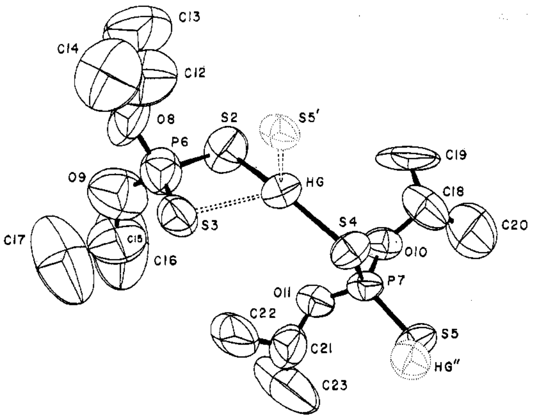

Figure 4.—A parallel projection of the $Hg[(i\text{-}C_3H_7O)_2PS_2]_2$ molecule illustrating the principal root-mean-square thermal displacements. Ellipsoidal boundaries are at the 60% probability level. Atoms S(5') at $^1/_2 - x$, $^1/_2 + y$, $^1/_2 - z$ and Hg'' at $^1/_2 - x$, $-^1/_2 + y$, $^1/_2 - z$ are related by symmetry to the parent molecule at x, y, z and are indicated by dotted lines.

with those in other phosphorodithioates.[1,21,22a-22f,23]

The two multidentate PS_2 ligands each form a nearly planar array of linkages with the mercury atom, the maximum deviation from planarity not exceeding 0.08 Å. Expressed in unit cell coordinates, the equation of the weighted plane[24] for the chelating ligand with mercury is $0.844x - 6.028y + 12.011z - 0.225 = 0$; distances of the defining atoms from this plane are as follows (Å): Hg(1), −0.0006 (8); S(2), 0.044 (6); S(3), 0.028 (5); P(6), −0.076 (7). The equation of the weighted plane for the bridging ligand with mercury is $19.836x - 6.634y - 11.351z - 0.305 = 0$; distances of the defining atoms from this plane are as follows (Å): Hg(1), 0.0012(8); S(4), −0.048(5); S(5), 0.059(5); P(7), −0.080 (5). The mercury atom Hg(1) is substantially out of the plane defined by atoms S(2), S(3), and S(4), however, by an amount 0.480 (1) Å. This deviation may be due to the presence of the Hg(1)–S(5') bridge as well as to crystal packing.

Thermal Motion.—As can be seen in Figure 4, atoms within the inner coordination sphere appear to undergo normal vibrational motions. The relative sizes and orientations of the derived thermal ellipsoids for the isopropyl groups, however, are so excessively large that it is doubtful the ellipsoidal model adequately describes actual motions of the atoms in these groups. It is more reasonable to expect that these groups undergo extensive libration. Significantly, the principal rms thermal displacements of the Hg, S, and P atoms range from 0.22 to 0.38 Å (Table II), indicating the presence of large lattice vibrations as well; such vibrations would be anticipated in a low-melting material (99.5°).

As was found in crystals of polymeric $Zn[(C_2H_5O)_2PS_2]_2$, the bridging group exhibits generally smaller thermal parameters than does the chelating group, reflecting the tight binding of atoms within the chains.

van der Waals Contacts.—The laterally stacked chains are held together by methyl···sulfur, methyl···oxygen, and methyl···methyl interactions, the latter being the most prevalent. All the distances are normal when compared with the expected values of 3.85, 3.4, and 4.0 Å, respectively.

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The Crystal and Molecular Structure of Chlorotris(N,N'-dimethylthiourea)copper(I)

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The crystal structure of chlorotris(N,N'-dimethylthiourea)copper(I) has been determined from counter diffractometer data at room temperature from 240 crystallographically independent reflections. The compound crystallizes in the rhombohedral space group $R3m$ with $a = b = c = 8.867 \pm 0.002$ Å, $\alpha = \beta = \gamma = 112.43 \pm 0.08°$ (hexagonal cell: $a = b = 14.741$ (3) Å, $c = 7.471$ (2) Å, $d_m = 1.44$ (3) g/cm³, and $d_c = 1.46$ g/cm³ with one molecule in the rhombohedral cell. The structure was solved by conventional heavy-atom techniques and refined by full-matrix least squares to a final conventional R of 0.030. The structure is composed of discrete "tetrahedral" molecules separated by ordinary van der Waals distances. The space group requires the molecule to have $3m$ (C_{3v}) symmetry. The Cu–S and Cu–Cl distances are 2.360 ± 0.001 and 2.406 ± 0.005 Å, respectively, while the S–Cu–S and S–Cu–Cl angles are 106.4 ± 0.1 and $112.4 \pm 0.1°$, respectively. The Cu–S–C angle is $111.1 \pm 0.3°$ and the metal–sulfur bond involves the sulfur sp² orbital. The analogous Ag complex has a cell six times as large.

