, P. G.; Bradley, D. C.; Hursthouse, M. B.; Meek, D. W. *Coord. Chem. Rev.* **1977**, *24*, 56−63 (an extensive review of Cu(I) complexes of tu and substituted thiourea derivatives). (s) Hall, S. R.; Kepert, D. L.; Raston, C. L. *Aust. J. Chem.* **1977**, *30*, 1955 (preparation and structure of $Cu(tu)_2$(*o*-phen)I. (t) Kamara, R.; Declercq, J. P.; Germain, G.; Van Meerssche, M. *Bull. Soc. Chim. Belg*. **1982**, *91*, 339 (preparation and structure of $Cu(detu)_3(SO_4)_{0.5}$). (u) Van Meerssche, M.; Kamara, R.; Declercq, J. P.; Germain, G. *Bull. Soc. Chim. Belg.* **1982**, *91*, 547 (preparation and structure of $Cu_2(tu)_6(SO_4){\cdot}H_2O$). (v) Van Meerssche, M.; Kamara, R.; Germain, G.; Declercq, J. P. *Bull. Soc. Chim. Belg.* **1982**, *91*, 553 (preparation and structure of $Cu_4(tu)_6(SO_4)_2{\cdot}2H_2O$ and $Cu_4(tu)_6(HSO_4)_2SO_4{\cdot}H_2O$). (w) Atkinson, E. R.; Gardiner, D. J.; Jackson, A. R. W.; Raper, E. S. *Inorg. Chim. Acta* **1985**, *98*, 35 (preparation and structure of $Cu(N\text{-}methyletu)_3NO_3$). (x) Dubler, E.; Bensch, W. *Inorg. Chim. Acta* **1986**, *125*, 37 (preparation and structure of $Cu(dmtu)_2NO_3$).

(3) At increased CuCN concentrations, a crystalline complex forms. The composition, properties, and crystal structure of this new complex will be reported in the literature in the near future.

(4) See footnote 2(l), p 708, where this interference was cited.

(5) This analysis was performed by Galbraith Laboratories, Inc., Knoxville, TN.

Table 1. Crystallographic Data[a]

complex no.	2	3	4	5	6	7
formula	$C_5H_{14}Cu_2N_8OS_3$	$C_9H_{16}Cu_3N_7S_2$	$C_7H_{14}Cu_2N_4OS$	$C_6H_{12}CuN_3S$	$C_6H_{12}CuN_3S$	$C_5H_6Cu_2N_4S$
fw	425.49	477.03	329.37	221.79	221.79	281.28
space group	$P\bar{1}$ (No. 2)	*Cc* (No. 9)	$P2_1/n$ (No. 14)	$P2_12_12_1$ (No. 19)	$P\bar{1}$ (No. 2)	$P2_1$ (No. 4)
temp, °C	24	−96	24	24	24	24
a, Å	7.696(5)	10.082(3)	7.969(5)	8.653(1)	9.660(4)	3.994(2)
b, Å	9.346(2)	14.984(5)	11.559(4)	9.426(1)	14.202(4)	13.886(3)
c, Å	10.772(2)	11.413(3)	13.736(5)	11.620(3)	16.03(1)	7.556(1)
α, deg	106.53(2)	90.0	90.0	90.0	101.68(5)	90.0
β, deg	91.11(4)	104.50(2)	100.48(4)	90.0	107.08(6)	97.07(2)
γ, deg	98.42(3)	90.0	90.0	90.0	70.07(2)	90.0
V, $Å^3$	733(1)	1669(2)	1244(2)	947.8(4)	1964(4)	415.2(4)
Z	2	4	4	4	8	2
ρ_{calcd} (g cm^{-3})	1.927	1.898	1.758	1.554	1.500	2.250
μ, cm^{-1}	33.24	40.44	35.72	24.67	23.81	53.25
R^b	0.040	0.056	0.049	0.040	0.051	0.027
$R_w{}^c$	0.049	0.057	0.052	0.044	0.045	0.027

[a] Radiation: Mo Kα (graphite monochromated, $\lambda = 0.71073$ Å). [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2)]^{1/2}$.

detu (132.2 mg, 1 mmol). As the detu dissolved, it was replaced by a fine white precipitate that was assumed to be the complex. After additional heating on the steam bath, the solution became nearly clear and was filtered while hot. This solution was placed in a 90 °C water bath on a steam cone, and the bath temperature was adjusted gradually to the 75−80 °C range and held there for 20 h. The product comprised clear colorless crystals (83.0 mg, 25.2%) which appeared in two different shapes (irregular spheres and rhombic prisms). Only the rhombic prisms were of adequate size and quality for X-ray studies. IR (KBr): 3633 m, 3551 w, 3345 s, 3264 m, 3189 w, 2972 w, 2946 w, 2115 m, 2105 s, 1603 s, 1513 s, 1469 w, 1448 w, 1380 w, 1335 w, 1309 w, 1288 w, 1253 m, 1173 w, 1139 w, 1090 w, 1055 w, 930 w, 794 w cm^{-1}. Anal. Calcd for $C_7H_{14}Cu_2N_4SO$: C, 25.53; H, 4.28; Cu, 38.59; N, 17.01; S, 9.73. Found: C, 26.90; H, 4.51; Cu, 35.69; N, 17.24; S, 16.60.

Preparation of (CuCN)(tmtu) (Polymorph a) (5).[6] Before the standard solution was adopted, **5** was prepared, using a solution made up of 30 mL of distilled water, $Na_2S_2O_3{\cdot}5H_2O$ (3.337 g, 13.44 mmol), and CuCN (270 mg, 3 mmol). The tmtu (132.2 mg, 1 mmol) was added, and as the suspension was stirred, it appeared that the tmtu dissolved rapidly and was replaced by a white precipitate of complex. The suspension was heated with periodic mixing at 75 °C on a steam bath until a virtually clear, colorless solution was obtained (approximately 30 min). Following a hot filtration, the flask (125 mL Erlenmeyer) containing the solution was placed in a 600 mL water bath at 90 °C which was set aside on an insulated surface and cooled slowly until it reached room temperature. The first crystals began to appear within 2 h. The nearly colorless product (65 mg, 29.3%), which was collected after 2 days, appeared to be made up of several crystal types, but only one type was of adequate size and quality for X-ray studies. IR (KBr): 3010 w, 2925 m, 2120 s, 1553 s, 1485 m, 1457 m, 1440 w, 1401 w, 1379 s, 1255 m, 1203 w, 1151 m, 1100 m, 1052 w, 873 m, 657 w, 600 w, 463 w, 390 w cm^{-1}. The prism crystal selected for X-ray structure analysis proved to have the composition (CuCN)(tmtu) or $C_6H_{12}CuN_3S$. The values found for the composition of the bulk product did not correspond within expected limits to the composition of the crystal used in the structure determination. Anal. Calcd for $C_6H_{12}CuN_3S$: C, 32.49; H, 5.45; Cu, 28.65; N, 18.95; S, 14.46. Found: C, 28.73; H, 4.49; Cu, 29.76; N, 18.30; S, 10.10.

