Contribution from the Department of Physical Chemistry and the School of
Biological Technology, University of New South Wales, Kensington, New South Wales, 2033, Australia

A New Series of Polynuclear Copper Dithiocarbamate–Copper Halide Polymers

R. M. GOLDING,* A. D. RAE, B. J. RALPH, and L. SULLIGOI

Two polymeric complexes of the type $Cu(pipdtc)_2(CuBr)_n$,[1] where $n = 4$ and 6, and the chloride complex $Cu(pipdtc)_2$-$(CuCl)_4$ have been prepared by the reaction of solutions of bis(piperidyldithiocarbamato)copper(II) (abbreviated to $Cu(pip$-$dtc)_2$) and copper(II) halide in a chloroform–ethanol mixture. These structures consist of polymeric sheets of individual $Cu(pipdtc)_2$ molecules linked to polymeric CuBr chains via Cu–S bonds. All three compounds crystallize in the monoclinic space group $C2/m$ with 2 formula units per unit cell. The compounds $Cu(pipdtc)_2(CuX)_4$ (X = Cl, Br) are isomorphous and the room-temperature crystal structures of $Cu(pipdtc)_2(CuBr)_n$ ($n = 4$, 6) have been determined by the least-squares refinement of $\Sigma w(\Delta F_0)^2$. Intensity data and unit cell dimensions were obtained on a Siemens automatic single-crystal diffractometer using Cu Kα radiation and Ni filters and attenuators. $Cu(pipdtc)_2(CuBr)_4$ has unit cell dimensions $a = 17.108$ (3) A, $b = 6.904$ (1) A, $c = 10.203$ (2) A, and $\beta = 102.5$ (2)° and was refined to a value of $R = \Sigma |\Delta F_0|/\Sigma |F_0| = 0.034$ for a total 1223 nonequivalent reflections, including unobserved reflections. $Cu(pipdtc)_2(CuBr)_6$ has unit cell dimensions $a = 13.796$ (4) A, $b = 6.839$ (2) A, $c = 13.813$ (4) A, and $\beta = 95.5$ (2)° and was refined to a value of $R = 0.047$ for a total 1346 nonequivalent reflections, including unobserved reflections. A Cu atom is disordered over three sites in this latter structure.

Introduction

The present investigation was initiated to study the reactions of copper(II) halides with bis(piperidyldithiocarbamato)copper(II) in an attempt to synthesize and characterize sulfur-bridged polynuclear complexes containing copper. It was hoped that any such polynuclear copper dithiocarbamate complexes would serve as mineral analogs and provide a model in our present studies of sulfide mineral degradation by microorganisms. Many polynuclear complexes have been characterized,[2-6] but as yet very few complexes containing the same metal ion in two apparently different oxidation states have been reported.[7]

Recently a number of new dithiocarbamate complexes have been reported.[8-21] Some of these complexes appear to contain metals with quite high oxidation numbers (Cu[III],[8,15,19] Cu[IV],[8,15] Ni[III],[21] Ni[IV],[8,10,13,15,19] and Fe[IV],[19,20]). It should be noted however that these oxidation numbers are

(1) dtc = dithiocarbamate; pip = piperidyl.
(2) (a) R. M. King, *Progr. Inorg. Chem.*, 15, 287 (1972); (b) T. W. Thomas and A. E. Underhill, *Chem. Soc. Rev.*, 1, 99 (1972).
(3) W. E. Hatfield and R. Whyman, *Transition Metal Chem.*, 5, 47 (1969).
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(14) P. T. Beurskens, J. A. Cras, J. H. Noordik, and A. M. Spruyt, *J. Cryst. Mol. Struct.*, 1, 93 (1971).
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(16) J. G. M. van der Linden, *Recl. Trav. Chim. Pays-Bas*, 90, 1027 (1971).
(17) J. G. M. van der Linden and H. G. J. van der Roer, *Inorg. Chim. Acta*, 5, 254 (1971).
(18) H. C. Brinkhoff and J. M. A. Dautzenberg, *Recl. Trav. Chim. Pays-Bas*, 11, 117 (1972).
(19) R. M. Golding, C. M. Harris, K. J. Jessop, and W. C. Tennant, *Aust. J. Chem.*, 25, 2567 (1972).
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(21) J. Willemse, P. H. F. M. Rouwette, and J. A. Cras, *Inorg. Nucl. Chem. Lett.*, 8, 389 (1972).

of formal significance only as the actual oxidation state of the metal is probably lower.[10,15] The dithiocarbamate ligand can stabilize a high oxidation state system by (1) delocalization of the charge[22]

and (2) formation of thiuram disulfide by ligand oxidation
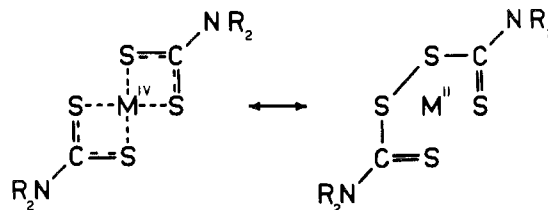
as has been shown in complexes of the type $M(dtc)_2X_2$ (M = Zn, Cd, or Hg)[11,14] and has been suggested to be a resonance structure in $Ni(Bu_2dtc)_3Br$.[10] In addition the dithiocarbamate ligand may be oxidized to a positive ion containing an s-tetrathiane ring
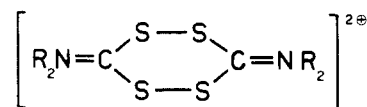
as has been suggested in the cases of $Fe(dtc)Cl_4$ and $Cu(dtc)$-X_3 (X = Br, Cl).[9] In a previous paper[19] we studied the reactions and products for several metal salt–metal dithiocarbamate systems and some of the results are summarized in Table I. In all but one of the examples given in the table the formal oxidation state of the metal ion of the metal dithiocarbamate has been increased. However, it was reported that the reaction of copper(II) halides with copper(II) dithiocarbamates involved the formation of polymeric species and in this paper the synthesis and the crystal structure analysis of two of these complexes is presented.