Introduction

It has been shown that the Cu(I) and Ag(I) complexes with thiourea, $SC(NH_2)_2$, hereafter tu, give rise to a multiplicity of stoichiometries and some unusual and unexpected bonding as well. $Cu(tu)_3Cl$[2] is a chain structure made up of almost regular tetrahedrally co-

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(2) (a) Y. Okaya, C. B. Knobler, and R. Pepinsky, *Z. Kristallogr., Kristallgeometrie, Kristallophys., Kristallchem.*, **111**, 385 (1959); (b) Y. Okaya and C. Knobler, *Acta Crystallogr.*, **17**, 928 (1964).

ordinated Cu(I) involving a bridging sulfur, two terminal Cu–S bonds, and a chloride ion well separated from the Cu(I). The sulfur utilizes its sp^2 lone pair or pairs of electrons to form the terminal and bridging metal–sulfur bonds. Although $Cu(tu)_2Cl$[3] and $Ag(tu)_2Cl$[4] also form chain structures, the metal is almost trigonal planar with very long metal–chlorine distances. Furthermore, in these cases two types of S–M–S bridges are found: (1) normal bridges involving two sp^2 sulfur lobes and electron pairs to form Lewis electron pair donor–acceptor bonds; (2) three-center electron deficient bonds involving thiourea π orbitals. The terminal metal–sulfur bonds are very similar to those found in $Cu(tu)_3Cl$. On the other hand $Cu(tu)_3BF_4$[5] and $Cu(tu)_3ClO_4$[6] are not chain structures but rather discrete dimers of the type $Cu_2(tu)_6^{2+}\cdot 2(XY_4^-)$ involving approximately regular tetrahedral Cu(I), in which the bridging sulfur atoms use both the π ligand orbitals as well as one of the sp^2 sulfur orbitals. Again, the terminal Cu–S bonds are similar to those found in $Cu(tu)_3Cl$. $Cu_4(tu)_9(NO_3)_4$[7] is a more complex structure but, nevertheless, is made up of tetrahedral Cu(I) with three-center electron pair bridge bonds using sulfur sp^2 orbitals and electron pairs. This particular structure also contains normal Cu–S terminal bonds, two electron pair bridge bonds utilizing both sp^2 lobes of a bridging sulfur as well as bridge bonds formed from both ligand π and sp^2 orbitals. As part of a program to determine the relative importance of various factors that determine the nature of the metal–sulfur bond with Cu(I) and Ag(I), we prepared the complex of stoichiometry $Cu(dmt)_3Cl$ (dmt = *N,N'*-dimethylthiourea) and determined its crystal structure.

Experimental Section

Crystals of chlorotris(*N,N'*-dimethylthiourea)copper(I) were prepared as follows: *N,N'*-Dimethylthiourea (dmt) (5 g) was dissolved in 100 ml of water at 80°. A 50-ml aqueous suspension containing 0.5 g of freshly prepared CuCl was added to the dmt solution and the resulting mixture was allowed to stand for several days. The translucent, colorless, air-stable, needle crystals which precipitated were of excellent quality for diffraction purposes. Preliminary Weissenberg photographs (*hk*0–*hk*5) indicated a trigonal system with systematic extinctions for hkl, $-h + k + l = 3n + 1, 3n + 2$ absent, indicating space groups $R3m$, $R32$, and $R\bar{3}m$ based on a hexagonal cell.[8] A single crystal, approximately hexagonal in cross section with prominent {100} faces, measuring 0.070 × 0.035 × 0.39 mm, was mounted with the long direction (*c* axis) vertical on an automated Picker diffractometer and aligned by variations of well-known methods.[9a,b] The lattice constants were determined by least-squares refinement[9c] of the setting angles (ϕ, θ, ω, χ) of 16 reflections that had been carefully centered. Using Mo Kα radiation (λ 0.71068 Å) the lattice constants of the hexagonal cell at room temperature were $a = b = 14.741$ (3) Å and $c = 7.471$ (2) Å.

The experimental density, 1.44 (3) g cm^{-3}, measured by flotation in a carbon tetrachloride–benzene mixture is in good agreement with the calculated value of 1.46 g cm^{-3} with three molecules per hexagonal cell. The hexagonal cell can easily be transformed[10] into a primitive obverse rhombohedral cell having the lattice constants $a = b = c = 8.867$ (2) Å and $\alpha = \beta = \gamma = 112.43$ (8)°.