Preparation of (CuCN)(tmtu) (Polymorph b) (6). To the warm standard solution of sodium thiosulfate and copper(I) cyanide was added tmtu (264.4 mg, 2 mmol). This solution was placed in a 90 °C water bath, which was cooled on an insulated surface until it reached room temperature. The product (149.1 mg, 33.6%) appeared as colorless needles of a variety of sizes. IR (KBr): 3001 w, 2956 w, 2920 w, 2900 w, 2857 w, 2800 w, 2199 s, 1537 s, 1489 m, 1462 m, 1440 m, 1408 w, 1384 s, 1369 s, 1270 m, 1212 w, 1151 m, 1110 m, 1095 m, 1053 w, 942 w, 881 m, 660 w, 625 w, 479 w cm^{-1}. Anal. Calcd for $C_6H_{12}CuN_3S$: C, 32.49; H, 5.45; Cu, 28.65; N, 18.95; S, 14.46. Found: C, 33.89, 32.74; H, 5.64, 5.66; Cu, 27.46, 28.32; N, 19.16, 19.02; S, 13.06, 14.13.

Preparation of $(CuCN)_2$(etu) (7).[6] To the warm standard solution of sodium thiosulfate and copper(I) cyanide was added etu (153.2 mg, 1.5 mmol). This solution was placed in a hot water bath which was brought to boil and then cooled on an insulated surface until it reached room temperature. The crystalline product (99.4 mg, 23.6%) was made up of colorless rhombic prisms in either singles or aggregates. IR (KBr): 3385 s, 3340 s, 3005 w, 2895 w, 2875 w, 2115 s, 2110 s, 1640 w, br, 1530 s, 1360 w, 1325 m, 1282 m, 1234 w, 1205 w, 1190 w, 1035 w, 990 w, 912 w, 660 m, 562 m, 502 w, 472 w, br cm^{-1}. Anal. Calcd for $C_5H_6Cu_2N_4S$: C, 21.35; H, 2.15; Cu, 45.18; N, 19.92; S, 11.40. Found: C, 21.57; H, 2.06; Cu, 43.96; N, 19.94; S, 11.75.

X-ray Structure Determinations

The crystals were mounted on a glass fiber, and measurements were made at 24 ± 1 °C (except for $(CuCN)_3(dmtu)_2$ (**3**) which was done at −96 ± 3 °C) on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The intensities of three representative reflections were measured after every 50−80 min of X-ray exposure time; in each of the six data sets these intensities remained constant throughout data collection indicating crystal and electronic stability (no decay corrections were applied). Crystallographic data for **2**−**7** are presented in Table 1. The structures were solved by direct methods using the programs MITHRIL[7] and DIRDIF.[8] The neutral atom scattering factors used include correction for the real and imaginary components of the effect of anomalous dispersion.[9] All calculations were performed using the TEXSAN[10] crystallographic software package. The non-hydrogen atoms were refined anisotropically. There is a tendency for the bridging CN groups to have end-for-end disorder in these compounds; each such group was refined with the degree of disorder as a variable. In all but three of the cases the disorder appeared to be complete within the experimental accuracy. In the remaining three cases the CN groups appeared to be completely ordered within the experimental accuracy; these three cases are discussed later after the section on hydrogen bonding. The atoms in all the bridging groups are labeled C1N, *etc.*, as a reminder of the possible

---

(6) We are indebted to Macalester student Lilla Bartkó for assistance in the preparation of complexes **5** and **7**.

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

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

(9) (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.

(10) TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corporation, 1985.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for the Non-hydrogen Atoms of $(CuCN)_2(tu)_3(H_2O)$ (**2**)

atom	*x*	*y*	*z*	B_{eq}[a]
Cu1	0.30703(5)	0.17235(5)	0.20113(4)	2.61(1)
Cu2	0.17892(6)	−0.24243(4)	−0.22050(4)	2.60(1)
C1N[b]	0.2559(4)	0.0022(4)	0.0452(3)	2.6(1)
N2C[b]	0.2246(4)	−0.0921(3)	−0.0518(3)	2.5(1)
C3	0.1199(4)	−0.4598(3)	−0.2658(3)	2.1(1)
N4	0.0891(4)	−0.5872(3)	−0.2899(3)	3.3(1)
S1	0.3703(1)	0.4103(1)	0.18087(8)	2.55(3)
C11	0.2437(4)	0.4277(4)	0.0558(3)	2.7(1)
N11	0.2586(6)	0.5580(5)	0.0294(4)	4.2(1)
N12	0.1321(5)	0.3118(5)	−0.0179(4)	4.0(1)
S2	0.0606(1)	0.17009(8)	0.33591(7)	1.92(2)
C21	0.0171(4)	−0.0173(3)	0.3312(3)	2.1(1)
N21	0.1439(5)	−0.0989(4)	0.3255(4)	3.9(1)
N22	−0.1443(4)	−0.0838(4)	0.3356(4)	3.5(1)
S3	0.5594(1)	0.16348(9)	0.32866(7)	2.14(2)
C31	0.5734(4)	0.2914(3)	0.4800(3)	1.94(9)
N31	0.4295(4)	0.3285(4)	0.5378(3)	3.0(1)
N32	0.7291(4)	0.3517(4)	0.5410(3)	2.8(1)
O1	0.5108(4)	0.8149(4)	0.1455(4)	5.4(1)

[a] In Tables 2−7, $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$. [b] Disordered CN group. Fraction oriented as shown 0.50(3).

Table 3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for the Non-hydrogen Atoms of $(CuCN)_3(dmtu)_2$ (**3**)

atom	*x*	*y*	*z*	*B*(eq)
Cu1	0	0.58548(7)	3/4	1.79(4)
Cu2	−0.2568(2)	0.43305(7)	0.3772(2)	1.65(4)
Cu3	0.2740(2)	0.41733(8)	1.1088(2)	1.85(5)
N1C[a]	−0.1788(7)	0.5071(5)	0.5152(7)	1.9(3)
C2N[a]	−0.1172(8)	0.5423(6)	0.6026(8)	1.6(3)
N3C[b]	0.1013(8)	0.5044(5)	0.8803(7)	1.6(3)
C4N[b]	0.1641(9)	0.4673(6)	0.9644(8)	2.0(4)
N5C[c]	−0.540(1)	0.4311(5)	0.2010(8)	2.0(3)
C6N[c]	−0.431(1)	0.4351(6)	0.2644(7)	1.7(3)
S1	0.1665(3)	0.6853(1)	0.7047(2)	1.69(8)
C11	0.2932(9)	0.7090(6)	0.8346(7)	1.7(3)
N12	0.3307(8)	0.6501(5)	0.9209(7)	2.2(3)
C12	0.443(1)	0.6594(8)	1.026(1)	3.7(5)
N13	0.3536(8)	0.7890(6)	0.8456(7)	2.6(3)
C13	0.318(1)	0.8617(7)	0.756(1)	3.2(4)
S2	−0.1288(3)	0.6868(1)	0.8487(2)	1.73(8)
C21	−0.0061(9)	0.7119(6)	0.9790(8)	1.7(3)
N22	0.0344(8)	0.6520(5)	1.0650(6)	2.0(3)
C22	0.139(1)	0.6659(7)	1.177(1)	3.2(4)
N23	0.0468(8)	0.7950(5)	0.9948(7)	2.1(3)
C23	0.008(1)	0.8673(7)	0.910(1)	3.2(5)

[a−c] Disordered CN groups. Fractions oriented as shown: *a*, 0.93(8); *b*, 0.66(9); *c*, 0.58(11).

disorder. Hydrogen atoms attached to nitrogen were refined with isotropic displacement parameters; H atoms attached to carbon were included in the structure factor calculation in idealized positions and were assigned isotropic displacement parameters which were 20% greater than the B_{eq} value of the atom to which they were bonded. In **2** and **4** the hydrogen in the water molecules could not be located in a difference Fourier map and were omitted from the calculations.