Experimental Section

(a) **Measurements.** Copper assays were carried out gravimetrically by digestion into hot nitric acid and precipitation of the copper as the ethylenediamine mercuriiodide.[23]

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(23) A. I. Vogel, "Quantitative Inorganic Analysis," 3rd ed, Longmans, Green and Co., London, 1962, p 499.

Table I. Reactions and Products for Several Metal Salt–Metal Dithiocarbamate Systems

Metal dithiocarbamate (benzene or chloroform soln)	Metal salt (alcohol or acetone)	Dithiocarbamate complex	Formal oxidn state
Copper(II)	FeCl₃	Cu(dtc)₂FeCl₄	Copper(III)
	Fe(ClO₄)₃·6H₂O	Cu(dtc)₂ClO₄	Copper(III)
	Cu(ClO₄)₂·6H₂O	Cu(dtc)₂ClO₄	Copper(III)
Nickel(II)	FeCl₃	Ni(dtc)₃FeCl₄	Nickel(IV)
	Fe(ClO₄)₃·6H₂O	Ni(dtc)₃ClO₄	Nickel(IV)
Iron(III)	FeCl₃ (ether soln)	Fe(dtc)₂Cl	Iron(III)
		Fe(dtc)₃FeCl₄	Iron(IV)
	Fe(ClO₄)₃	Fe(dtc)₃ClO₄	Iron(IV)

Infrared spectra were from paraffin mulls in the range 200–2000 cm⁻¹ on a Perkin-Elmer 521 recording spectrophotometer.

(b) **Preparation of Complexes.** Bis(piperidyldithiocarbamato)-copper(II) was prepared as follows. Copper(II) nitrate (0.05 mol) was dissolved in water (150 ml) and 15 *M* ammonia solution (0.1 mol) was added while stirring. Piperidine (0.1 mol) and carbon disulfide (0.1 mol) were added and the mixture was stirred well for 1 hr. The precipitate was filtered off, washed with water, and air-dried. The crude bis(piperidyldithiocarbamato)copper(II) was recrystallized from hot chloroform; yield 80%.

Cu(pipdtc)₂(CuX)ₙ. Copper(II) halide (0.01 mol) in absolute ethanol (100 ml) was diluted with dry chloroform (4 l.) and added while stirring to bis(piperidyldithiocarbamato)copper(II) (0.2 mol) in dry chloroform (4 l.). The mixture was allowed to stand for 7 days at room temperature, washed with ethanol and chloroform, and dried over silica gel. This yields 1–2 g of good-quality crystals of the complex Cu(pipdtc)₂(CuX)₄ (where X = Br, Cl). The bromine and chlorine analogs form isomorphic crystals.

If the total volume of the reaction mixture was decreased from 8 l. to 3 l., two easily distinguished crystal compounds were obtained.

As yet no method has been found for the preparation of pure samples of Cu(pipdtc)₂(CuBr)₆ and hence all subsequent studies other than the crystal structure determination were carried out on Cu(pipdtc)₂(CuBr)₄.

Different preparations were attempted by varying the Cu(pipdtc)₂: CuBr₂ ratio, the halide ion, the dithiocarbamate ligand, and the solvent system but meaningful characterization was hampered by the poor quality of crystals produced and the presence of more than a single crystalline product.

(c) **X-Ray Crystallography.** Approximate density measurements using the flotation method and examination of final electron density maps verified the formulas imposed by the structure determinations.

Intensity data and unit cell dimensions were obtained at 20° on a Siemens automatic single-crystal diffractometer using Cu Kα radiation and Ni filters and attenuators. The integrated intensities were recorded using the four-value method.[24,25] The scanning procedure utilized the moving-crystal, moving-detector method (θ–2θ scan). Nonequivalent data up to $2\theta = 140°$ were collected. At all stages scattering factors[26] were corrected for anomalous dispersion[27] using values of $\Delta f' = -2.15$, -0.96, and 0.31 and $\Delta f'' = 0.75$, 1.46, and 0.58 for Cu, Br, and S, respectively. Extinction corrections[28] were made using an isotropic extinction parameter $R^* = (e^2/mc^2 V)\lambda^3 r^*$ where the modified F_c is given by $F_c{}^* = k |F_c|(1 + 2r^*|F_c|^2\delta)^{-1/4}$ and where

$$\delta = \left(\frac{e^2}{mc^2 V}\right)^2 \left(\frac{\lambda^3}{\sin 2\theta}\right)\left(\frac{1 + \cos^4 2\theta}{1 + \cos^2 2\theta}\right)\overline{T}$$

and $\overline{T}$ is the mean path length (in cm) in the crystal. A value of $R^* = 0.00166$ (4) was obtained for Cu(pipdtc)₂(CuBr)₄ and a value of 0.00028 (2) was obtained for Cu(pipdtc)₂(CuBr)₆.

