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Crystal Structures of Two New Complexes Produced by Reaction of Copper(I) Cyanide with Thioacetamide. *In Situ* Formation of the Thiosulfate Anion

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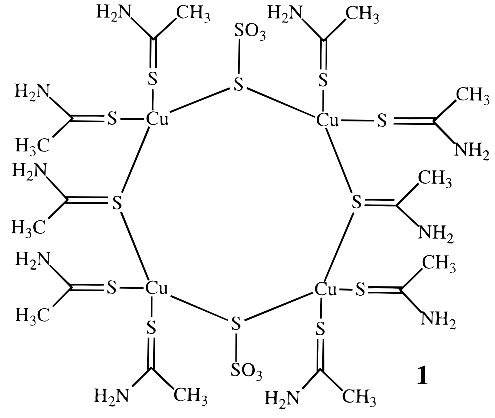
An attempt to synthesize a complex between copper(I) cyanide and thioacetamide (ta) by a direct combination in aqueous solution, surprisingly, produced instead $Cu_4(S_2O_3)_2(ta)_{10}\cdot ta$ (**1**), a complex lacking cyanide but including thiosulfate. We know of no precedent for the production of thiosulfate from an aqueous solution of ta. Using a new synthetic approach, a complex of CuCN and ta was subsequently prepared—(CuCN)(ta), **2**. In the new method, which has been found to be widely applicable to water-soluble ligands, CuCN is made "available" for coordination by dissolving it in aqueous sodium thiosulfate. Complex **1** crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with unit cell dimensions $a = 10.139(3)$ Å, $b = 12.230(4)$ Å, $c = 12.665(4)$ Å, $\alpha = 85.20(2)°$, $\beta = 67.32(2)°$, $\gamma = 68.47(2)°$, $V = 1345(2)$ Å^3, and $Z = 2$. Complex **2** crystallizes in the orthorhombic space group $Pna2_1$ (No. 33) with unit cell dimensions $a = 6.993(9)$ Å, $b = 8.744(3)$ Å, $c = 9.372(6)$ Å, $V = 573(1)$ Å^3, and $Z = 4$. Some possible pathways for the production of thiosulfate are discussed.

Introduction

During an extended research project which involved the synthesis of a family of complexes of copper cyanide with thiourea and several substituted thioureas,[1] we became interested in reactions of other thioamides with copper cyanide. We found, from a review of the literature, that thioacetamide was the most frequently studied thioamide outside of the thioureas themselves.

Our experimental work attempting a direct combination of thioacetamide (ta) and CuCN in aqueous media provided an unexpected outcome. The stable, pale-yellow, crystalline complex isolated was found to contain ta and Cu(I), but surprisingly, thiosulfate was present instead of cyanide. Somehow, sulfur had been released from ta and had been air-oxidized to thiosulfate. The reaction leading to $Cu_4(S_2O_3)_2(ta)_{10}\cdot ta$, **1**, is shown in Scheme 1.



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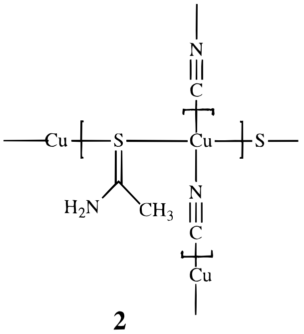
After we found from a literature search that little was known about copper(I) complexes containing thiosulfate, we began an experimental study of reactions of various copper(I) salts with sodium thiosulfate. During these investigations, we discovered that certain aqueous solutions of sodium thiosulfate that were nearly saturated with copper cyanide would not only deposit a new crystalline complex if left undisturbed but also acted as convenient sources of "available" copper cyanide, ready to form crystalline complexes with a variety of suitable, soluble ligands. (A paper providing details about the complex and about this new, convenient pathway to copper cyanide complexes will soon be submitted for publication.) It seemed probable to us that a reaction of thioacetamide with the aqueous copper cyanide/sodium thiosulfate system would provide an alternative pathway to **1**. After conducting the reaction and isolating the crystalline complex, we were, therefore, surprised to discover that it contained Cu(I), cyanide, and ta but *not* thiosulfate! The molecular formula proved to be (CuCN)(ta) (**2**), and therefore this complex was consistent with the type of complex we had expected initially when reacting CuCN and ta but had not found. The reaction pathway is outlined in Scheme 2. These reactions seemed to us, at this point, to represent a paradox; when thiosulfate was *not* provided as a reactant, it *did* appear in the product, and when it *was* provided as a reactant, it *did not* appear in the product.