$(CuCN)_3(dmtu)_2$ (**3**) occurs in a polar space group. The structure was refined in both possible polarities. The reported structure has the lower *R* value. For the rejected structure $R = 0.061$ and $R_w = 0.065$. The similarity of this structure to that of **1**, which has space group *C*2/*c*,[1] raises the question of whether **3** is actually a disordered structure in *C*2/*c* rather than an ordered one in *Cc*. Inspection of Figure 4 will show that the Cu and CN alone could be described in space group *C*2/*c*. All attempts to find a satisfactory alternative solution in *C*2/*c* were unsuccessful so we conclude that the *Cc* structure is correct. This is discussed at greater length in the Supporting Information.

Table 4. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for the Non-hydrogen Atoms of $(CuCN)_2(detu)(H_2O)$ (**4**)

atom	*x*	*y*	*z*	*B*(eq)
Cu1	0.1626(1)	0.57979(7)	0.06639(5)	3.99(4)
Cu2	0.0801(1)	0.81688(7)	0.35448(5)	3.64(3)
N1C[a]	0.3237(6)	0.6156(4)	−0.0184(4)	3.4(2)
C2N[a]	0.4217(7)	0.6388(5)	−0.0659(4)	3.5(2)
C3N[b]	0.1114(6)	0.6761(5)	0.1725(4)	3.4(2)
N4C[b]	0.0940(7)	0.7320(5)	0.2386(4)	3.8(3)
S1	0.1368(2)	0.3800(1)	0.0745(1)	2.87(5)
C11	0.0367(7)	0.3399(5)	0.1720(4)	2.9(2)
N12	0.0195(8)	0.4182(5)	0.2384(4)	5.1(3)
N13	−0.0224(7)	0.2352(5)	0.1793(4)	3.9(2)
C14	−0.072(2)	0.402(1)	0.3228(8)	11.1(7)
C15	0.015(2)	0.403(2)	0.406(1)	21(2)
C16	−0.025(1)	0.1452(7)	0.1067(6)	7.1(4)
C17	0.032(1)	0.0344(8)	0.1468(8)	9.3(6)
O1W	−0.1949(6)	0.1273(5)	0.3324(4)	6.4(3)

[a,b] Disordered CN groups. Fractions oriented as shown: *a*, 0.66(5); *b*, 0.52(6).

Table 5. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for the Non-hydrogen Atoms of (CuCN)(tmtu) (polymorph a) (**5**)

atom	*x*	*y*	*z*	*B*(eq)
Cu1	0.92277(8)	0.21893(7)	0.21810(7)	3.08(3)
N1C[a]	1.0021(6)	−0.0947(6)	0.2505(4)	3.3(3)
C2N[a]	0.9740(6)	0.0236(6)	0.2374(5)	2.7(3)
S1	0.6765(2)	0.2541(1)	0.1426(2)	5.2(1)
C11	0.6077(7)	0.0933(6)	0.0970(5)	3.1(3)
N12	0.4674(6)	0.0515(5)	0.1315(4)	3.4(3)
N13	0.6879(6)	0.0098(6)	0.0264(5)	3.6(3)
C12	0.3898(8)	0.1121(8)	0.2334(6)	4.8(4)
C13	0.3649(9)	−0.0338(8)	0.0602(6)	4.5(4)
C14	0.813(1)	0.062(1)	−0.0425(7)	5.9(5)
C15	0.679(1)	−0.1433(7)	0.0355(6)	5.3(4)

[a] Disordered CN group. Fraction oriented as shown 0.55(6).

For $(CuCN)_2(detu)(H_2O)$ (**4**) inspection of the anisotropic displacement ellipsoids (see Figure 5) shows that the two ethyl groups in this compound are disordered. Attempts were made to refine both groups with each anisotropic atom replaced by a pair of isotropic half-atoms for C14, C15, C16, and C17. The half-atom model led to poorer *R* values as well as less realistic bond lengths and angles. This suggests that the disorder is over a continuous range of possibilities, which we are unable to model in any straightforward way. The final refinement was made using the anisotropic whole-atom model.

Polymorph a of (CuCN)(tmtu) (**5**) occurs in a chiral space group. The structure was refined as both enantiomers, and the enantiomer leading to the lower *R* values is reported. For the rejected enantiomer, $R = 0.051$ and $R_w = 0.059$.

For polymorph b of (CuCN)(tmtu) (**6**) the conventional unit cell has $a = 9.660(4)$, $b = 14.195(4)$, $c = 16.034(12)$ Å, $\alpha = 90.15(5)$, $\beta = 107.08(5)$, $\gamma = 109.85(2)°$. Multiplying by the matrix 100/110/001 gives the unit cell reported in Table 1. The latter cell was chosen because it puts the CuCN helices parallel to the *b* axis rather than along a diagonal.

$(CuCN)_2(etu)$ (**7**) occurs in a chiral space group. The structure was refined as both enantiomers, and the enantiomer leading to the lower *R* values is reported. The opposite enantiomer refines to $R = 0.033$ and $R_w = 0.035$.

Atomic coordinates and equivalent isotropic displacement parameters for the non-hydrogen atoms of **2**−**7** are presented in Tables 2−7, respectively. Selected bond angles and bond

