Inorg. Chem. **2000,** *39,* 3479−3484

Crystal Structures of a Family of Silver Cyanide Complexes of Thiourea and Substituted Thioureas

Fred B. Stocker,*,† Doyle Britton,‡ and Victor G. Young, Jr.‡

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

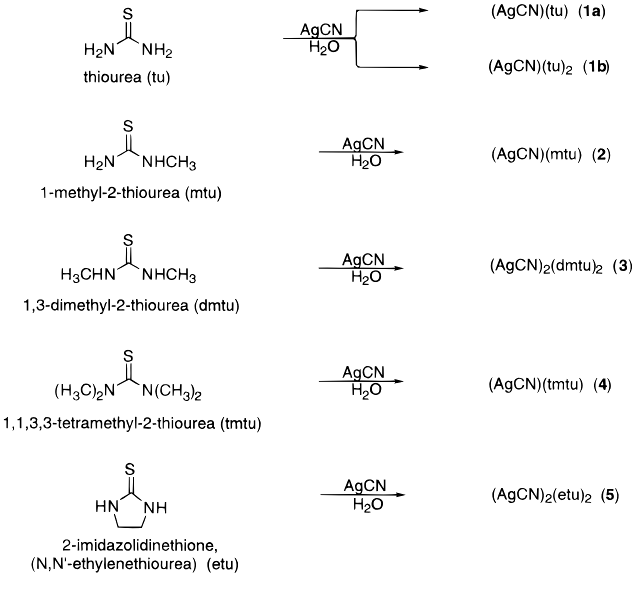
Received July 20, 1999

The syntheses and crystal structures of a family of silver cyanide complexes of thiourea and substituted thioureas are reported. The sulfur ligands include thiourea (tu), 1-methyl-2-thiourea (mtu), 1,3-dimethyl-2-thiourea (dmtu), 1,1,3,3-tetramethyl-2-thiourea (tmtu), and 2-imidazolidinethione (*N,N′*-ethylenethiourea, etu). Synthesis was effected by dissolving AgCN in an aqueous solution of ligand. Two different complexes were obtained by the reaction of AgCN with tu. Complex **1a**: (AgCN)(tu), monoclinic, $P2_1/c$, $a = 9.3851$ (6) Å, $b = 8.2782$ (5) Å, $c = 7.1178$ (5) Å, $\beta = 94.591$ (1)°, and $Z = 4$. Complex **1b**: $(AgCN)(tu)_2$, triclinic, $P\bar{1}$, $a = 7.9485$ (14) Å, $b = 9.431$ (2) Å, $c = 12.771$ (2) Å, $\alpha = 85.695$ (3)°, $\beta = 81.210$ (4)°, $\gamma = 77.987$ (2)°, and $Z = 4$. Complex **2**: (AgCN)(mtu), triclinic, $P\bar{1}$, $a = 4.113$ (2) Å, $b = 9.472$ (4) Å, $c = 9.679$ (4) Å, $\alpha = 113.918$ (5)°, $\beta = 98.188$ (6)°, $\gamma = 97.725$ (6)°, and $Z = 2$. Complex **3** $(AgCN)_2(dmtu)_2$, monoclinic, $P2_1/m$, $a = 7.1482$ (7) Å, $b = 14.776$ (2) Å, $c = 7.3366$ (7) Å, $\beta = 92.418$ (2)°, and $Z = 2$. Complex **4**: (AgCN)(tmtu), orthorhombic, $P2_12_12_1$, $a = 8.823(6)$ Å, $b = 10.209$ (2) Å, $c = 10.362$ (2) Å, and $Z = 4$. Complex **5**: $(AgCN)_2(etu)_2$, triclinic, $P\bar{1}$, $a = 6.8001$ (2) Å, $b = 8.6154$ (1) Å, $c = 13.4747$ (3) Å, $\alpha = 71.720$ (1)°, $\beta = 79.906$ (1)°, $\gamma = 75.885$ (2)°, and $Z = 2$. All of the structures involve either one- or two-dimensional polymeric arrays held together by bridging S and CN groups. There is, however, no similarity between any two of the arrays. Four of the five ligands used also form similar complexes with CuCN. For one ligand, tmtu, the structures are isomorphous. For the other three, not only are the structures not isomorphous, the m/n ratio in $(MCN)_mL_n$ when M is Ag is different from that when M is Cu.

Introduction

In 1996 we reported the syntheses and crystal structures of a family of copper(I) cyanide complexes of thiourea and substituted thioureas.[1] The present project was pursued in order to determine whether AgCN produced comparable structures when complexed with these same thiourea ligands. During the previous project direct synthesis from CuCN was generally an ineffective preparative method, and a thiosulfate-assisted procedure was used instead. In the current project we learned at the outset that thiosulfate binding of AgCN was too strong to permit complex formation with the thiourea compounds. However, all the thiourea compounds provided aqueous solutions capable of dissolving AgCN, allowing the subsequent deposit of crystalline complexes. The thioureas that reacted to produce crystalline complexes were thiourea (tu), 1-methyl-2-thiourea (mtu), 1,3-dimethyl-2-thiourea (dmtu), 1,1,3,3-tetramethyl-2-thiourea (tmtu), and 2-imidazolidinethione (*N,N′*-ethylenethiourea, etu). Another thiourea compound, 1,3-diethyl-2-thiourea (detu), which produced $(CuCN)_2(detu)(H_2O)$ with CuCN, gave no crystalline product with AgCN. Scheme 1 shows the transformations.