Intensity data were corrected for absorption effects using a

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(28) A. C. Larson in "Crystallographic Computing," F. R. Ahmed, Ed., Munskgaard, Copenhagen, 1970, p 291.

Table II. Analytical Data (%)

Compd		Cu	C	H	N	S	Br or Cl
Cu(pipdtc)₂(CuBr)₄	Calcd	33.18	15.04	2.09	2.93	13.34	33.37
	Found	34.4	15.61	2.15	2.99	13.70	34.1
Cu(pipdtc)₂(CuCl)₄	Calcd	40.72	18.47	2.58	3.59	16.44	18.60
	Found	40.3	18.62	2.68	3.59		19.0

weighted gaussian grid.[29] The Cu(pipdtc)₂(CuBr)₄ crystal used was bounded by planes at distances from an internal origin of 0.148 mm for (110), (1̄10), (11̄0), and (1̄1̄0), 0.063 mm for (100), 0.125 mm for (1̄00), and 0.016 mm for (001) and (001̄) giving a mean path length in the crystal $\overline{T}$ ranging between 0.003 and 0.012 cm ($\mu \overline{T}$ between 0.5 and 2.0). The Cu(pipdtc)₂(CuBr)₆ crystal used was bounded by planes at distances from an internal origin of 0.075 mm for (110), (1̄10), (11̄0), and (1̄1̄0) and 0.0063 mm for (001) and (001̄) making $\overline{T}$ range between 0.0006 and 0.008 cm ($\mu \overline{T}$ between 0.1 and 1.7). Estimation of errors was from counting statistics. Data with a count above background of less than 3σ were regarded as unobserved and given a value for I of σ and were included in the refinement of $\Sigma w(\Delta F_o)^2$ only if $|F_c| > |F_o|$. Weights of $w = 1/\sigma^2(F_o)$ were used.

Results and Discussion

(a) **Analytical Data.** Analytical data for the chloride and the bromide complexes Cu(pipdtc)₂(CuX)₄ are presented in Table II.

(b) **Chemical Properties.** These polymers are insoluble in all the common solvents including water, chloroform, ethanol, benzene, dioxane, ethyl acetate, and ether. The more polar organic solvents (dimethyl sulfoxide, dimethylformamide, and pyridine) decompose them to produce bis-(piperidyldithiocarbamato)copper(II) and the solvent complex of the copper(I) moieties. They are stable in water at neutral or acid pH but are attacked by alkalis and oxidizing agents. The copper(I) moiety is generally oxidized first whereas the dithiocarbamate ligand is only attacked by strong oxidizing agents such as concentrated nitric acid.

(c) **Infrared Spectra.** The infrared frequencies for ν(C$\cdots$N) and ν(C$\cdots$S) stretches in Cu(pipdtc)₂(CuBr)₄ were found to be 1520 and 955 cm⁻¹, respectively, compared with 1500 and 993 cm⁻¹, respectively, in Cu(pipdtc)₂. This indicates a weakening of the C–S bond and a strengthening of the C–N bond suggesting a delocalization of electrons from the nitrogen to the sulfur moieties.

Attempts to examine the Cu–S and Cu–Br stretches were unsuccessful due to the large number of vibrational frequencies observed in this region.

(d) **X-Ray Crystallography.** Cu(S₂CNC₅H₁₀)₂(CuBr)₄ has cell dimensions $a = 17.108$ (3) Å, $b = 6.904$ (1) Å, $c = 10.203$ (2) Å, and $\beta = 102.5$ (2)° and crystallizes in space group $C2/m$ with 2 formula units per unit cell; $\rho_{calcd} = 2.705$ g cm⁻³; μ(Cu Kα) = 172.2 cm⁻¹. The dark blue crystals are tabular on (001) with the faces (001), (001̄), (110), (11̄0), (1̄10), (1̄1̄0), (100), and (1̄00) all being well developed.

The Br atoms were located from a Patterson synthesis, and suspected locations of the Cu and S atoms were verified by a Fourier synthesis using phases determined by the Br atoms. All the atoms except the H atoms were then located from a further Fourier synthesis. A full-matrix least-squares refinement using isotropic temperature factors for two cycles and anistropic temperature factors for one cycle reduced the R factor to 0.053. Only data with $(\sin \theta)/\lambda > 0.3$ were used up to this stage.

A difference Fourier using all data then located all the hydrogen atoms which were given the same anisotropic tem-

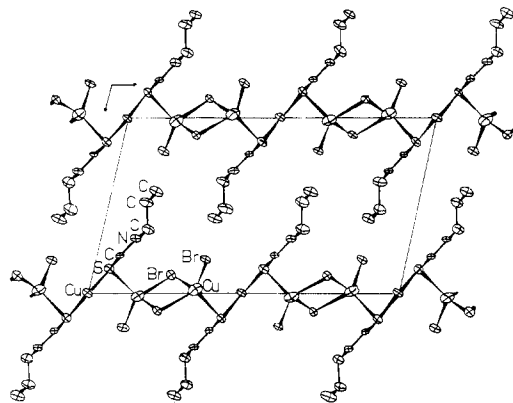(29) P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Crystallogr.*, **18**, 1035 (1965).