Table 6. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for the Non-hydrogen Atoms of (CuCN)(tmtu) (polymorph b) (**6**)

atom	*x*	*y*	*z*	*B*(eq)
Cu1	0.2170(1)	−0.07521(7)	0.90388(6)	4.66(6)
Cu2	−0.0189(1)	0.15556(7)	0.67454(6)	4.28(6)
Cu3	0.2764(1)	0.34116(7)	0.60379(6)	4.54(6)
Cu4	0.5117(1)	0.57086(7)	0.83016(6)	4.58(6)
N1C[a]	0.1087(9)	0.0178(6)	0.8189(5)	4.7(5)
C2N[a]	0.0504(8)	0.0729(6)	0.7669(5)	4.0(4)
N3C[b]	0.095(1)	0.2228(7)	0.6414(4)	5.0(5)
C4N[b]	0.161(1)	0.2676(7)	0.6244(5)	4.7(5)
N5C[c]	0.3770(9)	0.4279(6)	0.6877(6)	4.4(5)
C6N[c]	0.4323(9)	0.4806(6)	0.7402(6)	3.8(4)
N7C[d]	0.398(1)	0.705(1)	0.8676(4)	5.0(7)
C8N[d]	0.331(1)	0.787(1)	0.8837(5)	4.9(6)
S1	0.2297(3)	−0.0082(1)	1.0459(1)	5.2(1)
C11	0.3144(8)	−0.1025(5)	1.1123(4)	3.2(4)
N11	0.4251(7)	−0.0918(5)	1.1838(4)	4.7(4)
N12	0.2729(7)	−0.1859(4)	1.0978(4)	4.1(3)
C12	0.508(1)	−0.0204(7)	1.1938(6)	7.4(6)
C13	0.430(1)	−0.1197(9)	1.2689(6)	9.7(8)
C14	0.128(1)	−0.1922(6)	1.0400(6)	6.0(5)
C15	0.375(1)	−0.2804(6)	1.1278(7)	8.4(6)
S2	−0.2546(2)	0.1688(2)	0.5862(1)	5.2(1)
C21	−0.2735(8)	0.2421(6)	0.5084(4)	3.6(4)
N21	−0.2944(7)	0.2036(5)	0.4239(4)	5.0(4)
N22	−0.2684(7)	0.3358(5)	0.5290(4)	4.8(4)
C22	−0.261(1)	0.0945(8)	0.3985(6)	8.4(8)
C23	−0.393(1)	0.2652(9)	0.3534(5)	8.9(8)
C24	−0.287(1)	0.3919(6)	0.6130(6)	7.6(6)
C25	−0.209(1)	0.3839(6)	0.4790(6)	7.3(6)
S3	0.2888(3)	0.3343(2)	0.4635(1)	5.2(1)
C31	0.1829(8)	0.2581(5)	0.4010(5)	3.6(4)
N31	0.2123(7)	0.1637(4)	0.4181(4)	4.2(3)
N32	0.0712(8)	0.2912(5)	0.3319(4)	5.3(4)
C32	0.353(1)	0.1112(6)	0.4735(5)	5.7(5)
C33	0.091(1)	0.1174(6)	0.4035(5)	5.8(5)
C34	0.009(1)	0.3989(8)	0.3214(7)	9.1(7)
C35	0.033(1)	0.2223(9)	0.2524(6)	8.9(8)
S4	0.7589(3)	0.5163(1)	0.9035(1)	5.2(1)
C41	0.7673(8)	0.6104(6)	0.9909(5)	3.9(4)
N41	0.7857(8)	0.5913(5)	1.0713(4)	5.3(4)
N42	0.7555(7)	0.7035(5)	0.9777(4)	4.8(4)
C42	0.764(1)	0.4998(8)	1.0868(6)	9.4(8)
C43	0.870(1)	0.6420(8)	1.1475(6)	8.4(7)
C44	0.686(1)	0.7946(6)	1.0298(6)	6.6(6)
C45	0.772(1)	0.7233(6)	0.8968(6)	7.4(7)

[a−d] Disordered CN groups. Fractions oriented as shown: *a*, 0.61(9); *b*, 0.62(12); *c*, 0.58(10); *d*, 0.55(13).

Table 7. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for the Non-hydrogen Atoms of $(CuCN)_2(etu)$ (**7**)

atom	*x*	*y*	*z*	*B*(eq)
Cu1	0.1732(2)	1/4	0.24707(7)	2.85(2)
Cu2	0.0869(2)	0.40608(5)	−0.34766(7)	3.45(3)
N1C[a]	0.101(1)	0.3007(3)	0.0062(5)	3.0(2)
C2N[a]	0.086(1)	0.3342(3)	−0.1331(6)	2.6(2)
C3N[b]	0.064(1)	0.1240(3)	0.3155(5)	2.4(2)
N4C[b]	0.007(1)	0.0446(3)	0.3422(5)	2.6(2)
S1	0.4339(3)	0.36335(8)	0.4409(1)	2.10(4)
C11	0.481(1)	0.4626(3)	0.3086(5)	1.9(1)
N12	0.387(1)	0.5513(3)	0.3429(5)	2.5(2)
N15	0.632(1)	0.4608(3)	0.1625(5)	2.6(2)
C13	0.524(1)	0.6211(3)	0.2237(7)	2.8(2)
C14	0.620(1)	0.5563(4)	0.0778(6)	2.8(2)

[a,b] Disordered CN groups. Fractions oriented as shown: *a*, 0.97(5); *b*, 1.00(5).

distances for **2**−**7** are provided in Table 8. The labeling of the atoms and the anisotropic displacement ellipsoids for the six structures are shown in Figures 1, 3, 5, 7, 9, and 11. The packing is shown in Figures 2, 4, 6, 8, 10, and 12.

Table 8. Selected Bond Angles (deg) and Bond Distances (Å)