Scheme 1



Experimental Section

General. Commercial chemicals were used without further purification. Infrared spectra were recorded as KBr pellets with a Perkin-Elmer model 1430 spectrometer. Elemental analyses were determined by Galbraith Laboratories, Knoxville, TN. The crystal structures were determined by the X-Ray Crystallography Laboratory, Department of Chemistry, University of Minnesota, Minneapolis, MN.

General Preparation Procedures. Magnetic mixing was used until both the thiourea compound and AgCN were dissolved (distilled water). When heating was used, temperatures were limited to 70−80 °C. After the thiourea and AgCN were dissolved, the solution was filtered by gravity and transferred to a set of 4 in. test tubes. The covered tubes were stored in the dark while awaiting crystal formation. The products were collected by suction filtration and washed several times with

---

* To whom correspondence should be addressed.

† Macalester College.

‡ University of Minnesota.

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

10.1021/ic990859l CCC: $19.00

Table 1. Crystallographic Data[a]

	complex					
	(AgCN)(tu), **1a**	(AgCN)(tu)$_2$, **1b**	(AgCN)(mtu), **2**	(AgCN)$_2$(dmtu)$_2$, **3**	(AgCN)(tmtu), **4**	(AgCN)$_2$(etu)$_2$, **5**
formula	$C_2H_4AgN_3S$	$C_3H_8AgN_5S_2$	$C_3H_6AgN_3S$	$C_8H_{16}Ag_2N_6S_2$	$C_6H_{12}AgN_3S$	$C_8H_{12}Ag_2N_6S_2$
fw	210.01	286.12	224.04	476.13	266.11	472.10
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/m$	$P2_12_12_1$	$P\bar{1}$
temp, °C	24(2)	−100(2)	−100(2)	25(2)	24(2)	20(2)
a, Å	9.3851(6)	7.9485(14)	4.113(2)	7.1482(7)	8.823(6)	6.8001(2)
b, Å	8.2782(5)	9.431(2)	9.472(4)	14.776(2)	10.209(2)	8.6154(1)
c, Å	7.1178(5)	12.771(2)	9.679(4)	7.3366(7)	10.362(2)	13.4747(3)
α, deg	90	85.695(3)	113.918(5)	90	90	71.720(1)
β, deg	94.591(1)	81.210(4)	98.188(6)	92.418(2)	90	79.906(1)
γ, deg	90	77.987(2)	97.725(6)	90	90	75.885(2)
V, Å^3	551.22(11)	924.5(3)	333.4(3)	774.24(13)	933(1)	722.76(3)
Z	4	4	2	2	4	2
ρ_{calcd} (Mg m^{-3})	2.531	2.056	2.232	2.042	1.894	2.169
μ, cm^{-1}	39.02	25.26	32.33	27.91	22.99	29.89
R^b	0.056	0.058	0.020	0.037	0.038	0.038
wR2^c	0.153	0.163	0.050	0.076	0.089	0.094

[a] Radiation: Mo Kα (graphite monochromated, $\lambda = 0.710\,73$ Å). [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$, includes $I > 2.00\sigma(I)$. [c] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2]\}^{1/2}$, includes all I.

distilled water; they were stored in the dark. Although most of the complexes were relatively stable the crystals of (AgCN)(tu) (**1a**) and (AgCN)(mtu) (**2**) gradually darkened and in a few days became gray in color.

a. Preparation of the Complexes of AgCN/tu. The tu (381 mg, 5 mmol) dissolved readily at room temperature in 15 mL of water. To dissolve the AgCN (134 mg, 1.0 mmol), mild heating was required. Within hours crystal growth was evident. After 48 h the crystalline product was filtered while taking care not to dilute the mother liquor (colorless plates, 80 mg, 38%). (AgCN)(tu) (**1a**): IR: 3460 m, 3405 s, 3300 s, 3190 m, 2130 s, doublet 1632, 1618 s, 1497 w, 1427 m, 1398 m, 1060 w, 707 m, 640 w, 520 s, 477 m, 325 w cm^{-1}. Anal. Calcd for $C_2H_4AgN_3S$: C, 11.44; H, 1.92; Ag, 51.37; N, 20.01; S, 15.27. Found: C, 11.52; H, 1.92; Ag, 52.11; N, 19.77; S, 15.60. The mother liquor (stored in the dark) showed the first sign of new crystal growth after 60 days. Eleven days later the product was collected (colorless needles, 15 mg, 5.5%). Subsequently, when this preparation was run as a double batch, 4 months passed before crystals of **1b** appeared.

(AgCN)(tu)$_2$ (**1b**). IR: 3410 s, 3270 m, 3180 m, 3110 w, 2130 s, 1637 w, sh, 1615 s, 1520 w, 1490 m, 1450 w, 1430 w, 1390 m, 1120 w, 1095 w, 715 m, 640 w, 560 s, 470 s, 320 w cm^{-1}. Anal. Calcd for $C_3H_8AgN_5S_2$: C, 12.59; H, 2.82; Ag, 37.7; N, 24.48; S, 22.41. Found: C, 12.46; H, 2.76; Ag, 37.44; N, 24.09; S, 24.22.

b. Preparation of (AgCN)(mtu) (2). The mtu (595 mg, 6.60 mmol) dissolved readily in 20 mL of water at room temperature. To dissolve the AgCN (268 mg, 2 mmol), mild heating was required. Within 24 h the solutions were filled with colorless crystals (needles). On the fourth day the product (184 mg, 41.1%) was collected. IR: 3295 s, 3140 s, 2115 s, 1663 s, 1585 s, 1522 w, 1457 w, 1427 w, 1308 m, 1255 w, 1173 w, 1135 w, 985 w, 777 m, 715 w, 652 w, 614 m, 493 m, 410 w cm^{-1}. Anal. Calcd for $C_3H_6AgN_3S$: C, 16.08; H, 2.70; Ag, 48.15; N, 18.76; S, 14.31. Found: C, 16.03; H, 2.83; Ag, 48.39; N, 18.83; S, 14.44.