Scheme 1

$$2CuCN + ta_{satd\ aq} \xrightarrow{[O]} Cu_4(S_2O_3)_2(ta)_{10}\cdot ta$$

Scheme 2

$$CuCN + ta \xrightarrow[H_2O]{Na_2S_2O_3} (CuCN)(ta)$$



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Later, an experimental variant of Scheme 1 showed that it was possible to produce a mixture of **1** and **2**. This occurred

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

(1) A paper describing this research has been submitted for publication.

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Scheme 3

$$3\mathrm{CuCN} + \mathrm{ta}_{\mathrm{satd\ aq}} \xrightarrow{[\mathrm{O}]} (\mathrm{CuCN})(\mathrm{ta}) + \mathrm{Cu}_4(\mathrm{S}_2\mathrm{O}_3)_2(\mathrm{ta})_{10}\cdot(\mathrm{ta})$$

when the CuCN loading, relative to the original experiment, was increased by 50%, as is shown in Scheme 3. There is a marked difference in stability between **1** and **2**. In the presence of air, **1** is stable indefinitely, whereas **2** begins to show signs of decomposition within 24 h of preparation. In the absence of air, **2** shows no evidence of breakdown.

Experimental Section

General Information. Commercial reagent grade chemicals were used without further purification. Infrared spectra were recorded as KBr pellets with a Perkin-Elmer Model 283 or Model 1430 spectrometer. Elemental analyses were determined by either Galbraith Laboratories, Knoxville, TN, or M-H-W Laboratories, Phoenix, AZ. The crystal structures were determined by the X-Ray Service Laboratory, Department of Chemistry, University of Minnesota, Minneapolis, MN.

Preparation of $Cu_4(S_2O_3)_2(ta)_{10}\cdot ta$ (1). To a solution of thioacetamide (3.00 g, 39.9 mmol) in 30 mL of distilled water was added CuCN (180 mg, 2 mmol). Initially the CuCN clumped up into a jelly-like mass that was broken up with a glass stirring rod. Mixing with a magnetic stir bar caused the solid to dissolve slowly, giving a light-yellow solution, which was filtered by gravity. After 2 h, the solution had darkened to a yellow-gray and microscopic black particles were evident (these particles were not removed). The flask (125 mL Erlenmeyer) was arranged to allow for slow evaporation by covering the mouth with filter paper. Over several days, the pale-yellow color returned. Crystal growth began in a few days and was substantial after about 10 days. After 14 days, the transparent yellow, prism-shaped crystals (278 mg, 42.6%) were collected by suction filtration and washed with distilled water. A sample of this product appeared to be unchanged after over a year in storage while exposed to air. IR: 3300 s, br, 3170 s, br, 1635 s, sh, 1620 s, 1464 m, 1402 w, 1372 m, 1307 m, 1172 s, 1142 s, 1008 s, 970 m, 704 s, 628 s, 532 w, 512 w, 463 m, 384 w cm^{-1}. Anal. Calcd for $C_{22}H_{55}Cu_4N_{11}S_{15}O_6$: C, 20.25; H, 4.25; Cu, 19.48; N, 11.81; S, 36.86. Found: C, 20.45; H, 4.58; Cu, 19.54; N, 11.54; S, 36.45.