The intensities of 904 crystallographically independent reflections ($2\theta_{max} = 66°$) were recorded by the θ–2θ scan technique using Zr-filtered Mo Kα radiation at room temperature. The peaks were scanned for 240 sec (2.0° in 2θ) and backgrounds were estimated by stationary counting for 40 sec at ±1.0° in 2θ of the peak maxima. Integrated intensities were calculated assuming a linear variation in background from the function $I_{net} = I_{scan} - 3.0(B_1 + B_2)$ where B_1 and B_2 are the background counts. Reflections were considered absent if I_{net} was less than $2.5 \times 3(B_1 + B_2)^{1/2}$. Based on the above considerations 240 independent data points were used in the solution of the structure. A standard reflection was measured every 67 min to ensure stability of operation.

Stability as measured by total variation in the standard peak during data collection was excellent at 2% (0.5σ) of the total integrated intensities. Peak to peak variations were even smaller, indicating good electronic stability and little crystal decomposition throughout the data collection. The takeoff angle, source to crystal, and crystal to counter values were 3.7°, 18 cm, and 23 cm, respectively, and the receiving aperature at the counter was 6 mm wide and 8 mm high. The peak width at half-peak-height for an average reflection was 0.34° (2θ) at the 3.7° takeoff angle indicating a reasonable mosaic width for the peaks. The counting rate never exceeded 5000/sec and no attenuators were used. Ten equivalent reflections were measured, and these showed less than 2% deviation among the 12 equivalent segments of the reciprocal lattice. The linear absorption coefficient (μ) for this compound with Mo Kα radiation was calculated to be 16.28 cm^{-1}. No absorption corrections were made, but the effect on the intensities would probably not exceed 10%. Corrections for Lorentz–polarization effects were made, and the intensity data were reduced to structure factors.

Structure Solution

With three $Cu(dmt)_3Cl$ entities in the hexagonal cell the center of the molecule must lie on special positions of $R32$, $R\bar{3}m$, or $R3m$. In $R32$ the molecule would be required to have D_3 symmetry or be disordered. Correspondingly in $R\bar{3}m$ the molecule would be required to have D_{3d} symmetry or be disordered. However, in $R3m$ the molecule would be required to have only C_{3v} symmetry. If the structure were composed of discrete molecules, C_{3v} would be a likely molecular symmetry. Hence, $R3m$ was chosen as the correct space group, and the structure was solved and refined on this basis.

Space group requirements placed the copper and chlorine atoms on the special position 0, 0, *z* and the sulfur on *x*, 2*x*, *z*. The origin in the *z* direction is arbitrary and the Cu was placed at 0, 0, 0. A three-dimensional Patterson function[11] yielded trial coordinates for the chlorine, sulfur, and carbon(1) atoms which after

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[9] (a) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **22**, 457 (1967); (b) K. Knox in "Master Card Program for Picker Four-Angle Programmer," prepared by F. C. Carter, Picker Instruments, Cleveland, Ohio, 1967, p 11. (c) The least squares program which computes the lattice dimensions is based upon ref 9a, b, by W. A. Spofford, III, for the IBM 1620.

[10] M. J. Buerger, "X-Ray Crystallography," Wiley, New York, N. Y., 1942, p 504.

[11] Patterson and electron density calculations done on an IBM 7040 with ERFR-3 program. A modification of the ERFR-2 of Sly, Shoemaker, and van den Hende by D. R. Harris.

TABLE I

FINAL ATOMIC POSITIONAL AND THERMAL PARAMETERS AND ESTIMATED STANDARD DEVIATIONS[a]

Atom	x^b	z	Atom	x^b	z
Cu	0^c	0^d	N(1)	0.1832 (4)	−0.0077 (8)
S	0.0854 (1)	0.1203 (4)	N(2)	0.1195 (4)	−0.2137 (12)
Cl	0^d	−0.3220 (6)	C(2)	0.2027 (6)	0.1798 (19)
C(1)	0.1314 (4)	0.0448 (15)	C(3)	0.1571 (6)	−0.3628 (19)

Atom	β_{11}	β_{22}	β_{33}	β_{23}
Cu	40 (1)	e	145 (6)	e
S	52 (2)	29 (2)	150 (6)	2 (2)
Cl	42 (2)	e	139 (11)	e
C(1)	71 (7)	34 (8)	182 (29)	5 (11)
N(1)	183 (14)	27 (7)	273 (29)	−34 (13)
N(2)	179 (13)	28 (7)	136 (23)	41 (10)
C(2)	297 (27)	41 (9)	717 (36)	−40 (14)

[a] Esd of last figure in parentheses. Anisotropic temperature factors of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)] \times 10^4$. [b] For all atoms $y = 2x$. [c] Arbitrarily fixed equal to zero to define origin. [d] Special position fixed parameter. [e] $\beta_{22} = \beta_{11}$, $\beta_{12} = \beta_{11}$, $^1/_2\beta_{13} = \beta_{23} = 0$ for Cu, Cl; $\beta_{12} = {}^1/_2\beta_{22}$, $\beta_{13} = {}^1/_2\beta_{23}$ for all other atoms.