c. Preparation of (AgCN)$_2$(dmtu)$_2$ (3). The dmtu (2084 mg, 20 mmol) dissolved readily at room temperature (20 mL water), but the AgCN (134 mg, 1 mmol) required the application of mild heating. Within 24 h tiny "blocklike" crystals were evident. During the next few weeks the size of the crystals increased. After a total of 8 weeks 75 mg (32%) of product was isolated. IR: 3350 s, 3030 w, 2950 w, 2130 s, 1590 s, 1525 s, 1457 m, 1427 w, 1383 w, 1300 s, 1195 w, 1043 m, 1027 m, 723 m, 545 s, 450 w, 365 w cm^{-1}. Anal. Calcd for $C_8H_{16}Ag_2N_6S_2$: C, 20.18; H, 3.39; Ag, 45.31; N, 17.65; S, 13.47. Found: C, 20.01; H, 3.10; Ag, 44.94; N, 17.61; S, 14.07.

d. Preparation of (AgCN)(tmtu) (4). The tmtu (600 mg, 4.54 mmol) dissolved slowly (30 min) at room temperature in 20 mL of water. To dissolve the AgCN (94 mg, 0.70 mmol), mild heating was required. Crystal growth was evident after 24 h, and a good crop of crystals (colorless prisms) was present within 3 days. The product, which was collected after 6 days, amounted to 116 mg (62.4%); mp, 118−120 °C. IR: 3035 w, 2940 m, 2140 s, 1550 s, 1498 m, 1473 m, 1447 w, 1415 w, 1395 s, 1380 s, 1280 m, 1227 w, 1267 s, 1128 w, 1105 m, 1070 w, 960 w, 900 m, 620 w, 485 m, 375 w cm^{-1}. Anal. Calcd for $C_6H_{12}AgN_3S$: C, 27.08; H, 4.55; Ag, 40.54; N, 15.79; S, 12.05. Found: C, 26.49; H, 4.57; Ag, 40.38; N, 15.59; S, 12.51.

e. Preparation of (AgCN)$_2$(etu)$_2$ (5). The etu (531 mg, 5.0 mmol) dissolved slowly at room temperature in 30 mL of water. To dissolve the AgCN (100 mg, 0.75 mmol), mild heating was required. Within 24 h a large number of small crystals were evident. The size of the crystals increased during the first week, but the product (colorless prisms) was not collected for 8 weeks. The total yield amounted to 79 mg (45%). IR: 3370 s, 3200 br, w, 3170 w, 2970 w, 2890 m, 2128 m, 1695 br, w, 1527 s, 1480 m, 1354 w, 1315 m, 1278 s, 1203 m, 1040 w, 990 w, 970 w, 917 w, 720 br, w, 655 w, 550 m, 493 w, 375 w, 333 w cm^{-1}. Anal. Calcd for $C_8H_{12}Ag_2N_6S_2$: C, 20.35; H, 2.56; Ag, 45.70; N, 17.80; S, 13.58. Found: C, 20.31; H, 2.63; Ag, 48.14; N, 17.83; S, 14.93.

X-ray Structure Determinations. Data were collected on a Siemens SMART system (**1a**, **1b**, **2**, **3**, **5**) or an Enraf-Nonius CAD-4 (**4**) using graphite monochromated Mo Kα radiation ($\lambda = 0.710\,73$). Checks showed no decay in intensity for any of the crystals. Crystallographic data are in Table 1. The structures were solved by direct methods using SHELXTL[2] or MITHRIL[3] and DIRDIF.[4]

All crystals of **1b** that were examined were nonmerohedrally twinned. Data were collected on a twinned crystal, the correct unit cell was identified using programs by Sparks,[5] and the intensities were corrected for the twinning using UNTWIN.[6] The twin law is (−1 0 0/−0.474 1 −0.064/0 0 −1). The twin components are related by a 180° rotation about (010) in reciprocal space. The final refinements for all of the structures were done using SHELXTL. The only nonroutine feature of the refinement was the consideration of disorder in the cyanide groups (see below). H atoms were included at idealized positions with isotropic displacement parameters 20% larger than the B_{eq} value of the atom to which they were bonded. AgCN(tmtu) (**4**) occurs in a chiral space group; a Flack[7] parameter of −0.03(5) shows the reported enantiomer to be the correct one.

The possibility of disorder was considered for every cyanide group. The cyanide groups in **4**, coordinated to equivalent Ag atoms with equal

---

(2) Sheldrick, G. M. *SHELXTL*, version 5.0*;* Siemens Analytical X-Ray Instruments, Inc.: Madison, WI, 1994.

(3) Gilmore, C. J. *J. Appl. Crystallogr.* **1984**, *17*, 42.

(4) Beurskens, P. T. Technical Report 1984/1; Crystallography Laboratory: Toernooiveld, The Netherlands, 1984.

(5) Sparks, R. A. Bruker-AXS, Inc., 6300 Enterprise Lane, Madison, WI 53719, 1996.

(6) Young, V. G., Jr. Unpublished work, University of Minnesota, 1997.

(7) Flack, H. D. *Acta Crystallogr.* **1984**, *A39*, 876.