Preparation of (CuCN)(ta) (2). To a solution of $Na_2S_2O_3\cdot 5H_2O$ (2.482 g, 10 mmol) in 30 mL of distilled water was added CuCN (270 mg, 3 mmol). After the CuCN was dissolved with the aid of a magnetic mixer, thioacetamide (225 mg, 3 mmol) was added. With continued mixing, the thioacetamide soon dissolved to give a clear yellow solution. Shortly thereafter, a pale yellow precipitate formed, which was redissolved by warming the solution on a steam bath. The solution, having a greenish-yellow color, was filtered by gravity to remove a slight amount of brownish precipitate. Over a 10 day period, the stoppered solution deposited the yellow crystalline product (177 mg, 35.8%), which was filtered off by suction and washed with distilled water. This complex had a short shelf-life in air; after 24 h, a barely perceptible darkening of the color was observed, which became very noticeable over several days. Within a few weeks the material became nearly black. When this complex was stored under argon or under a hydrocarbon oil, stability was increased dramatically. In fact, a sample under oil appeared to be unchanged after over a year in storage. IR: 3345 m, 3280 w, 3160 m, 2105 s, 1637 s, 1480 m, 1363 w, 1300 m, 970 m, 705 m, 677 m, 504 w, 458 w cm^{-1}. Anal. Calcd for $C_3H_5CuN_2S$: C, 21.88; H, 3.06; Cu, 38.58; N, 17.01; S, 19.47. Found: C, 21.89; H, 2.89; Cu, 36.85; N, 16.83; S, 19.10.

Preparation of a Mixture of $Cu_4(S_2O_3)_2(ta)_{10}\cdot ta$ (1) and (CuCN)(ta) (2). To a solution of thioacetamide (3.005 g, 40 mmol) was added CuCN (270 mg, 3 mmol). After 45 min of stirring at room temperature with a magnetic mixer, nearly all of the CuCN was dissolved. After about 16 h, an amorphous yellow precipitate was noted, which was redissolved by warming the slurry briefly on the steam bath. During the warming process, the following observations were made: (a) The solution produced fumes with a hydrogen sulfide-like odor (b) The solution darkened from a yellow to an amber color. (c) A small amount of very fine black precipitate was produced. After the latter was removed by filtration, the flask was stoppered and set aside. The first tiny yellow crystals were noted after about 24 h. On the 13th day, a product mixture was isolated that consisted of 131 mg (26.5%) of **2** and 23 mg (2.3%) of **1.** The latter appeared as two large transparent yellow prism crystals, which were easily separated from the bulk of the product. Each product was identified by comparing its IR spectrum with that of an authentic sample.

Table 1. Summary of X-ray Diffraction Data[a]

	$Cu_4(S_2O_3)_2(ta)_{10}\cdot ta$ (**1**)	(CuCN)(ta) (**2**)
formula	$Cu_4C_{22}N_{11}S_{15}O_6H_{55}$	$CuC_3H_5N_2S$
fw	1304.84	164.69
space group	$P\bar{1}$ (No. 2)	$Pna2_1$ (No. 33)
a, Å	10.139(3)	6.993(9)
b, Å	12.230(4)	8.744(3)
c, Å	12.665(4)	9.372(6)
α, deg	85.20(2)	90.0
β, deg	67.32(2)	90.0
γ, deg	68.47(2)	90.0
V, Å^3	1345(2)	573(1)
Z	1	4
D(calcd), g/cm^3	1.611	1.909
temp, °C	22	−101
μ, cm^{-1}	21.68	40.41
R^b	0.050	0.032
$R_w{}^c$	0.062	0.035
transm factors	0.85−1.10	0.70−1.50

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

General Procedures for X-ray Structure Determinations. The crystals were mounted on a glass fiber, and measurements were made on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$). The intensities of three representative reflections, which were measured after every 60−75 min of X-ray exposure time, remained constant throughout data collection, indicating crystal and instrumental stability (no decay corrections were applied). The data were corrected for Lorentz and polarization effects. Crystallographic data for **1** and **2** are presented in Table 1. The structures were solved by direct methods using the programs MITHRIL[2] and DIRDIF.[3] The neutral-atom scattering factors used include correction for the real and imaginary components of anomalous dispersion.[4] All calculations were performed using the TEXSAN[5] crystallographic software package.

The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation in idealized positions that most closely corresponded to peaks on the difference Fourier map and were assigned isotropic thermal parameters 20% greater than the B_{eq} values of the atoms to which they were bonded. The atomic coordinates and isotropic displacement parameters for the non-hydrogen atoms of **1** and **2** are presented in the Supporting Information. Table 2 contains selected bond distances and bond angles for **1** and **2**.