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $Cu(dmt)_3Cl$[a]

* H 0 0 *	* H 6 0 *	* H 2 1 *	8 282 291	12 210 212	* H 8 2 *	10 210 221	0 603 640	* H 13 3 *	2 187 182	8 267 245	* H 9 5 *	2 161 155	* H 3 7 *
3 771 798	0 518 514	0 692 679	* H 8 1 *	* H 2 2 *	4 332 332	13 192 203	3 335 347	1 181 174	8 333 338	* H 1 5 *	2 154 140	5 184 186	4 299 281
12 476 486	3 539 530	3 319 319	3 355 350	1 568 566	7 257 266	* H 2 3 *	6 303 324	* H 5 3 *	11 187 165	0 181 174	* H 0 6 *	8 237 239	* H 4 7 *
* H 1 0 *	6 208 205	6 404 419	6 177 190	4 350 339	* H 9 2 *	2 970 923	* H 7 3 *	2 324 324	* H 5 4 *	3 451 447	0 567 561	* H 6 6 *	5 215 207
1 724 744	* H 7 0 *	12 197 194	* H 9 1 *	7 345 340	2 243 237	5 457 461	1 354 357	* H 1 3 *	0 452 455	6 208 228	3 584 592	0 355 359	8 175 168
10 440 430	1 527 527	* H 3 1 *	1 143 142	10 191 178	5 186 163	8 368 365	4 494 495	1 494 493	3 171 169	* H 2 5 *	6 260 247	3 174 173	* H 5 7 *
13 212 209	4 279 263	1 906 905	4 303 306	* H 3 2 *	* H 10 2 *	11 160 158	7 177 186	* H 0 3 *	6 348 351	1 211 207	* H 1 6 *	6 182 169	3 207 215
* H 2 0 *	7 323 362	4 807 800	7 174 181	2 504 481	0 180 161	14 187 151	* H 8 3 *	12 158 168	* H 6 4 *	7 190 187	1 237 238	* H 7 6 *	* H 6 7 *
22016 1229	10 188 186	7 190 203	* H 10 1 *	5 600 588	3 213 219	* H 3 3 *	2 420 422	* H 0 4 *	1 262 257	* H 3 5 *	4 377 373	1 356 351	1 153 147
5 602 583	* H 8 0 *	10 193 191	2 305 312	8 175 172	* H 11 2 *	01055 1044	5 355 349	1 153 131	4 225 230	2 153 161	7 149 141	* H 9 6 *	* H 11 7 *
11 375 370	2 228 240	* H 4 1 *	* H 11 1 *	11 153 149	1 348 362	3 351 343	* H 9 3 *	4 545 536	* H 7 4 *	8 185 180	10 164 170	0 263 254	0 164 171
* H 3 0 *	8 395 387	2 565 571	0 320 329	* H 4 2 *	* H 13 2 *	6 277 270	0 207 207	7 370 369	2 383 391	* H 4 5 *	* H 2 6 *	* H 10 6 *	* H 1 8 *
31150 1162	* H 9 0 *	5 433 442	* H 12 1 *	0 586 597	0 179 157	9 236 245	3 438 436	* H 1 4 *	5 187 204	0 482 492	2 390 375	4 159 144	0 165 176
9 310 312	0 380 383	11 256 252	1 192 181	3 575 581	* H 0 2 *	12 320 325	* H 10 3 *	2 447 470	* H 8 4 *	9 177 156	5 241 240	* H 11 6 *	* H 0 9 *
12 178 164	6 317 317	* H 5 1 *	7 161 143	12 219 200	2 325 342	* H 4 3 *	1 240 242	5 380 375	0 554 552	* H 5 5 *	8 207 191	5 176 169	0 228 217
15 177 186	* H 0 1 *	0 770 759	* H 14 1 *	* H 5 2 *	5 133 145	1 779 790	4 173 175	8 349 361	3 222 224	1 317 313	* H 3 6 *	* H 12 6 *	* H 4 9 *
* H 4 0 *	4 480 479	3 330 348	0 188 172	1 481 476	* H 0 3 *	4 436 421	* H 11 3 *	14 175 172	* H 9 4 *	7 222 228	0 323 329	3 177 166	4 187 174
1 585 570	7 540 526	6 228 227	* H 0 2 *	4 438 432	0 541 574	7 292 287	2 152 158	* H 2 4 *	4 214 211	* H 6 5 *	3 242 239	* H 8 6 *	
4 949 955	10 235 237	9 145 142	0 569 568	* H 6 2 *	3 428 446	10 184 211	8 187 180	3 430 429	* H 10 4 *	5 198 185	6 199 210	2 220 213	
10 204 205	13 153 152	* H 6 1 *	11 365 353	2 301 302	6 744 768	13 170 177	* H 12 3 *	9 209 203	5 150 142	* H 7 5 *	9 240 243	* H 0 7 *	
* H 5 0 *	* H 1 1 *	4 370 365	* H 1 2 *	5 311 311	9 486 517	* H 5 3 *	0 243 235	* H 3 4 *	* H 12 4 *	0 282 289	* H 4 6 *	1 278 283	
5 645 628	2 560 489	10 175 176	0 829 800	8 165 166	15 155 159	5 276 293	* H 15 3 *	1 504 502	4 176 167	3 256 243	1 199 203	4 253 272	
8 286 286	5 271 256	* H 7 1 *	3 170 150	* H 7 2 *	* H 1 3 *	8 195 197	0 235 226	7 270 266	* H 0 5 *	* H 8 5 *	4 253 238	* H 1 7 *	
11 206 190	8 609 610	2 181 171	6 438 428	3 343 351	4 342 373	11 274 274	* H 16 3 *	10 194 174	2 257 272	1 303 290	7 276 270	2 229 225	
14 175 182	11 319 331	5 396 403	9 179 186	9 194 205	7 562 584	* H 6 3 *	1 196 186	* H 4 4 *	5 282 310	4 242 228	* H 5 6 *	5 152 161	