bond angles		bond distances	
	$(CuCN)_2(tu)_3(H_2O)$ (**2**)		
C1N−Cu1−S1	118.9(1)	Cu1−C1N	1.944(3)
C1N−Cu1−S2	108.8(1)	Cu1−S1	2.279(1)
C1N−Cu1−S3	113.4(1)	Cu1−S2	2.412(2)
S1−Cu1−S2	107.04(4)	Cu1−S3	2.382(2)
S1−Cu1−S3	101.08(4)		
S2−Cu1−S3	106.85(5)		
N2C−Cu2−C3	130.5(1)	Cu2−N2C	1.943(3)
N2C−Cu2−S2	106.8(1)	Cu2−C3	1.931(3)
N2C−Cu2−S3	99.6(1)	Cu2−S2	2.481(1)
C3−Cu2−S2	103.11(9)	Cu2−S3	2.470(2)
C3−Cu2−S3	111.7(7)		
S2−Cu2−S3	101.99(5)		
	$(CuCN)_3(dmtu)_2$ (**3**)		
C2N−Cu1−N3C	122.6(4)	Cu1−C2N	1.910(8)
C2N−Cu1−S1	109.5(3)	Cu1−N3C	1.993(8)
C2N−Cu1−S2	109.4(3)	Cu1−S1	2.400(3)
N3C−Cu1−S1	106.6(2)	Cu1−S2	2.448(3)
N3C−Cu1−S2	105.5(2)		
S1−Cu1−S2	101.12(8)		
N1C−Cu2−C6N	131.6(3)	Cu2−N1C	1.926(8)
N1C−Cu2−S2	116.1(2)	Cu2−C6N	1.897(9)
C6N−Cu2−S2	112.0(3)	Cu2−S2	2.282(3)
C4N−Cu3−N5C	135.5(3)	Cu3−C4N	1.895(9)
C4N−Cu3−S1	115.7(3)	Cu3−N5C	1.91(1)
N5C−Cu3−S1	108.8(3)	Cu3−S1	2.309(3)
	$(CuCN)_2(detu)(H_2O)$ (**4**)		
S1−Cu1−N1C	108.5(2)	Cu1−S1	2.323(2)
S1−Cu1−C3N	120.2(2)	Cu1−N1C	1.929(5)
N1C−Cu1−C3N	125.9(2)	Cu1−C3N	1.936(6)
S1−Cu2−C2N	111.1(2)	Cu2−S1	2.403(2)
S1−Cu2−N4C	107.8(2)	Cu2−C2N	1.885(6)
C2N−Cu2−N4C	141.1(2)	Cu2−N4C	1.891(6)
	(CuCN)(tmtu) (polymorph a) (**5**)		
N1C−Cu1−C2N	141.9(2)	Cu1−N1C	1.909(6)
N1C−Cu1−S1	104.6(2)	Cu1−C2N	1.907(6)
C2N−Cu1−S1	113.2(2)	Cu1−S1	2.328(2)
	(CuCN)(tmtu) (polymorph b) (**6**)		
C8N−Cu1−N1C	127.5(3)	Cu1−C8N	1.90(1)
C8N−Cu1−S1	116.8(2)	Cu1−N1C	1.909(9)
N1C−Cu1−S1	115.4(2)	Cu1−S1	2.269(3)
C2N−Cu2−N3C	126.8(3)	Cu2−C2N	1.899(9)
C2N−Cu2−S2	117.9(2)	Cu2−N3C	1.92(1)
N3C−Cu2−S2	115.1(2)	Cu2−S2	2.269(3)
C4N−Cu3−N5C	127.3(3)	Cu3−C4N	1.89(1)
C4N−Cu3−S3	117.7(2)	Cu3−N5C	1.91(1)
N5C−Cu3−S3	115.0(2)	Cu3−S3	2.268(3)
C6N−Cu4−N7C	125.3(3)	Cu4−C6N	1.89(1)
C6N−Cu4−S4	118.1(2)	Cu4−N7C	1.92(1)
N7C−Cu4−S4	116.6(2)	Cu4−S4	2.268(3)
	$(CuCN)_2(etu)$ (**7**)		
N1C−Cu1−C3N	125.5(2)	Cu1−N1C	1.940(4)
N1C−Cu1−S1	110.6(1)	Cu1−C3N	1.888(5)
C3N−Cu1−S1	123.9(1)	Cu1−S1	2.307(1)
C2N−Cu2−N4C	118.4(2)	Cu2−N4C	1.959(4)
C2N−Cu2−S1	113.4(1)	Cu2−C2N	1.904(5)
N4C−Cu2−S1	121.2(1)	Cu2−S1	2.317(1)

Discussion

The only previously reported copper(I) cyanide complex that includes a sulfur-containing ligand is $(CuCN)_2(DMSO)_2$,[11] but here the DMSO is coordinated to copper through the oxygen atom. Thus, prior to our study, no copper(I) complex had been reported which included coordination of both cyanide and sulfur. In our article[1] reporting the structure and properties of $(CuCN)_3(HMTA)_2$ (**1**), reference was made to 13 articles appearing from 1957 to 1986 which reported crystal structures for a total of 18

---

[11] Emokpae, T. A.; Ukwueze, A. C.; Walton, D. R.; Hitchcock, P. B. *Synth. React. Inorg. Met.-Org. Chem.* **1986**, *16*, 387.

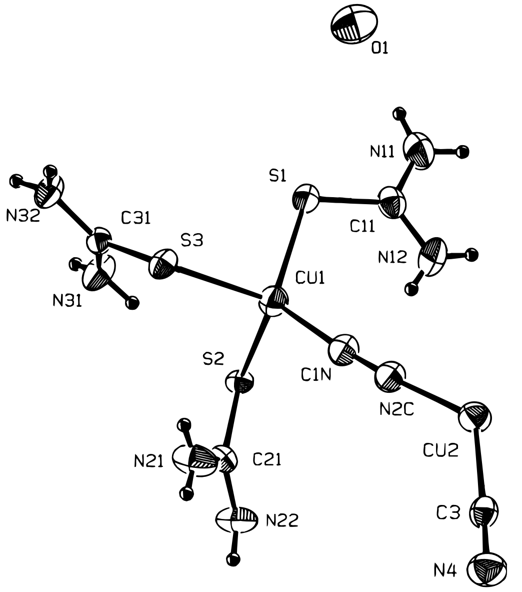

Figure 1. ORTEP plot of the structure of $(CuCN)_2(tu)_3(H_2O)$ (**2**), showing the atom labeling scheme and 50% probability ellipsoids. Hydrogen atoms have been given arbitrary radii.

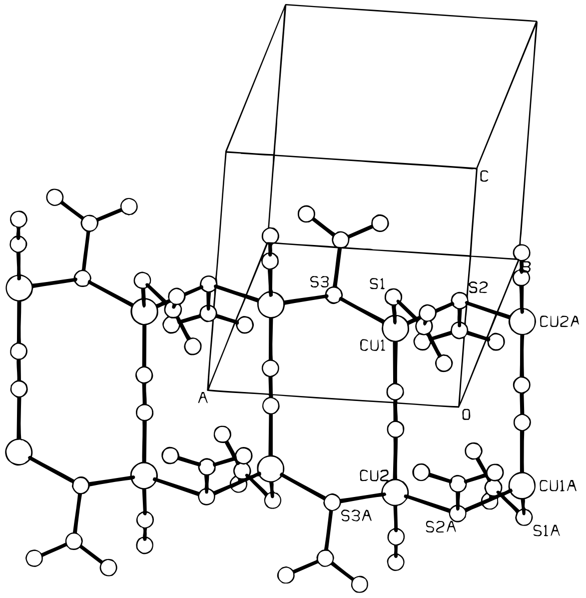

Figure 2. The extended structure of $(CuCN)_2(tu)_3(H_2O)$ (**2**). The view is normal to the $(01\bar{1})$ plane of the $(Cu_2CNS_2)_n$ ladder arrangement. In this and Figures 4, 6, 8, and 10, H atoms and the H_2O molecule have been omitted for clarity and Cu atoms have been shown larger than the rest.

copper(I) cyanide complexes. Except for the DMSO case, all of the ligands (other than cyanide) cited in those articles were nitrogen bases. Included among the latter were NH_3, $HNEt_2$, NEt_3, N_2H_4, ethylenediamine, 4-methylpyridine, 1,10-phenanthroline, and 2,9-dimethyl-1,10-phenanthroline. More recently the crystal structure of another complex of the same type, $(CuCN)(py)_2$ (py = pyridine), was reported.[12]

As can be seen in Figures 1 and 2 the structure of the thiourea complex **2** is a ladder arrangement with the sides of the ladder consisting of infinite chains of Cu1−S2−Cu2−S3−Cu1, bound together with rungs of C≡N between Cu1 and Cu2. The ladder is puckered rather than flat with the mean plane of the ladder parallel to $(01\bar{1})$. Each Cu1 also has a nonbridging S, and each

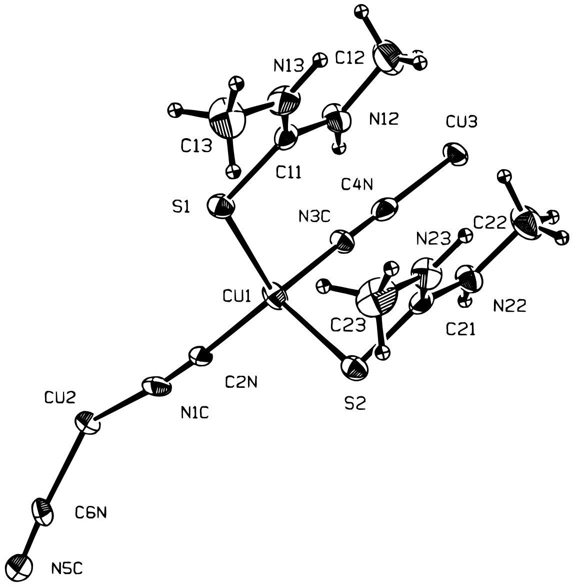

Figure 3. ORTEP plot of the structure of $(CuCN)_3(dmtu)_2$ (**3**), showing the atom labeling scheme and 50% probability ellipsoids.