X-ray Structure Determination of $Cu_4(S_2O_3)_2(ta)_{10}\cdot ta$ (1). A yellow prismatic crystal of **1** having approximate dimensions 0.60 × 0.50 × 0.40 mm was mounted on a glass fiber. Cell constants were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $23 < 2\theta < 45°$ and were found to correspond to a triclinic cell. The space group was shown to be $P\bar{1}$ (No. 2) by the eventual solution of the structure. The occupancy for O21, O22, O23 was 0.822(6), and that for O24, O25, O26 was 0.178(6). The data were collected at a temperature of 22 ± 1 °C using the $\omega-2\theta$ scan technique to a maximum 2θ value of 59.9°.

Of the 7803 unique reflections, the 5559 with $I > 2.00\sigma(I)$ were used in the calculations. The linear absorption coefficient for Mo Kα is 21.7 cm^{-1}. An empirical absorption correction, using the program

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

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

(4) (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.

(5) *TEXSAN-TEXRAY Structure Analysis Package*; Molecular Structure Corporation.: The Woodlands, TX, 1985.

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

bond angles		bond distances	
	A. $Cu_4(S_2O_3)_2(ta)_{10}$·ta (**1**)		
S1−Cu1−S3	105.21(5)	Cu1−S1	2.353(2)
S1−Cu1−S4	113.24(6)	Cu1−S3	2.320(1)
S1−Cu1−S5	105.14(5)	Cu1−S4	2.313(2)
S3−Cu1−S4	108.32(5)	Cu1−S5	2.300(2)
S3−Cu1−S5	109.76(6)		
S4−Cu1−S5	114.73(5)		
S1−Cu2−S3	95.57(5)	Cu2−S1	2.339(1)
S1−Cu2−S6	119.47(5)	Cu2−S3	2.381(2)
S1−Cu2−S7	123.37(5)	Cu2−S6	2.299(2)
S3−Cu2−S6	102.64(6)	Cu2−S7	2.302(1)
S3−Cu2−S7	111.99(6)		
S6−Cu2−S7	101.97(5)		
	B. (CuCN)(ta) (**2**)		
N1−Cu-C2	139.3(2)	Cu-N1	1.924(5)
N1−Cu−S1	112.4(2)	Cu-N2	1.942(5)
C2−Cu−S1	103.9(2)	Cu−S1	2.345(2)
		Cu−S1′	2.708(4)

DIFABS,[6] was applied, which resulted in correction factors ranging from 0.85 to 1.10. A correction for secondary extinction was applied (coefficient = 0.52750E−06).

X-ray Structure Determination of (CuCN)(ta) (2). A light-yellow platelike crystal of **2** having approximate dimensions 0.55 × 0.26 × 0.06 mm was mounted on a glass fiber. Cell constants were obtained from a least-squares refinement using the setting angles of 24 carefully centered reflections in the range $23 < 2\theta < 58°$ and were found to correspond to an orthorhombic cell. Systematic absences were consistent with space group $Pna2_1$ (No. 33) or *Pnam*. The former was shown to be correct by the eventual solution of the structure. Refinement for the structure reported converged with $R = 0.0319$ and $R_w = 0.0347$. Refinement using the other polarity converged with $R = 0.0324$ and $R_w = 0.0352$. Refinement of the occupancies for N1 and C2 converged at 0.90(6). This is not significantly different from complete order, so in the final refinement, the CN group was treated as completely ordered. The data were collected at a temperature of −101 ± 1 °C using the $\omega-2\theta$ scan technique to a maximum 2θ value of 60.1°.

Of the 1008 unique reflections, the 747 with $I > 2.00\sigma(I)$ were used in the calculations. The linear absorption coefficient for Mo Kα is 40.4 cm^{-1}. An empirical absorption correction, using the program DIFABS, was applied, which resulted in correction factors ranging from 0.70 to 1.50.

Discussion

Only a few crystal structures have been reported for copper(I) complexes containing thioacetamide or thiosulfate ligands. The complex $[Cu(ta)_4]Cl$ has a straightforward tetrahedral structure[7] for the $Cu(ta)_4{}^+$ ion. The structure of [Cu(ta)]Cl contains six-atom rings made up of alternating copper and sulfur atoms with a chlorine atom attached to each copper.[8] The geometry at each copper site is approximately trigonal planar. A single example of a copper(I) complex containing thiosulfate coordination is found in $Na_4[Cu^{II}(NH_3)_4][Cu^{I}(S_2O_3)_2]_2$, which contains infinite chains of ---CuS_2Cu--- with tetrahedral coordination about the Cu and four-atom Cu_2S_2 rings.[9]

The preliminary work on the X-ray crystal structure of **1** showed it to be $Cu_2(S_2O_3)(ta)_5$. There was a question as to whether water or some other molecule was also present in a disordered state. To resolve the question, a complete sphere of data were collected out to 30°.