Table 2. Selected Bond Distances (Å)

(AgCN)(tu) (**1a**)			
Ag1−C1	2.123(8)	Ag1−S1	2.578(2)
		Ag1−S1′	2.674(2)
		Ag1−S1″	2.804(2)
(AgCN)(tu)$_2$ (**1b**)			
Ag1−C1	2.110(10)	Ag1−S1	2.547(2)
Ag2−C2	2.128(9)	Ag1−S2	2.594(2)
		Ag1−S4	2.885(3)
		Ag2−S3	2.505(2)
		Ag2−S4	2.662(2)
		Ag2−S2	2.779(2)
(AgCN)(mtu) (**2**)			
Ag1−C1	2.173(3)	Ag1−S1	2.637(1)
Ag1−C1′	2.603(3)	Ag1−S1′	2.498(1)
(AgCN)$_2$(dmtu)$_2$ (**3**)			
Ag1−N1′	2.514(6)	Ag1−S1	2.504(1)
Ag1−N2′	2.410(6)	Ag1−S1′	2.504(1)
Ag2−C1	2.081(7)	Ag2−S1	3.143(1)
Ag2−C2	2.090(7)	Ag2−S1′	3.143(1)
(AgCN)(tmtu) (**4**)			
Ag1−C1(N1)	2.156(4)	Ag1−S1	2.708(2)
Ag1−C2(N2)	2.155(4)		
(AgCN)$_2$(etu)$_2$ (**5**)			
Ag1−N2	2.255(6)	Ag1−S1	2.589(1)
Ag2−C1	2.110(8)	Ag1−S2	2.620(1)
Ag2−C3	2.089(8)	Ag1−S2′	2.700(1)
		Ag2−S1	2.725(2)

distances at both ends, were completely disordered within experimental limits. The bridging cyanide in **5**, coordinated to nonequivalent Ag atoms with unequal distances, was found to be 87(7)% as shown in Figure 5 (below) and 13% in the opposite orientation; this amount of disorder was included in the refinement, although complete order is a distinct possibility. All the remaining cyanide groups were found to be completely ordered within experimental limits.

Discussion

General. The bond distances to Ag are given in Table 2. In the seven cases where Ag is attached to C in an ordered CN group, the distances range from 2.08 to 2.13 Å with an average of 2.104(18) Å; the largest deviation from linearity in the Ag−C−N angle is 3.3(9)°. In three of these cases where the N atom in the CN is bonded to another Ag, the Ag−N distances vary from 2.26 to 2.51 Å and the angles from 135 to 173°, suggesting that if the Ag−C bond is normal, the bond from the N to another Ag is secondary with a much wider range of distances and angles.

In the one case (**2**) where an ordered CN group is bonded to two Ag at the C atom, the Ag−C distances differ by 0.43 Å. For comparison, when ordered CN groups were similarly bonded to two Cu,[8] the differences between the two Cu−C distances varied from 0.18 to 0.68 Å.

The Ag−S distances show a wider variation. Most are between 2.50 and 2.80 Å, but in **3** there is a recognizable Ag−S interaction at 3.14 Å. There is no obvious pattern in the variation.

Packing. In **1a** (see Figure 1) the Ag atoms have irregular tetrahedral coordination with one cyanide N atom and three S atoms in the coordination sphere. The corollary to this is that each S atoms also has irregular tetrahedral coordination. The overall aggregation is into two-dimensional layers with alternating Ag_4S_4 and Ag_2S_2 rings. The layers are held together through hydrogen bonds (see Table 3).

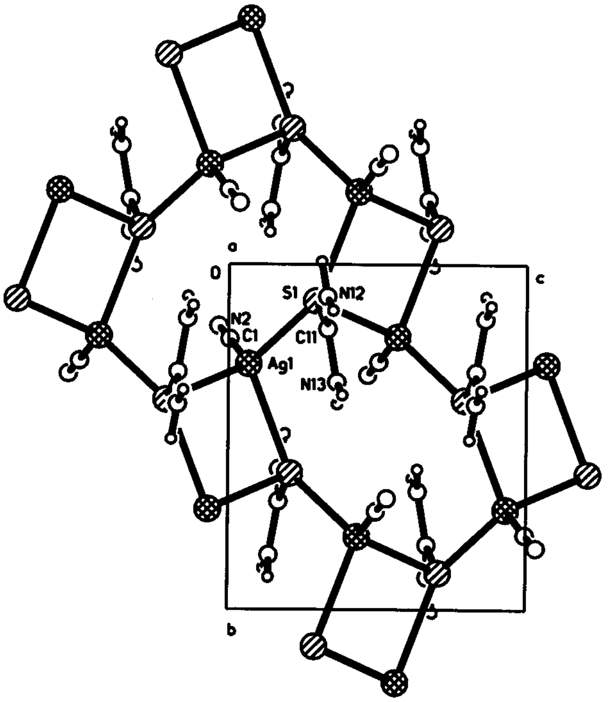


Figure 1. Extended structure of (AgCN)(tu) (**1a**). The Ag and S atoms are larger, the Ag atoms are crosshatched, and the S atoms are shaded. The view is normal to the (100) plane. Hydrogen bonds (not shown) connect adjacent layers.