Figure 1. The (010) projection of the structure of $Cu(pipdtc)_2(CuBr)_4$. Only atoms between the mirror planes at $y = 0$ and $y = \frac{1}{2}$ are shown. H atoms are not shown.
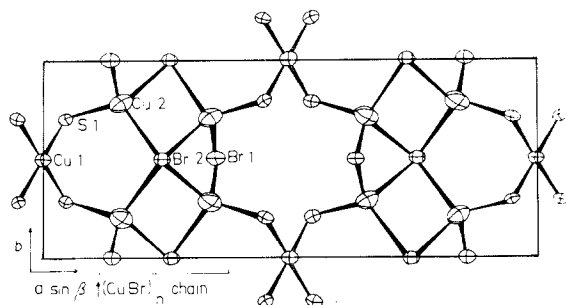

Figure 2. The (001) projection of the structure of $Cu(pipdtc)_2(CuBr)_4$. Only Cu, S, and Br atoms are shown to aid the visualization of the polymeric sheets.

Figure 3. The (010) projection of the structure of $Cu(pipdtc)_2(CuBr)_6$. Only atoms between the mirror planes at $y = 0$ and $y = \frac{1}{2}$ are shown. H atoms are not shown. The Cu atom Cu(3) is randomly distributed over three sites (see text). For visualization unoccupied sites are denoted by dotted lines.

perature factors as the carbon atoms to which they were attached. Further least-squares refinement of the total data, including refinement of an extinction parameter, reduced the R factor to 0.034 for the total 1223 independent reflections including unobserved reflections. In the final refinement cycle the largest positional parameter shift was 0.8σ. The atomic coordinates, anisotropic temperature factors, and bond distances and angles are given in Table III.

$Cu(S_2CNC_5H_{10})_2(CuBr)_6$ has cell dimensions $a = 13.796$ (4) Å, $b = 6.839$ (2) Å, $c = 13.813$ (4) Å, and $\beta = 95.5$ (2)° and crystallizes in space group $C2/m$ with 2 formula units per unit cell; $\rho_{calcd} = 3.184$ g cm^{-3}; μ(Cu Kα) = 213.8 cm^{-1}. The dark blue crystals are tabular on (001) with the faces (001), (00$\bar{1}$), (110), ($\bar{1}$10), (1$\bar{1}$0), and ($\bar{1}\bar{1}$0) all being well developed.

Two of the three nonequivalent Br atoms were located from the Patterson synthesis using peaks at (0.117, 0.0, 0.267), (0.113, 0.5, 0.117), (0.225, 0.5, 0.392), and (0.012, −0.5, 0.150) to predict Br atoms at (0.362, 0.5, 0.192) and (0.254, 0.0, 0.075).

In the Fourier synthesis obtained using the phases predicted by these two atoms there were seven nonequivalent peaks of about the electron density of a sulfur atom, including one peak very close to the origin (0.025, 0.0, 0.035).

Knowing the general chemical features of the compound $Cu(S_2CNC_5H_{10})_2(CuBr)_4$ it was possible to interpret this pattern of peaks by assuming the space group Cm rather than $C2/m$ and assuming that atoms at points (x, y, z) appear as half-weight atoms at both (x, y, z) and $(-x, -y, -z)$ because of the centric arrangement of the Br atoms used to phase the data. It was noted that the space group could again become $C2/m$ by shifting the origin by (−0.057, 0.0, −0.136), giving three nonequivalent Br atoms at (0.419, 0.5,
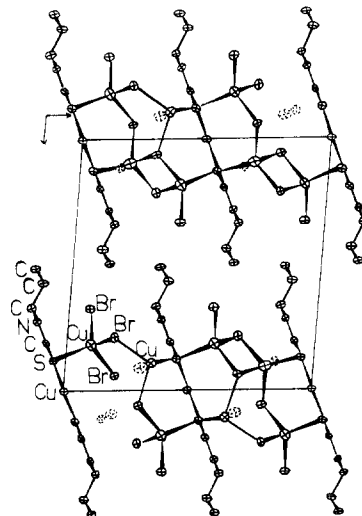
0.328), (0.311, 0.0, 0.211), and (0.303, 0.5, 0.061). It was thus possible to locate all the Cu, Br, and S atoms and to infer the remainder of the structure.

It should be noted at this juncture that the atom Cu(2) in the final parameter list when inverted through ($\frac{1}{4}$ + 0.057, $\frac{1}{4}$, 0 + 0.136) creates an atom Cu(3) at (0.206, 0.203, 0.089). But, by placing full-weight Cu atoms at (0.0, 0.5, 0.0), (0.408, 0.297, 0.183), and (0.206, 0.203, 0.089) a formula unit of $Cu(S_2CNC_5H_{10})_2Cu_8Br_6$ would be obtained which would require a nonintegral valency for some of the Cu atoms. By varying the occupancy in a least-squares refinement cycle it was quickly shown that the Cu at (0.206, 0.203, 0.089) was not a full-weight atom and in two cycles refined to give a third-weight atom at $y = 0.15$.

At this stage anisotropic refinement was begun using a half-weight atom in space group $C2/m$, employing a formula unit of $Cu(S_2CNC_5H_{10})_2(CuBr)_6$. Such refinement could not reduce the R factor below 0.10. The half-weight atom became highly anisotropic. A difference Fourier indicated a peak of about one-third the electron density of a Cu atom at (0.16, 0.0, 0.11). Distributing the Cu atom as a unit-weight atom in space groups Cm and $C2$ gave even less successful refinements. Using a unit-weight Cu atom at (0.16, 0.0, 0.11) in $C2/m$ allowed a refinement to an R factor of 0.12 but this atom was even more anisotropic than before, giving residual electron density in a difference Fourier of a third of a Cu atom at (0.20, ±0.15, 0.09).