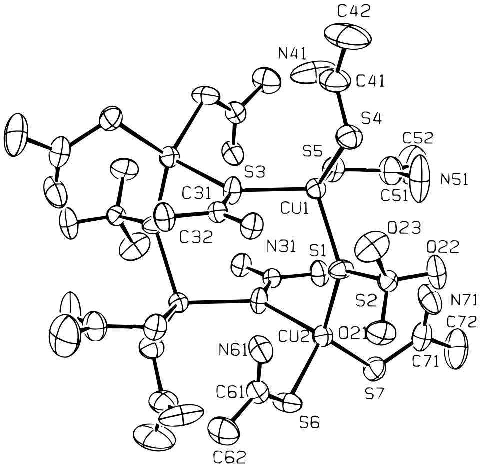

Figure 1. ORTEP plot of the structure of $Cu_4(S_2O_3)_2(ta)_{10}$·ta, **1**, showing the atom-labeling scheme and 50% probability ellipsoids. Hydrogen atoms are given arbitrary radii. Only the major component of the disordered SO_3 groups is shown.

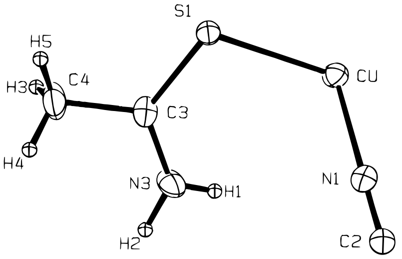

Figure 2. ORTEP plot of the structure of (CuCN)(ta), **2**, showing the atom-labeling scheme and 50% probability ellipsoids. Hydrogen atoms are given arbitrary radii.

The crystal of **1** consists of discrete $Cu_4(S_2O_3)_2(ta)_{10}$ units and uncoordinated thioacetamides. If the Cu_4 units are centered at 0, 0, 0, the extra thioacetamide is disordered on a center at 0, $^1/_2$, $^1/_2$. Figure 1 shows that the Cu_4 unit is based on an eight-membered ring of alternate Cu and S atoms, with two S atoms from thiosulfate and two from thioacetamide. The remaining eight thioacetamides are bound to the four Cu atoms as monodentate ligands, making all the Cu sites four-coordinate. The thiosulfate group bridges two Cu atoms through the terminal S atom. The SO_3 group is disordered by a 60° rotation about the S−S axis. The major orientation has a fractional occupancy of 0.822(6) and is the one shown in the figure. The O atoms in the major component were refined anisotropically; the O atoms in the minor component, isotropically.

The extra thioacetamide lies on a center of symmetry, so it must be disordered. In fact, it seems to occur with four different orientations, two pairs each related by the center. When the independent orientations were refined with variable occupancies, the refinement converged with the same occupancy for each orientation within experimental error. In view of the disorder, the extra thioacetamide was treated as a rigid group, with bond lengths and angles taken as the average values of those found in the five molecules bound to the Cu atoms.

As can be seen in Figures 2 and 3, the structure of **2** consists of infinite chains of ---Cu−CN−Cu−CN--- with nonbridging S from ta coordinated at each Cu with a Cu−S distance of 2.345(2) Å. There is, however, a Cu−S distance of 2.708(4) Å to a S atom in an adjacent chain, which makes the coordination around the Cu distorted tetrahedral.[10] Alternate Cu atoms in a particular chain for these contacts to S atoms are

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(6) DIFABS: Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.

(7) Truter, M. R.; Rutherford, K. W. *J. Chem. Soc.* **1962**, 1748.

(8) De Ranter, C. J.; Rolies, M. *Cryst. Struct. Commun.* **1977**, *6*, 399.

(9) Ferrari, A.; Braibanti, A.; Tiripicchio, A. *Acta Crystallogr.* **1966**, *21*, 605.

(10) We are indebted to a reviewer for calling our attention to this contact.