Table 3. Hydrogen Bond Lengths (Å) and Angles (deg) for X−B···H−Y

X	B	Y	X−B···H	B···H	B···H−Y	B···Y
H-Bonds to Cyanide N						
(AgCN)(tu) (**1a**)						
C1	N1	N12′	117	2.20	151	2.985
C1	N1	N12′	176	2.33	146	3.081
(AgCN)(tu)$_2$ (**1b**)						
C1	N1	N32′	162	2.07	175	2.944
C2	N2	N21′	160	2.13	155	2.948
C2	N2	N22′	140	2.33	146	3.095
(AgCN)(mtu) (**2**)						
C1	N1	N3′	157	2.14	161	2.981
C1	N1	N3″	110	2.25	166	3.109
(AgCN)$_2$(dmtu)$_2$ (**3**)						
C1	N1	N13′	99	2.40	145	3.144
C2	N2	N12′	103	2.22	165	3.056
(AgCN)$_2$(etu)$_2$ (**5**)						
C3	N4	N11′	135	2.11	165	2.947
H Bonds to S						
(AgCN)(tu) (**1b**)						
C11	S1	N32′	110	2.44	171	3.313
C21	S2	N42′	102	2.57	171	3.445
C31	S3	N11′	107	2.49	178	3.370
C41	S4	N21′	108	2.59	168	3.456
(AgCN)(mtu) (**2**)						
C2	S1	N2′	109	2.54	164	3.391

In **1b** there are two AgCN(tu)$_2$ formula units in the asymmetric unit, which behave chemically in a similar fashion, as can be seen from Figure 2 and from the bond lengths in Table 2. Both Ag atoms have irregular tetrahedral coordination with one cyanide, one unidentate thiourea, and two bridging thioureas in the coordination sphere. It should be noted, however, that there are small but significant differences between corresponding bond lengths and angles. The most prominent structural feature is the zigzag one-dimensional chain −Ag1−S2−Ag2−S4−Ag1−, parallel to the *a* axis, in which the Ag−S distances

---

[8] Stocker, F. B.; Staeva, T. P.; Rienstra, C. M.; Britton, D. *Inorg. Chem.* **1999**, *38*, 984.

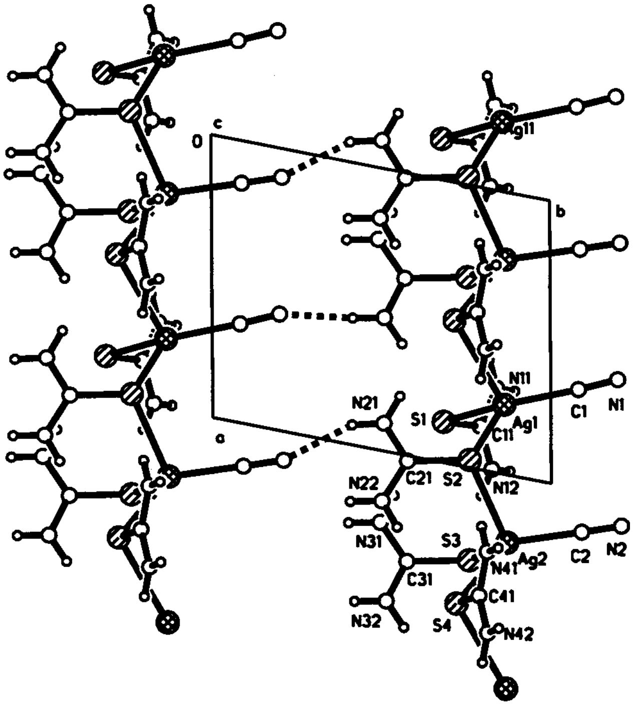


Figure 2. Extended structure of (AgCN)(tu)$_2$ (**1b**). The Ag and S atoms are larger, the Ag atoms are crosshatched, and the S atoms are shaded. The view is normal to the (001) plane. The dotted lines show hydrogen bonds between adjacent chains.

alternate between a short distance, near 2.6 Å, and a longer one, near 2.8 Å. The chains form two-dimensional sheets parallel to (110) through N−H···N−C hydrogen bonds (see Table 3). There are also four short N−H···S distances within each chain that are probably hydrogen bonds, although in two of the four cases the H···S−Ag angles are far from tetrahedral.

In **2** the Ag atoms have irregular tetrahedral coordination with two bridging thioureas, one strongly bound cyanide, and one weakly bound cyanide in the coordination sphere. There is a zigzag one-dimensional chain −Ag1−S1−Ag1− parallel to the *a* direction (see Figure 3). Two such chains are held together by two cyanide carbon atoms asymmetrically bridging pairs of Ag atoms. The asymmetric bridging is similar to that found in some CuCN·L complexes.[8] A sometime consequence of this M−C−M bridging is that the M···M distance is less than it is in the pure metal. This is the situation here, where the Ag···Ag distance is 2.832(1) Å versus a distance of 2.889 Å in the silver metal.[9] The double chains are assembled into two-dimensional sheets parallel to (011) through N−H···N−C hydrogen bonds. There are short N−H···S distances between adjacent sheets that appear to be hydrogen bonds.

In **3** there are two AgCN(dmtu) formula units in the asymmetric unit. The Ag atoms, however, are chemically quite different. Ag1 is strongly bonded to two S atoms and weakly bonded to two cyanide N atoms. Ag2 is strongly bonded to two cyanide C atoms and weakly bonded to two S atoms. The overall aggregation is into two-dimensional layers parallel to the (010) plane (see Figure 4). There are weak hydrogen bonds N−H···NC between adjacent layers. The dmtu from adjacent layers are stacked face-to-face.