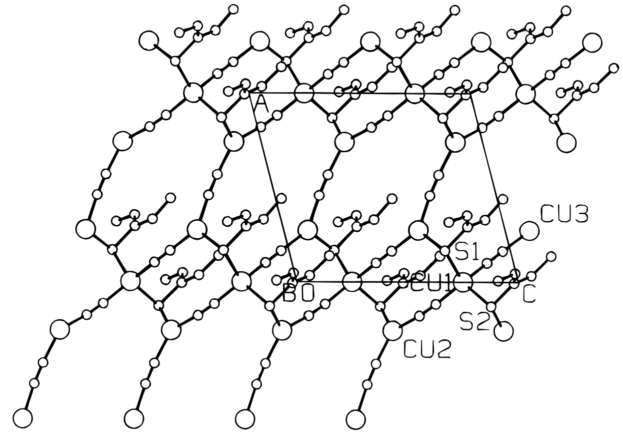

Figure 4. The extended structure of $(CuCN)_3(dmtu)_2$ (**3**). The view is along the *b* axis, normal to the two-dimensional sheet, $[(CuCN)_3S_2]_n$.

Cu2 has a nonbridging CN group, making both copper sites four-coordinate. A water molecule is present with the O atom 2.816(5) Å from N11 in an N−H···O hydrogen bond.

The crystal structure (see Figures 3 and 4) of $(CuCN)_3(dmtu)_2$ (**3**) resembles that of $(CuCN)_3(HMTA)_2$ (**1**). A hypothetical exchange of HMTA by dmtu converts structure **1** into **3**. The structure consists of infinite chains of Cu−CN−Cu−CN along the [101] direction with the chains bound into infinite sheets by bridging S atoms of dmtu. Two-thirds of the Cu atoms are three-coordinate, and one-third is four-coordinate. The sheets, which are considerably puckered, have a mean plane parallel to (010).

In $(CuCN)_2(detu)(H_2O)$ (**4**) (see Figures 5 and 6) there are two independent Cu atoms, each bonded to two bridging CN groups and one bridging S atom. The structure can be thought of as infinite chains Cu−CN−Cu−CN along the $[10\bar{1}]$ direction with the chains bound into puckered sheets by Cu−S−Cu bridges. The mean planes are parallel to (101). A water molecule is present with the O atom 2.987(7) Å from N13 but with no other contacts less than 3.3 Å. This is due to an N−H···O hydrogen bond. The H atoms bound to the O atom could not be found.

(CuCN)(tmtu) occurs in two polymorphic forms (see Figures 7−10). In both polymorphs there are infinite chains Cu−CN−Cu−CN with nonbridging S on each Cu to make the Cu three-

---

[12] Olmstead, M. M.; Speier, G.; Szabó, L. *Acta Crystallogr., Sect. C* **1993**, *49*, 370.

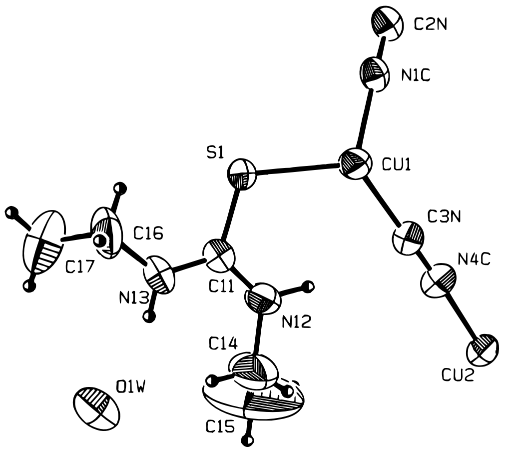

Figure 5. ORTEP plot of the structure of $(CuCN)_2(detu)(H_2O)$ (**4**), showing the atom labeling scheme and 50% probability ellipsoids.

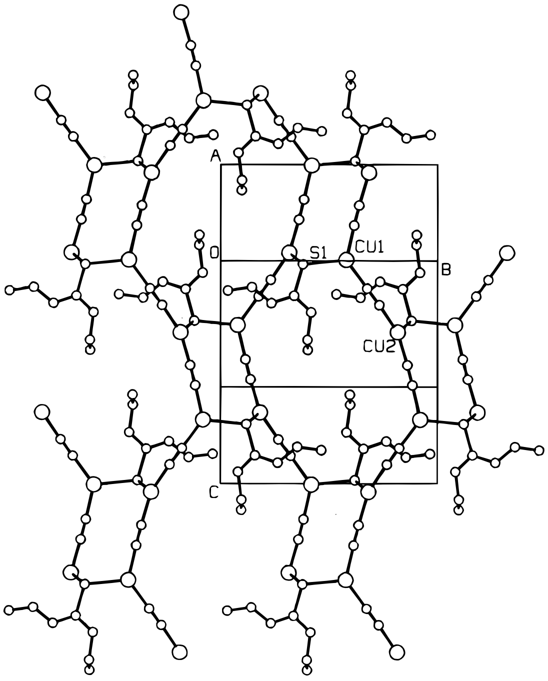

Figure 6. The extended structure of $(CuCN)_2(detu)(H_2O)$ (**4**). The view is normal to (101), the mean plane of the two dimensional sheet, $[(CuCN)_2S]_n$.

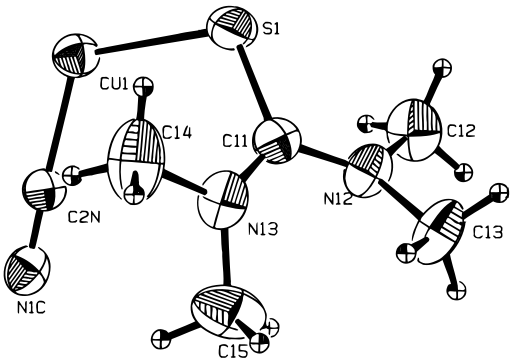

Figure 7. ORTEP plot of the structure of (CuCN)(tmtu) (polymorph a) (**5**), showing the atom labeling scheme and 50% probability ellipsoids.