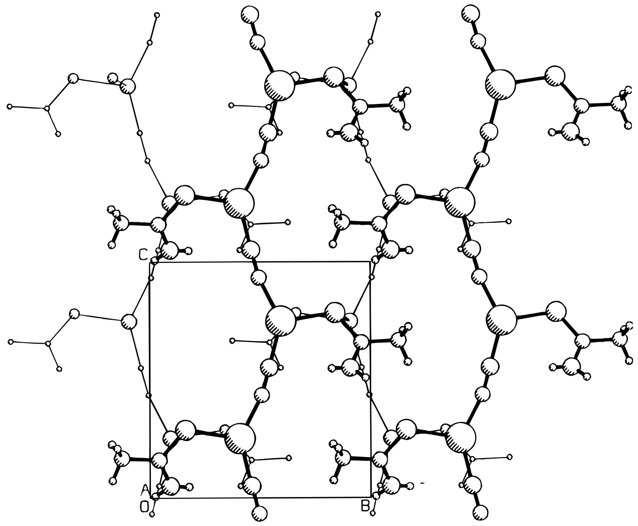

Figure 3. The extended structure of (CuCN)(ta), **2**. The view is normal to the *bc* plane. $(CuCN)_n$ chains occur parallel to the *c* axis. A thioacetamide molecule attached through a Cu−S bond completes an apparent 3-fold coordination around the Cu. There is, however, a weaker (longer) Cu−S bond roughly parallel to the *a* axis, which makes the Cu coordination tetrahedral and which leads to an overall three-dimensional structure. In the figure, two chains attached through these weaker bonds are shown with light lines.

on opposite sides of the first chain, leading to a three-dimensional structure. If we focus only on the Cu atoms, with each Cu bonded to four other Cu atoms through two CN bridges and two S bridges, the connectivity of the Cu atoms is the same as the connectivity of the carbon atoms in the diamond structure.

The spontaneous production of the thiosulfate anion in a neutral, aqueous, room-temperature solution of CuCN and thioacetamide was totally unexpected. We were well aware of the long established use of thioacetamide in qualitative analysis[11] as a source of hydrogen sulfide, which is used for the pH-dependent, selective precipitation of metal sulfides. The hydrolysis of ta in acidic or neutral conditions is described by the following equation:

$$CH_3CSNH_2 + H_2O \rightarrow CH_3CONH_2 + H_2S$$

Aqueous solutions of pure thioacetamide (typically 8−10%) have been found to be stable for months at room temperature, and the hydrolysis procedure to generate hydrogen sulfide is ordinarily conducted at temperatures above 80 °C. Some metal sulfides are believed to form by an alternative pathway that is initiated by the formation of a coordination complex between ta and the metal, which subsequently decomposes giving the metal sulfide directly.[12] These considerations have led us to believe that the complex (CuCN)(ta) in solution has the potential (1) to be air-oxidized directly or (2) to produce sulfide, either in the form of hydrogen sulfide or as copper sulfide (presumably Cu_2S). The literature of thiosulfate chemistry[13] reveals that air oxidation of the sulfide, hydrogen sulfide, or polysulfide salts of sodium or calcium produces the respective thiosulfate salts. Some examples are shown in the following equations:

$$2Na_2S + 2O_2 + H_2O \rightarrow Na_2S_2O_3 + 2NaOH$$

$$2NaHS + 2O_2 \rightarrow Na_2S_2O_3 + H_2O$$

$$2CaS_5 + 3O_2 \rightarrow 2CaS_2O_3 + 6S$$

Examples can also be found where thiosulfate was produced either by the reaction of sulfites and free sulfur or by the reaction of hydrogen sulfide and sulfur trioxide at low temperature:

$$SO_3^{2-} + S \rightarrow S_2O_3^{2-}$$

$$H_2S + SO_3 \rightarrow H_2S_2O_3$$

Pathways that might lead to the appearance of sulfur trioxide or of sulfites (the latter presumably dependent on the appearance of sulfur dioxide) in the ta/CuCN solution employed in this research are not easy to rationalize.