Successful refinement was achieved by placing three third-weight Cu atoms, Cu(3), at (0.16, 0.0, 0.11) and (0.20, ±0.15, 0.09) and allowing the occupancy, coordinates and temperature parameters to refine along with the remaining atomic parameters. A single full-matrix least-squares refinement cycle reduced the R factor to 0.054 using data with (sin θ)/ $\lambda > 0.3$ only.

A difference Fourier using all data then located all the H atoms which were given the same anisotropic temperature factors as the C atoms to which they were attached. A further least-squares refinement of the total data including refinement of an extinction parameter reduced the R factor to 0.047 for the total 1346 data, including unobserved data.

The occupancies of the Cu(3) sites are 0.365 (8) for the position (0.1584, 0.0, 0.1107) and 0.310 (5) for the posi-

Table III. Structural Parameters for $Cu(pipdtc)_2(CuBr)_4$

Atomic Coordinates

	x/a (σ)	y/b (σ)	z/c (σ)	Site symmetry
Br(1)	0.14086 (4)	0.0	0.19258 (5)	m
Br(2)	0.24082 (4)	0.5	0.10151 (5)	m
Cu(1)	0.0	0.5	0.0	$2/m$
Cu(2)	0.15814 (5)	0.21302 (13)	0.01779 (7)	1
S(1)	-0.04810 (6)	0.29097 (15)	0.14165 (8)	1
N(1)	-0.1179 (3)	0.5	0.3096 (4)	m
C(1)	-0.0787 (3)	0.5	0.2116 (4)	m
C(2)	-0.1443 (3)	0.3206 (8)	0.3644 (4)	1
C(3)	-0.1205 (4)	0.3209 (10)	0.5170 (4)	1
C(4)	-0.1482 (6)	0.5	0.5763 (6)	m
H(1)	-0.122 (4)	0.213 (11)	0.327 (6)	1
H(2)	-0.206 (4)	0.307 (10)	0.333 (5)	1
H(3)	-0.152 (4)	0.196 (12)	0.548 (6)	1
H(4)	-0.055 (5)	0.313 (12)	0.539 (6)	1
H(5)	-0.117 (7)	0.5	0.663 (9)	m
H(6)	-0.206 (8)	0.5	0.549 (9)	m

Anisotropic Temperature Factors $[\exp(-(\beta_{11}h^2 + 2\beta_{12}hk + ...))]$

	β_{11} (σ)	β_{22} (σ)	β_{33} (σ)	β_{12} (σ)	β_{13} (σ)	β_{23} (σ)
Br(1)	0.00336 (3)	0.01163 (14)	0.00490 (5)	0.0	0.00148 (3)	0.0
Br(2)	0.00237 (2)	0.01098 (14)	0.00675 (6)	0.0	0.00112 (2)	0.0
Cu(1)	0.00224 (4)	0.0137 (3)	0.00457 (9)	0.0	0.00128 (5)	0.0
Cu(2)	0.00518 (4)	0.0191 (2)	0.00893 (8)	-0.00209 (7)	-0.00044 (4)	0.00529 (9)
S(1)	0.00259 (4)	0.0113 (2)	0.00530 (7)	0.00057 (7)	0.00130 (4)	0.00006 (9)
N(1)	0.0027 (2)	0.0134 (11)	0.0039 (3)	0.0	0.0010 (2)	0.0
C(1)	0.0019 (2)	0.0129 (12)	0.0031 (4)	0.0	0.0003 (2)	0.0
C(2)	0.0037 (2)	0.0169 (11)	0.0055 (3)	-0.0013 (4)	0.0015 (2)	0.0016 (5)
C(3)	0.0046 (2)	0.0298 (16)	0.0053 (4)	0.0004 (5)	0.0020 (2)	0.0044 (6)
C(4)	0.0052 (4)	0.039 (3)	0.0052 (6)	0.0	0.0023 (4)	0.0

Bond Distances[a]

Bond	Value (σ), Å	Bond	Value (σ), Å
Cu(1)-S(1)	2.3163 (9)	C(2)-H(1)	0.95 (7)
S(1)-C(1)	1.740 (3)	C(2)-H(2)	1.04 (7)
C(1)-N(1)	1.320 (6)	C(3)-H(3)	1.10 (8)
N(1)-C(2)	1.470 (5)	C(3)-H(4)	1.09 (8)
C(2)-C(3)	1.521 (5)	C(4)-H(5)	0.93 (10)
C(3)-C(4)	1.499 (7)	C(4)-H(6)	0.97 (12)
Cu(2)-Br(1)	2.3790 (8)	Cu(2)-Br(2)	2.4761 (8)
Cu(2)-Br(2)$_c$	2.7472 (10)	Cu(2)-S(1)$_b$	2.2692 (10)
Cu(2)-Cu(2)$_c$	3.2813 (16)	Cu(2)-Cu(1)	3.3265 (9)
Cu(2)-Cu(2)$_a$	2.9414 (17)		

Bond Angles[a]