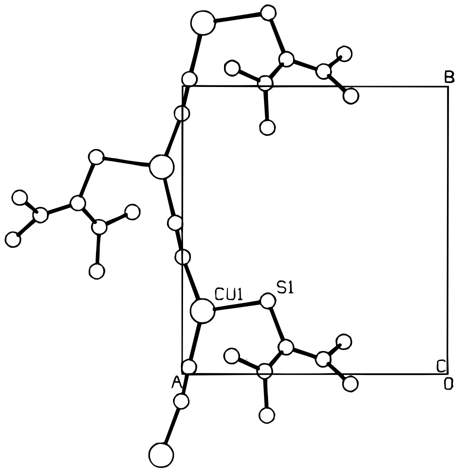

Figure 8. The extended structure of (CuCN)(tmtu) (polymorph a) (**5**). The view is along *c* showing the one-dimensional $(CuCN)_n$ chain.

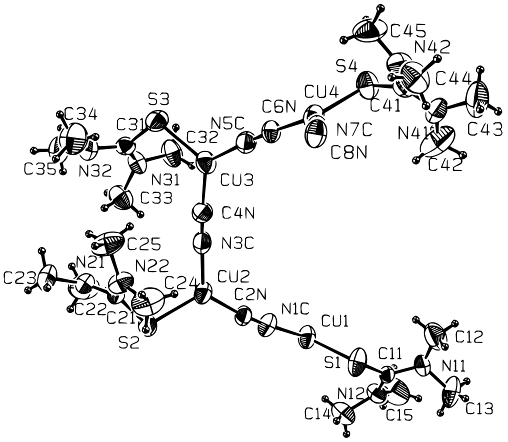

Figure 9. ORTEP plot of the structure of (CuCN)(tmtu) (polymorph b) (**6**), showing the atom labeling scheme and 50% probability ellipsoids.

coordinate. In polymorph a (**5**) these chains are parallel to the *b* axis with alternate CN−Cu−S residues related by the 2_1 axis. In polymorph b (**6**) the chains are again parallel to the *b* axis but with a helical arrangement involving four CN−Cu−S residues in the repeat unit. The four residues are not related by any crystallographic symmetry. A comparison of the molecular volumes, 237.0(1) Å^3 for **5** and 245.5(1) Å^3 for **6**, shows that the overall packing is more efficient in **5**.

The structure of $(CuCN)_2(etu)$ (**7**) (see Figures 11 and 12) can be thought of as infinite chains Cu−CN−Cu−CN bound into infinite sheets by bridging S atoms of etu. There are two independent Cu atoms, each three-coordinate and bonded to two bridging CN and one bridging S.

There are N−H bonds in **2**, **3**, **4**, and **7** and water molecules in **2** and **4**, so extensive hydrogen bonding might be expected. The short distances involving possible hydrogen bonds are shown in Table 9. Both water molecules are involved in N−H···O bonds with distances less than 3.00 Å, but there are no other O···N or O···O distances less than 3.00 Å, which suggests that none of the O−H hydrogens are involved in well-defined H-bonds. Only compound **2** has a terminal CN group and the lone pair in this group appears to H-bond to two H atoms. The rest of the N−H hydrogen bonds are to the π electrons in CN groups, to urea N atoms, or in one case to an S atom. None of these bonds is particularly short, which would imply that none is particularly strong. It would appear that the H-bonding, though extensive, is weak and, except for holding in the two water molecules, is not having a significant effect on the packing.

As mentioned above, all of the bridging CN groups appeared to be completely disordered within experimental error, except for N1C−C2N in **3** and both CN groups in **7**, all of which appear to be completely ordered within experimental error. In each of

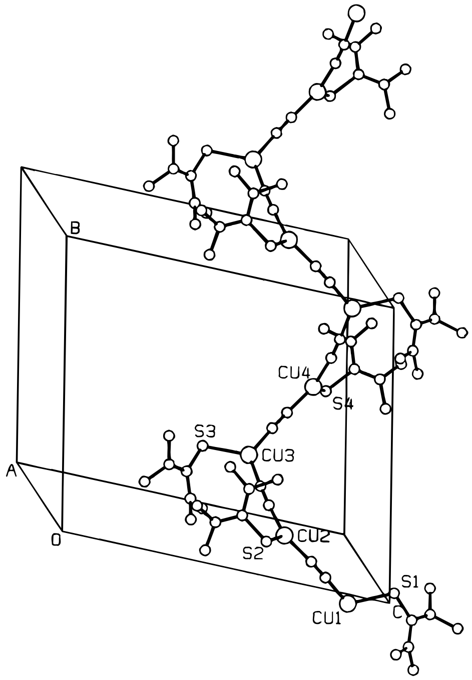

Figure 10. The extended structure of (CuCN)(tmtu) (polymorph b) (**6**). The view is normal to the *bc* plane showing the one-dimensional $(CuCN)_n$ chain. This arrangement has the same one-dimensional chain as shown in Figure 8, but here it repeats in a four-unit helix rather than as a two-unit zig-zag.

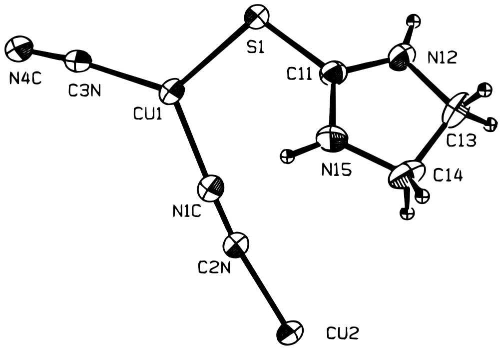

Figure 11. ORTEP plot of the structure of $(CuCN)_2$(etu) (**7**), showing the atom labeling scheme and 50% probability ellipsoids. Hydrogen atoms have been given arbitrary radii.

the latter three cases there is an N−H bond pointing nearly directly at the nitrogen atom in the CN with an H···N distance less than 2.5 Å, and it is tempting to argue that this interaction is energetic enough to order the CN group. Unfortunately, there are three other similar interactions where the CN group does not seem to be ordered. It appears that the degree of ordering in the CN groups is not well enough determined to allow any definitive conclusions to be drawn.