In **4** the Ag is trigonally coordinated with two strong bonds to disordered cyanide atoms and a weaker bond to sulfur (see Figure 5). The arrangement is slightly nonplanar. There is a one-dimensional chain −Ag1−CN−Ag1− parallel to the *b* axis. This structure is isomorphous with one of the two polymorphs of CuCN(tmtu).[1]

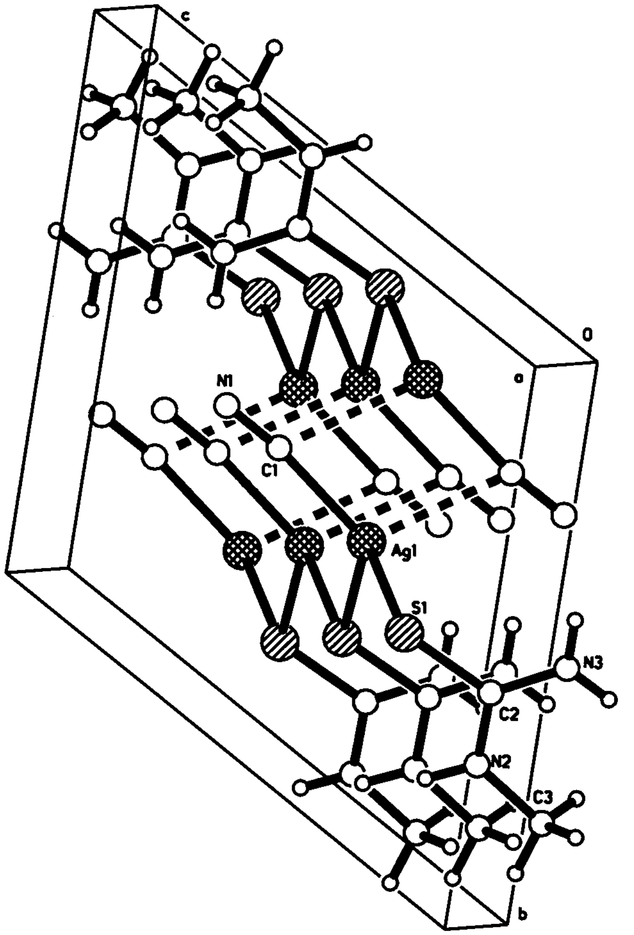


Figure 3. Extended structure of (AgCN)(mtu) (**2**). The Ag and S atoms are larger, the Ag atoms are crosshatched, and the S atoms are shaded. The view is approximately 15° away from the normal to the (100) plane. The −Ag−S−Ag− chains are parallel to the *a* axis.

In **5** the situation is similar to that in **3** (see Figure 6). There are two AgCN(etu) formula units in the asymmetric unit with two different chemical environments for the Ag atoms. Ag1 has irregular tetrahedral coordination with three S atoms and one cyanide N atom in the coordination sphere. Ag2 has irregular planar trigonal coordination with one S and two cyanide C atoms in the coordination sphere. The overall aggregation is into double chains parallel to the *a* axis with the mean plane of the chain parallel to (011).

Ag−S−Ag Bridges. While some of the S atoms in the above complexes are bonded to only one Ag atom, most are bonded to two (and in **1a** to three). These bridging S atoms show a variety of behaviors. Sometimes two Ag are connected by a single S; other times the two Ag are connected by two S. Furthermore, the bridging S appear to act in two different ways, with the Ag−S−Ag angle 90° or larger in about half the cases, leading to Ag···Ag distances of 3.6 Å or larger, and with the Ag−S−Ag angle significantly less than 90° in the other half, leading to Ag···Ag distances of 3.3 Å or less. The metrical details of these bridges are collected in Table 4, where they are compared with similar data for thiourea complexes of other silver salts.

There is no obvious pattern to these Ag−S−Ag bridges. In the structure of AgCl(tu)$_2$,[10] the earliest example of a thiourea complex of a silver salt, both kinds of bridges are found. The

---

[9] Wyckoff, R. W. G. *Crystal Structures*; Interscience: New York, 1963; Vol. 1, p 10.

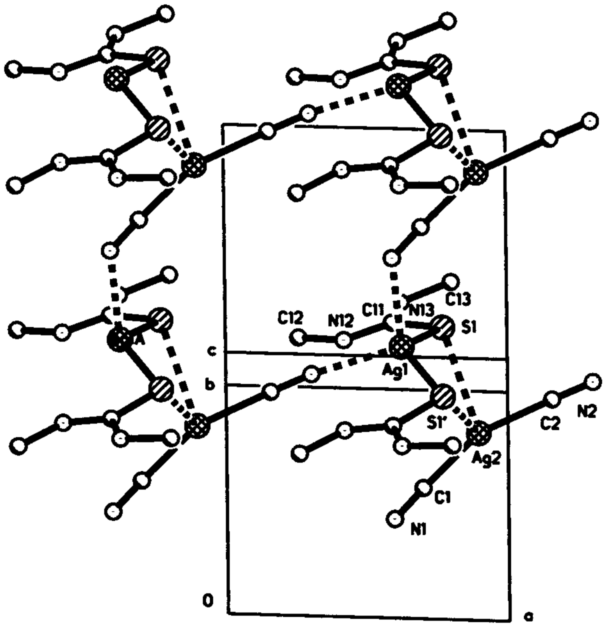


Figure 4. Extended structure of $(AgCN)_2(dmtu)_2$ (**3**). The Ag and S atoms are larger, the Ag atoms are crosshatched, and the S atoms are shaded. The view is approximately normal to the (011) plane. The dotted lines show Ag−L distances that are longer than usual. Hydrogen atoms have been omitted for clarity.