Angle	Value (σ), deg	Angle	Value (σ), deg
S(1)-Cu(1)-S(1)$_a$	77.08 (5)	C(2)-N(1)-C(2)$_a$	114.9 (5)
Cu(1)-S(1)-C(1)	85.32 (13)	N(1)-C(2)-C(3)	110.6 (4)
S(1)-C(1)-S(1)$_a$	112.1 (3)	C(2)-C(3)-C(4)	112.1 (5)
S(1)-C(1)-N(1)	123.95 (13)	C(3)-C(4)-C(3)$_a$	111.2 (6)
C(1)-N(1)-C(2)	122.5 (2)		
Cu(1)-S(1)$_b$-Cu(2)	93.00 (4)	C(1)$_b$-S(1)$_b$-Cu(2)	102.4 (2)
S(1)$_b$-Cu(2)-Br(1)	117.71 (4)	S(1)$_b$-Cu(2)-Br(2)	112.35 (4)
S(1)$_b$-Cu(2)-Br(2)$_c$	108.26 (4)	Br(1)-Cu(2)-Br(2)	113.00 (3)
Br(1)-Cu(2)-Br(2)$_c$	101.18 (3)	Br(2)-Cu(2)-Br(2)$_c$	102.36 (3)

[a] Atoms at equivalent positions $(x, 1-y, z)$, $(-x, y, -z)$, and $(^1/_2 - x, ^1/_2 - y, -z)$ are denoted by subscripts a, b, and c, respectively.

tions (0.1963, ±0.1496, 0.0933), giving a total occupancy of 0.985 (13) verifying the formulation of $Cu(S_2CNC_5H_{10})_2$-$(CuBr)_6$. A difference Fourier showed the residual electron density near these fractional atoms was no worse than near the other atoms. In the final cycle only two positional parameters shifted by more than σ, neither shift being greater than 1.2σ. This excludes shifts in the H coordinates for which a limited refinement capability is to be expected. The atomic coordinates, anisotropic temperature factors, and bond distances and angles are given in Table IV.

Both structures consist of polymeric sheets parallel to the (001) plane. (Both crystals are tabular on this plane.) The sheets consist of individual $Cu(S_2CNC_5H_{10})_2$ molecules link-

ing together $(CuBr)_n$ polymeric chains which run parallel to the (010) direction (see Figures 1-4). A Cu-S bond distance of 2.2692 (10) Å gives this linkage for $Cu(S_2CNC_5H_{10})_2$(Cu-Br)$_4$ while distances of 2.3046 (15), 2.476 (3), and 2.284 (4) Å are evidenced for $Cu(S_2CNC_5H_{10})_2$(CuBr)$_6$. The $Cu(S_2$-$CNC_5H_{10})_2$ molecules are on sites of $2/m$ symmetry and stack on edge parallel to the $(CuBr)_n$ polymeric chains, explaining the similarity of the unique b axis measurement for the two crystals, *viz.*, 6.904 (1) and 6.839 (2) Å. The $Cu(S_2CNC_5H_{10})_2$ molecule has 13 atoms in a plane, the planarity extending to the first three atoms of the six-membered rings. The central Cu atom has a four-coordinate square-planar environment whereas the Cu atoms in the $(CuBr)_n$

Table IV. Structural Parameters for $Cu(pipdtc)_2(CuBr)_6$

Atomic Coordinates

	x/a (σ)	y/b (σ)	z/c (σ)	Site symmetry
Br(1)	0.41894 (6)	0.5	0.32863 (5)	m
Br(2)	0.31242 (6)	0.0	0.21281 (5)	m
Br(3)	0.30255 (6)	0.5	0.06042 (5)	m
Cu(1)	0.0	0.5	0.0	$2/m$
Cu(2)	0.40762 (6)	0.29637 (15)	0.18280 (5)	1
Cu(3)^a	0.1584 (3)	0.0	0.1107 (2)	m
Cu(3)* ^{a}	0.1969 (3)	0.1496 (9)	0.0933 (3)	1
S(1)	0.05273 (9)	0.2894 (2)	0.12436 (7)	1
N(1)	0.1264 (4)	0.5	0.2823 (4)	m
C(1)	0.0847 (5)	0.5	0.1923 (4)	m
C(2)	0.1526 (4)	0.3186 (9)	0.3355 (3)	1
C(3)	0.1133 (4)	0.3187 (9)	0.4351 (3)	1
C(4)	0.1467 (6)	0.5	0.4926 (5)	m
H(1)	0.231 (5)	0.342 (12)	0.337 (4)	1
H(2)	0.119 (5)	0.183 (13)	0.294 (4)	1
H(3)	0.042 (5)	0.308 (13)	0.424 (4)	1
H(4)	0.127 (5)	0.170 (13)	0.464 (4)	1
H(5)	0.253 (7)	0.5	0.479 (5)	m
H(6)	0.140 (7)	0.5	0.559 (6)	m

Anisotropic Temperature Factors [$\exp(-(\beta_{11}h^2 + 2\beta_{12}hk + ...))$]

	β_{11} (σ)	β_{22} (σ)	β_{33} (σ)	β_{12} (σ)	β_{13} (σ)	β_{23} (σ)
Br(1)	0.00353 (5)	0.0125 (2)	0.00252 (4)	0.0	0.00019 (3)	0.0
Br(2)	0.00250 (4)	0.0089 (2)	0.00318 (4)	0.0	0.00043 (3)	0.0
Br(3)	0.00320 (5)	0.0104 (2)	0.00235 (3)	0.0	0.00005 (3)	0.0
Cu(1)	0.00255 (9)	0.0132 (4)	0.00162 (6)	0.0	0.00019 (5)	0.0
Cu(2)	0.00431 (5)	0.0122 (2)	0.00473 (5)	0.00023 (10)	0.00097 (4)	−0.00027 (8)
Cu(3)	0.0031 (2)	0.027 (2)	0.0031 (2)	0.0	0.0001 (1)	0.0
Cu(3)*	0.0063 (2)	0.040 (2)	0.0035 (2)	0.0098 (6)	−0.0005 (2)	−0.0049 (4)
S(1)	0.00260 (6)	0.0127 (3)	0.00199 (5)	0.00074 (13)	0.00032 (4)	−0.00054 (10)
N(1)	0.0020 (3)	0.014 (2)	0.0019 (3)	0.0	0.0000 (2)	0.0
C(1)	0.0019 (4)	0.017 (2)	0.0016 (3)	0.0	0.0006 (3)	0.0
C(2)	0.0030 (3)	0.014 (1)	0.0022 (2)	0.0015 (6)	0.0000 (2)	0.0005 (5)
C(3)	0.0042 (3)	0.014 (1)	0.0020 (2)	0.0000 (6)	0.0003 (2)	0.0009 (4)
C(4)	0.0036 (5)	0.015 (2)	0.0015 (3)	0.0	0.0000 (3)	0.0