A comparison of the structures of the six complexes provides some useful correlations. Only the tu complex **2** has exclusively four-coordinate copper—the dmtu complex **3** is made up of one-third four-coordinate and two-thirds three-coordinate copper. All of the other ligands (detu, tmtu, and etu) gave complexes (**4**−**7**) containing exclusively three-coordinate copper. Where rings are present in the structures, ring sizes are limited to either 10, 16, or 22 atoms total, and although copper and cyanide content vary with ring size, the sulfur count is always 2 atoms per ring. The family of sulfur ligands used in this research, although chemically similar in most respects, differs significantly in their steric requirements. For a working hypothesis, we estimated the following order of increasing steric hindrance among the ligands: tu < dmtu < etu < detu < tmtu. The two smallest ligands (tu and dmtu) are found to occupy either three or two of the available coordination sites at copper and permit

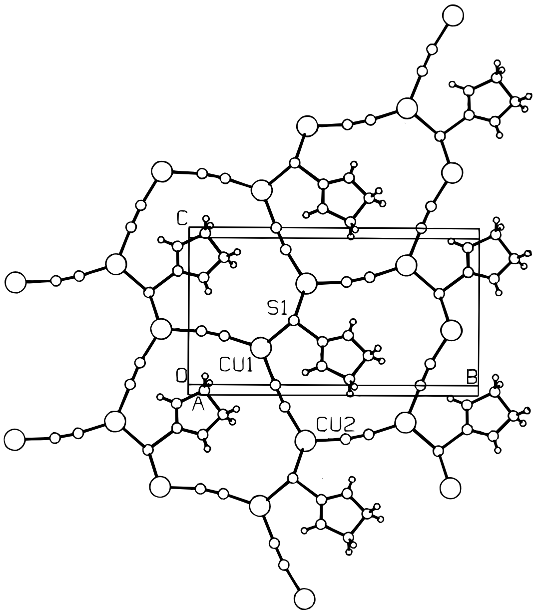

Figure 12. The extended structure of $(CuCN)_2$(etu) (**7**). The view is normal to the *bc* plane showing the two dimensional $[(CuCN)_2S]_n$ sheet.

Table 9. Hydrogen Bonds[a] D−H···A

D−H	A[b]	H···A (Å)	D−H···A (deg)	D···A (Å)
		Compound **2**		
N11−H1	O1	1.99	179	2.82
N11−H2	C3′−N4′	2.45	172	3.29
N12−H3	C1N−N2C	2.78	142	3.41
N12−H3	N2C′−C1N′	2.89	127	3.41
N12−H4	N4′−C3′	2.66	147	3.35
N12−H4	N11′	2.95	120	3.42
N21−H5	N4′−(C3′)	2.50	146	3.12
N21−H5	N32′	2.78	136	3.34
N22−H7	N4′−(C3′)	2.30	152	3.07
N22−H8	S′	2.75	165	3.49
O1[c]	N22′			3.18
O1[c]	C1N′−N2C′			3.18
O1[c]	C1N″−N2C″			3.41
O1[c]	N12′			3.32
		Compound **3**		
N12−H1	N3C−C4N	2.22	161	3.13
N22−H9	N1C′−C2N′	2.26	158	3.16
N22−H9	N3C−C4N	2.83	107	3.24
N23−H13	N5C′−C6N′	3.07	102	3.39
		Compound **4**		
N12−H1	C3N−N4C	2.29	167	3.24
N13−H2	O1W	2.16	162	2.99
O1W[d]				
		Compound **7**		
N12−H12	N4C′−C3N′	2.27	155	3.01
N15−H15	N1C′−C2N′	2.44	149	3.22

[a] Short distances are listed if D···A is less than 3.45 Å (3.5 Å if A is S) and D−H···A is greater than 120°. The esd's for the H···A distances are about 0.04 Å, for the D−H···A angles about 4°, and for the D···A distances all less than 0.01 Å. [b] If the H-bond acceptor is the N atom of a CN group, the name of the C atom is given in parentheses. If the H-bond acceptor is the π system of the CN group, both atoms are listed without parentheses with the closer atom named first. [c] Neither of the H atoms in the H_2O molecule in **2** could be located. The angles N11···O1···X are 140, 86, 119, and 99°, for X equal to N22′, C1N′, C1N″, and N12′, respectively. [d] Neither of the H atoms in the H_2O molecule in **4** could be located. The nearest N or O atom other than N13 is N12′ at a distance of 3.54 Å with an N13···O1W···N12′ angle of 119°.

four-coordination, whereas the three larger ligands (etu, detu, and tmtu) are found to occupy only one of the available coordination sites and presumably play a role in limiting copper to three-coordination. Only in the tu complex does the number of sulfur atoms exceed the number of copper atoms.

In 1986, Dubler and Bensch[13] published a useful summary and classification of all of the known structures of copper(I) complexes of thiourea and substituted thioureas. This classification scheme, which can only accommodate complexes with exclusively Cu−S linkages, obviously cannot be applied to the new complexes described here because they all contain at least one Cu−(CN) bond.

Examination of Table 8 shows a range of Cu−S bond distances of 2.27−2.48 Å which falls within the range of Cu−S distances (2.19−2.52 Å) reported for the 20 copper(I) complexes of thiourea and substituted thioureas described in the survey article by Dubler and Bensch. No simple correlation was observed between the Cu−S bond distance and the thiourea derivative used, the Cu coordination level, or the Cu−S−Cu bond angle. As has been previously described,[14] the Cu−(CN) distances vary with coordination number of the Cu and with C versus N linkage to Cu. The results here are consistent with those previous observations.

Among the most important data from the infrared spectra are the stretch frequencies for the C≡N bond. As can be seen in Table 10, all of the C≡N frequencies, except one, fall within the narrow range 2087−2120 cm^{-1}. A weak absorption at 2213 cm^{-1} appears as one of the two cyanide absorptions in $(CuCN)_2(tu)_3(H_2O)$ (**2**)—this one probably arises from the nonbridging C≡N unique to that compound.

For some of the new complexes (i.e., **2**, **3**, **5**, and **6**) it was possible to make direct comparisons of their key IR absorptions (especially the C−S stretch frequencies) to those of previously prepared copper(I) complexes with comparable ligands. IR data for copper(I) complexes of tu,[15] tmtu,[16] dmtu,[17] and mtu (1-methyl-2-thiourea)[18] were available for comparison. No appreciable differences were noted.

Conclusion

The first examples of sulfur, cyanide mixed ligand copper(I) complexes are reported. Synthesis was effected by adding the ligand to a solution of CuCN in aqueous sodium thiosulfate. The significance of this new procedure is that it is widely applicable beyond the limited scope reported here.

Acknowledgment. The authors are indebted Professor Wayne C. Wolsey of Macalester College for encouragement and helpful discussions. Financial support from the Howard Hughes Medical Institute is gratefully acknowledged.

Supporting Information Available: Tables of complete crystallographic data, discussion of the determination of the space group for $(CuCN)_3(dmtu)_2$ (**3**), atomic positional parameters, anisotropic thermal parameters, and bond distances and angles for **2**−**7** (29 pages). Ordering information is given on any current masthead page.

IC9511027

---

[13] Dubler, E.; Bensch, W. *Inorg. Chim. Acta* **1986**, *125*, 37.

[14] See the article cited in footnote 1 for a full set of references on crystal structures of CuCN complexes published through 1990. Reference to a more recently reported CuCN complex can be found in footnote 12.

[15] Swaminathan, K.; Irving, H. M. N. H *J. Inorg. Nucl. Chem.* **1964**, *26*, 1291.

[16] Schafer, M.; Curran, C. *Inorg. Chem.* **1966**, *5*, 265.

[17] Gosavi. R. K.; Rao, C. N. R. *J. Inorg. Nucl. Chem.* **1967**, *29*, 1937.

[18] Lane, T, J.; Yamaguchi, A.; Quagliano, J. V.; Ryan, J. A.; Mizushima, S. *J. Am. Chem. Soc.* **1959**, *81*, 3824.