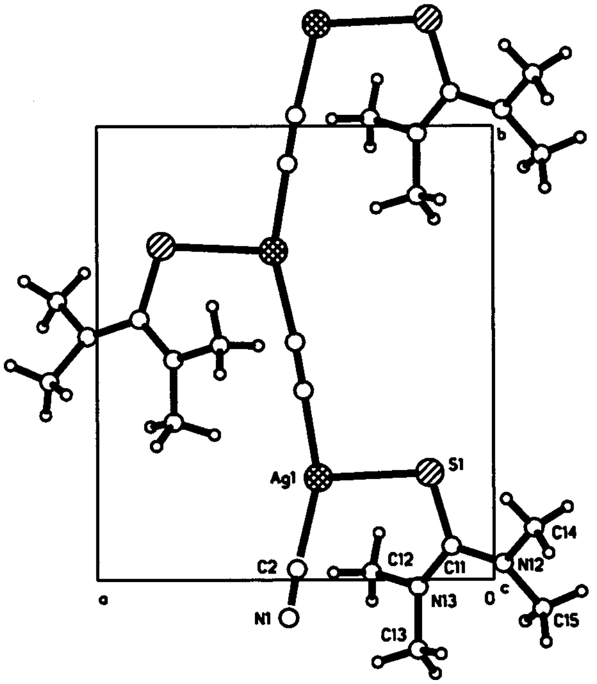


Figure 5. Extended structure of (AgCN)(tmtu) (**4**). The Ag and S atoms are larger, the Ag atoms are crosshatched, and the S atoms are shaded. The view is normal to the (001) plane.

authors suggested that the wide-angled bridge involves two normal Ag−S bonds, but the acute-angled bridge involves three-centered bonding using only a single orbital on the S atom. The most acute angle and shortest Ag⋯Ag distance are found to date in $AgClO_4(tu)_3$.[11] The authors here offer an alternative explanation involving two different kinds of two-center bonds. The conditions favoring such bonds are quite unclear because the change from $AgCl(tu)_2$ to $AgCl(etu)_2$ [12] leads to only a single

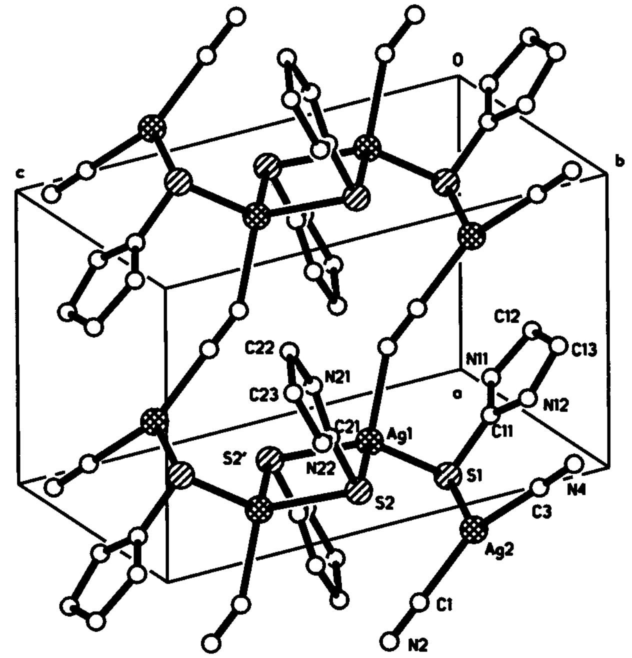


Figure 6. Extended structure of $(AgCN)_2(etu)_2$ (**5**). The Ag and S atoms are larger, the Ag atoms are crosshatched, and the S atoms are shaded. The view is normal to the (011) plane. Hydrogen atoms have been omitted for clarity.

S wide-angle bridge, and the change from $AgCl(etu)_2$ to $AgBr(etu)_2$ [13] leads to Br bridges replacing the S bridges. As another example of variable behavior, $AgClO_4(dmtu)_2$ [13] contains infinite chains of double acute-angled bridges, while $AgClO_4(dmtu)_3$ contains isolated dimers with essentially the same double acute-angled bridge. It would appear both from the above examples and from our work that the differences in energy among the various packing modes seen are small and that the actual structures are affected significantly by the weak interactions as well as the strong ones, with the probable consequence that the structures of $AgXL_n$ complexes are unpredictable.

The complexes of one silver chloride with three mtu,[14] silver iodide with three *N,N′*-diethylthioureas,[15] and silver hydrogen sulfide with three 1,1-diethyl-3-benzoylthioureas[16] all form discrete tetrahedral molecules that have no analogues in these silver cyanide complexes. The complexes of silver thiocyanate with two tu[17] or with two etu[18] both form isolated trigonal molecules, again with no analogues in these silver cyanide complexes. The compound of silver nitrate with three 1-methyl-2-imidazolidinethiones[19] forms a salt with a trigonal silver cation, also with no analogue here.

Comparison of Cu and Ag Analogues. Previously we reported the structures of five CuCN complexes with various thioureas.[1] In Table 5 these previous results are compared with

---

(10) Vizzini, E. A.; Taylor, I. F.; Amma, E. L. *Inorg. Chem.* **1968**, *7*, 1351.

(11) Udupa, M. R.; Krebs, B. *Inorg. Chim. Acta* **1973**, *7*, 271.

(12) Battaglia, L. P.; Corradi, A. B.; Mardelli, M. *Croat. Chem. Acta* **1984**, *57*, 545.

(13) Pakawatchai, C.; Kandasamy, S.; Fun, H.-K. *Acta Crystallogr.* **1996**, *C52*, 1954.

(14) Lee, T. C.; Amma, E. L. *J. Cryst. Mol. Struct.* **1972**, *2*, 125.

(15) Fun, H.-K.; Razak, I. A.; Pakawatchai, C.; Khaokong, C.; Chantrapromma, S.; Saithong, S. *Acta Crystallogr.* **1998**, *C54*, 453.

(16) Braun, U.; Richter, R.; Sieler, J.; Yanofsky, A. I.; Struchkov, Yu. T. *Z. Anorg. Allg. Chem.* **1976**, *529*, 201.

(17) Udupa, M. R.; Henkel, G.; Krebs, B. *Inorg. Chim. Acta* **1976**, *10*, 571.

(18) Ferrari, M. B.; Fava, G. G.; Tani, M. E. V. *Cryst. Struct. Commun.* **1981**, *10*, 571.