Bond Distances^b

Bond	Value (σ), Å	Bond	Value (σ), Å
Cu(1)–S(1)	2.3059 (11)	C(2)–H(1)	1.09 (7)
S(1)–C(1)	1.753 (4)	C(2)–H(2)	1.16 (8)
C(1)–N(1)	1.319 (7)	C(3)–H(3)	0.99 (7)
N(1)–C(2)	1.470 (6)	C(3)–H(4)	1.10 (8)
C(2)–C(3)	1.525 (6)	C(4)–H(5)	1.49 (10)
C(3)–C(4)	1.520 (7)	C(4)–H(6)	0.93 (8)
Cu(2)–Br(1)	2.4416 (10)	Cu(2)–Br(2)	2.4716 (10)
Cu(2)–Br(3)	2.5360 (11)	Cu(2)–S(1)$_b$	2.3046 (15)
Cu(3)–Br(2)	2.436 (4)	Cu(3)–Br(3)$_c$	2.474 (4)
Cu(3)–S(1)	2.476 (3)	Cu(3)–S(1)$_d$	2.476 (3)
Cu(3)*–Br(2)	2.411 (3)	Cu(3)*–Br(3)$_c$	2.357 (3)
Cu(3)*–Br(3)	2.863 (7)	Cu(3)*–S(1)	2.284 (4)
Cu(2)–Cu(1)$_b$	3.5667 (8)	Cu(2)–Cu(3)*	3.210 (5)
Cu(2)–Cu(2)$_a$	2.785 (2)	Cu(3)–Cu(3)*	1.188 (6)

Bond Angles^b

Angle	Value (σ), deg	Angle	Value (σ), deg
S(1)–Cu(1)–S(1)$_a$	77.32 (6)	C(2)–N(1)–C(2)$_a$	115.1 (5)
Cu(1)–S(1)–C(1)	86.03 (17)	N(1)–C(2)–C(3)	111.1 (5)
S(1)–C(1)–S(1)$_a$	110.6 (3)	C(2)–C(3)–C(4)	110.8 (5)
S(1)–C(1)–N(1)	124.72 (17)	C(3)–C(4)–C(3)$_a$	109.3 (6)
C(1)–N(1)–C(2)	122.4 (3)		
Cu(1)–S(1)–Cu(3)	126.08 (9)	C(1)–S(1)–Cu(3)	125.3 (2)
Cu(1)–S(1)–Cu(3)*	109.86 (13)	C(1)–S(1)–Cu(3)*	105.4 (3)
Cu(1)$_b$–S(1)$_b$–Cu(2)	101.36 (5)	C(1)$_b$–S(1)$_b$–Cu(2)	101.8 (2)
Br(1)–Cu(2)–Br(2)	108.82 (3)	S(1)$_b$–Cu(2)–Br(1)	116.40 (5)
Br(1)–Cu(2)–Br(3)	102.96 (4)	S(1)$_b$–Cu(2)–Br(2)	110.08 (5)
Br(3)–Cu(2)–Br(2)	106.44 (4)	S(1)$_b$–Cu(2)–Br(3)	111.51 (4)
Br(2)–Cu(3)*–Br(3)	98.6 (2)	S(1)–Cu(3)*–Br(2)	125.4 (2)
Br(2)–Cu(3)*–Br(3)$_c$	111.9 (2)	S(1)–Cu(3)*–Br(3)	98.4 (2)
Br(3)–Cu(3)*–Br(3)$_c$	100.1 (2)	S(1)–Cu(3)*–Br(3)$_c$	115.4 (2)
Br(2)–Cu(3)–Br(3)$_c$	107.2 (2)	S(1)–Cu(3)–Br(2)	116.3 (1)
S(1)–Cu(3)–S(1)$_d$	106.1 (2)	S(1)–Cu(3)–Br(3)$_c$	104.8 (1)
Cu(2)–S(1)$_b$–Cu(3)$_b$	111.1 (1)	Cu(2)–S(1)$_b$–Cu(3)*$_b$	139.5 (2)