The observation that pure, solid (CuCN)(ta) (**2**) is sensitive to the atmosphere and becomes black over time suggests to us that it has a tendency to decompose into copper sulfide. During the preparation of **1** from a solution of CuCN in aqueous ta, the transitory appearance of both a fine black precipitate and a gray coloration to the solution suggests that dissolved **2** may also have a tendency to break down into copper sulfide. The latter is presumably susceptible to air oxidation, slowly producing $Cu_2S_2O_3$, which would then respond to the high concentration of ta by undergoing complexation to form insoluble $Cu_4(S_2O_3)_2(ta)_{10}\cdot ta$ (**1**). The fact that substantial amounts of black precipitate never accumulated could be explained by a slow but steady rate of oxidation of copper sulfide (causing its dissolution) that was approximately equal to the rate of its production.

An alternative explanation of thiosulfate production could be based on a direct air oxidation of the (CuCN)(ta) complex. In such a pathway, the sulfur atom coordinated to copper would undergo oxidation either prior to or simultaneous with the scission of the thioacetamide C−S bond. Of course, such a pathway would not require the formation of copper sulfide. To gain a better understanding of the actual reaction pathway used in the preparation of **1**, a prolonged and detailed study of the process would be required. Such a study was beyond the scope of our project, which was limited to the synthesis of new copper(I) complexes.

In our laboratories during the last few years, we have prepared over two dozen new copper(I) complexes using CuCN and various ligands. Among all of the new complexes we have synthesized, only **1** and one other complex failed to contain cyanide. In the latter case, when thiocyanate was shown to be present in the complex,[14] it was clear that it had been produced by a reaction of cyanide and thiosulfate, the latter being the only sulfur-containing species present. Examples of analogous reactions have been reported in the literature.[15] In the preparation of **1**, we, likewise, believe that cyanide is lost through its reaction with the newly formed thiosulfate. Any thiocyanate formed in this instance is not incorporated into the structure of the insoluble complex.

With the help of the literature, we have been able to make assignments for Cu−S absorptions in the infrared spectra of

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(11) (a) Barber, H. H.; Grzeskowiak, E. *Anal. Chem.* **1949**, *21*, 192. (b) Rosenthal, D.; Taylor, T. I. *J. Am. Chem. Soc.* **1960**, *82*, 4169. (c) Clifford, A. F. *Inorganic Chemistry of Qualitative Analysis*; Prentice-Hall, Inc.: Englewood Cliffs, NJ, 1961; pp 148−150.

(12) See ref 11b.

(13) (a) Schmidt, M.; Siebert, W. In *Comprehensive Inorganic Chemistry*; Bailar, J. C., Jr., Emeléus, H. J., Nyholm, R., Trotman-Dickenson, A. F., Eds.; Pergamon Press: Oxford, England, 1974; Vol. 2, pp 884−887. (b) Remy, H. In *Treatise on Inorganic Chemistry*; Kleinberg, J., Ed.: Elsevier: New York, 1960; Vol. 1, pp 720−721. (c) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, England, 1984; pp 846−848. (d) Brasted, R. C. *Comprehensive Inorganic Chemistry*; Van Nostrand: New York, 1961; Vol. VIII, pp 158−165.

(14) Unpublished work by the authors. A crystal structure proved the presence of thiocyanate.

(15) See ref 13a, p 887.

the two complexes. In the infrared spectrum of **1**, the strong peak at 1172 cm^{-1} correlates with thiosulfate S-bridging as reported by Freedman and Straughan,[16] and the strong peak at 704 cm^{-1} correlates with thioacetamide S-coordination as reported by Iyengar *et al.*[17] The 705 cm^{-1} peak of medium intensity in the IR spectrum of **2** is, likewise, attributable to thioacetamide S-coordination.

Acknowledgment. The authors are indebted to Professor Doyle Britton, X-Ray Service Laboratory, University of Minnesota, for determining the crystal structures and for reading this paper and providing helpful comments. We are also grateful 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: Tables of additional X-ray experimental details, atomic positional parameters and equivalent isotropic displacement parameters, anisotropic displacement parameters, bond distances and angles, intermolecular distances, and torsion or conformation angles for **1** and **2** (13 pages). Ordering information is given on any current masthead page.

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(16) Freedman, A. N.; Straughan, B. P. *Spectrochim. Acta* **1971**, *27A*, 1455.

(17) Iyengar, R. R.; Sathyanarayana, D. N.; Patel, C. C. *J. Inorg. Nucl. Chem.* **1972**, *34*, 1088.