(19) Casas, J. S.; Martinez, E. G.; Sanchez, A.; Gonzalez, A. S.; Sordo, J.; Casellato, U.; Graziani, R. *Inorg. Chim. Acta* **1996**, *241*, 117.

Table 4. S Bridges Connecting Two Ag

compound	Ag−S−Ag	Ag−S, Å	S−Ag, Å	Ag−Ag, Å	Ag−S−Ag, deg	type of bridge[a]	ref
1a[b]	Ag1−S1−Ag1′	2.58	2.67	3.62	87	1	this
	Ag1′−S1−Ag″	2.67	2.80	3.96	92	2i	
	Ag″-S1−Ag1	2.80	2.58	5.06	140	1	
1b	Ag1−S2−Ag2	2.59	2.78	3.88	92	1	this
	Ag2−S4−Ag1′	2.66	2.89	4.07	94	1	
2	Ag1−S1−Ag1′	2.50	2.64	4.11	106	1	this
3	Ag1−S1−Ag2	2.50	3.14	3.12	66	2m	this
5	Ag1−S1−Ag2	2.59	2.73	3.20	74	1	this
	Ag1−S2−Ag1′	2.62	2.70	3.14	72	2i	
AgCl(tu)$_2$	Ag2−S2−Ag1	2.48	2.53	3.13	77	1	11
	Ag2′−S3−Ag1	2.54	2.59	4.71	133	1	
AgCl(etu)$_2$	Ag1−S2−Ag1′	2.55	2.66	4.45	118	1	13
AgNO$_3$L$_2$ [c]	Ag1−S1−Ag2	2.41	3.05	3.14	69	2i[d]	*e*
	Ag2−S3−Ag1	2.41	3.03	3.14	69	2i[d]	
AgClO$_4$(dmtu)$_2$	Ag1−S1−Ag1′	2.54	2.73	3.21	75	2i	14
	Ag1″−S2−Ag1	2.59	2.60	3.21	77	2i	
AgClO$_4$(dmtu)$_3$	Ag1−S1−Ag1′	2.64	2.67	3.31	77	2i	14
AgClO$_4$(tu)$_3$	Ag−S1−Ag′	2.66	2.68	2.85	64	22	12

[a] 1 = single S; 2i = two S related by a center of symmetry; 2m = two S related by a mirror; 22 = two S related by a 2-fold axis. [b] The S in **1a** is bonded to three Ag. [c] L = *N*-(diethylaminothiocarbonyl)benzamidine-S. [d] The two Ag and two S are only related by a pseudocenter. [e] Braun, U.; Sieler, J.; Richter, R.; Hettich, B.; Simon, A. *Z. Anorg. Allg. Chem.* **1988**, *557*, 134.

Table 5. Comparison of the (CuCN)$_m$L$_n$ and (AgCN)$_m$L$_n$ Structures[a]

	(CuCN)$_m$L$_n$				(AgCN)$_m$L$_n$			
L	*m*/*n*	Cu coord	CN coord	S coord	*m*/*n*	Ag coord	CN coord	S coord
tu	2/3	CuS$_3$(CN) [2]	CuCN CuCNCu	Cu$_2$S [2]	1/1	AgS$_3$(CN)	AgCN	Ag$_3$S
					1/2	AgS$_3$(CN) [2]	AgCN [2]	AgS [2] Ag$_2$S [2]
mtu	no crystals				1/1	AgS$_2$(CN)$_2$	Ag$_2$CN	Ag$_2$S
dmtu	3/2	CuS$_2$(CN)$_2$ CuS(CN)$_2$ [2]	CuCNCu [3]	Cu$_2$S [2]	1/1	AgS$_2$(CN)$_2$ Ag(CN)$_2$S$_2$	AgCNAg AgCNAg	Ag$_2$S
tmtu	1/1	CuS(CN)$_2$	CuCNCu	CuS	1/1	AgS(CN)$_2$	AgCNAg	AgS
	1/1[b]	CuS(CN)$_2$ [4]	CuCNCu [4]	CuS [4]				
etu	2/1	CuS(CN)$_2$ [2]	CuCNCu [2]	Cu$_2$S	1/1	AgS$_3$(CN) AgS(CN)$_2$	AgCNAg AgCN	Ag$_2$S [2]
detu	2/1	CuS(CN)$_2$[2]	CuCNCu [2]	Cu$_2$S	no crystals			

[a] Numbers in brackets tell how many crystallographically independent times the arrangement occurs. [b] There are two polymorphs of CuCN(tmtu).

those found in this work. With four thioureas, crystalline complexes were found for both metals. In one case, with tmtu, the silver complex was isomorphous with the copper complex. For the other three, not only were the complexes not isomorphous, they did not have the same ratio of MCN to thiourea. Some general differences can be seen. For Cu, three-coordinate Cu was slightly more common than four-coordinate; for Ag, four-coordinate Ag was found in every case, although the details of the coordination varied significantly. With Cu, the CN group was generally involved in a Cu−CN−Cu bridge; with Ag, terminal CN groups (Ag−CN) were as common as bridging. These terminal groups were hydrogen-bonded to thiourea (N)H atoms. In one case, with mtu, there was an Ag$_2$CN bridge; while this has no counterpart in the CuCN/thiourea complexes, similar Cu$_2$CN bridges were found in some CuCN/diamine complexes.[8] With Cu, the S was bonded to one or two Cu; with Ag, the S was bonded to one, two, or three Ag. In retrospect, it seems surprising that even one isomorphic pair of compounds was found.

Acknowledgment. We are indebted to 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: X-ray crystallographic files in CIF format for the structure determinations of **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC990859L