^{a} Cu(3) has fractional occupancy (see text). ^{b} Atoms at equivalent positions $(x, 1 - y, z)$, $(^1/_2 + x, ^1/_2 - y, z)$, $(^1/_2 - x, ^1/_2 - y, -z)$, and $(x, -y, z)$ are denoted by subscripts a, b, c, and d, respectively.
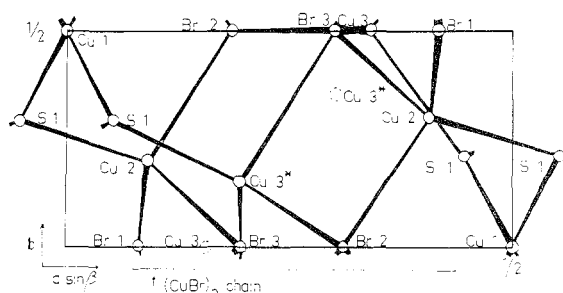
Figure 4. The (001) projection of the structure of Cu(pipdtc)$_2$(CuBr)$_6$ showing one-fourth of the unit cell. To aid visualization of the polymeric sheets only Cu, S, and Br atoms are shown. The Cu atom Cu(3) is randomly distributed over three sites (see text).

polymeric chains have a four-coordinate tetrahedral environment allowing formal valences of +2 and +1, respectively. Individual Cu atoms are linked by either Br or S atoms, an S atom bridging between Cu(I) and Cu(II) atoms and Br atoms bridging between Cu(I) atoms.

Comparisons of bond lengths and angles between the Cu-(S$_2$CNC$_5$H$_{10}$)$_2$ molecules in both structures show good agreement. The Cu-S distances of 2.3163 (9) and 2.3059 (11) Å are the only distances significantly different statistically, and these differ by only 0.01 Å and indicate an alteration in the environment of the S atom.

The Cu atom Cu(3) in Cu(S$_2$CNC$_5$H$_{10}$)$_2$(CuBr)$_6$ is of interest, being an atom disordered over three sites, Cu(3) at (0.1584, 0.0, 0.117) and Cu(3)* at (0.1969, ±0.1496, 0.933) with occupancies 0.365 and 0.310 (twice). The rate of interchange between these sites is not known but the potential barrier would not appear to be very high. The root-mean-square value of the thermal displacement has a maximum component of 0.255 (9) Å for the Cu(3) site and 0.369 (9) Å for the Cu(3)* site while these sites are 1.188 (6) Å apart.

The Cu(3) site is the more favorable site and is the site which most closely approaches tetrahedral symmetry of all the Cu(I) sites, having Cu–Br distances of 2.436 and 2.474 Å and two Cu–S distances of 2.476 Å. The Cu is bonded to equivalent S atoms on different S$_2$CNC$_5$H$_{10}$ ligands. The Cu(3)* site is like the remaining Cu(I) sites in the two structures except that the equivalent atom at (x, $-y$, z) will be absent, allowing a significantly smaller value of y for this atom (0.1496 (9) compared with 0.2036 (2)). This reduction in Cu(I)–Cu(I) repulsion is evidenced in the shorter b axial length of Cu(S$_2$CNC$_5$H$_{10}$)$_2$(CuBr)$_6$ and also in the Cu–Br bond distances about the Cu(2) site. These distances are 2.4416 (10), 2.4716 (10), and 2.5360 (11) Å compared with 2.3790 (8), 2.4761 (8), and 2.7472 (1) Å for Cu(S$_2$CNC$_5$-H$_{10}$)$_2$(CuBr)$_4$. The Cu(3) site is only available because of the lack of atoms at both (x, y, z) and (x, $-y$, z).

The Cu(I)–S bonds are in the correct directions for approximately tetrahedral coordination about the S, all S atoms being bonded to three different atoms in Cu(S$_2$CNC$_5$H$_{10}$)$_2$-(CuBr)$_4$ and to three or four atoms in Cu(S$_2$CNC$_5$H$_{10}$)$_2$(CuBr)$_6$ dependent on the location of the Cu(3) atom.

When considering what other ligands could form such a

structure, it is quickly evident that a severe restriction is imposed by the b-axis repeating distance. However, these two structures provide ample evidence that further coordination about the S atoms of dithiocarbamate and similar complexes is quite possible.

(e) Leaching Experiments. The structure of the polymeric Cu(pipdtc)$_2$(CuBr)$_4$ compound and its content of reducible copper suggests that it could be regarded as an analog of sulfide minerals such as covellite, a copper(I) copper(II) sulfide. The compound is stable at pH 2.5 for periods of at least 1 month and could serve as a substrate for low-pH optimum microorganisms such as *Thiobacillus ferrooxidans* which are known to be able to derive energy for growth from the oxidation of Fe(I) or reduced sulfide species. When so employed the compound was in fact degraded by a *T. ferrooxidans* strain but was unaffected by other *Thiobacillus* species such as *T. thiooxidans* and *T. concretovorus*. Cu(II) ions were released into the suspending medium in concentrations equivalent to the Cu(I) content of the complex, and the copper–piperidyl–dithiocarbamate moiety was recovered quantitatively from the residue. The increase in cell numbers during the course of the experiment was slight and does not provide unequivocable evidence of the derivation of energy for growth by the organism from the oxidation of Cu(I) to Cu(II). In view, however, of the difficulty of carrying out cell number counts in the presence of a solid insoluble substrate, the possibility of growth and of catabolic reactions is not positively excluded. This matter is being further investigated in experiments involving the uptake of radioactive carbon. Should growth not be occurring these observations are still explicable as an example of cometabolism phenomena. These experiments are being separately reported. It is interesting to speculate that the degradation of this compound may be a further example of energy derivation by an autotrophic microorganism by change of valence state of a metal other than iron. The complex used in these experiments has slight conducting properties and the mechanism of biological degradation may be analogous to that postulated for covellite and other copper sulfide minerals. The results are sufficiently encouraging to suggest that complexes of this type may have some utility as "mineral analogs" in the elucidation of biodegradative mechanisms.