[a] First column is h followed by F_o and F_c. $F_c = 10F_c$(absolute). The 220 reflection was not used in the refinement since it is in error due to machine malfunction but is listed nonetheless.

three cycles of least-squares refinement[12] gave an unweighted discrepancy index, R,[13] of 0.167. Phase assignments based on the four atoms were used to calculate a three-dimensional electron density function[11] and a difference map. The rest of the carbon and nitrogen atoms were easily located, and subsequent isotropic least-squares refinement of atoms resulted in $R = 0.102$. After conversion to anisotropic temperature factors and weighting the reflections,[13] the refinement converged to a final R, wR, and standard error of 0.0297, 0.0330, and 0.573, respectively.

The function minimized in the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$ where F_o and F_c are the observed and calculated structure factors, respectively. Scattering factors for Cu^+, Cl^-, and neutral sulfur, carbon, and nitrogen were from Cromer and Waber.[14] The effects of anomalous dispersion were included in the structure factor calculations by addition to F_c;[15] the values for $\Delta f'$ and $\Delta f''$ for copper, chlorine, and sulfur were those given by Cromer.[16] Since $|F(hkl)| \neq F|(\bar{h}\bar{k}\bar{l})|$ in the presence of anomalous dispersion, it is possible to determine the polarity of the space group. With the appropriate coordinate changes we refined the structure with opposite polarity and found that R, wR, and standard error converged to 0.0331, 0.0371, and 0.646, respectively. The ratio of $wR_{\bar{h}\bar{k}\bar{l}}/wR_{hkl}$ is 1.12 and Hamilton's R factor test[17] indicates that the orientation as given by the coordinates in Table I is the correct polarity at greater than the 99.5% confidence level. A final difference map showed some general spreading of the electron density in the z direction that was not completely compensated by anisotropic thermal parameters but was sufficiently small that no further interpretation is sensible. The final tabulation of observed and calculated structure factors is listed in Table II. Unobserved data were not used in the structure refinement but are given in Table III. Final atomic posi-

TABLE III

UNOBSERVED REFLECTIONS WITH CALCULATED VALUES GREATER THAN $F_{\min}$[a]

$F_{MIN} \le |F(\mathrm{CALC})| < 2.0 \times F_{MIN}$

L = 0	12 2 194	5 6 311	5 7 204	4 8 228	5 5 186	L = 8
4 7 263	11 4 252	9 7 205	4 9 211	L = 6	L = 7	0 1 176
5 8 264	1 12 181	L = 3	L = 5	6 0 247	4 0 272	
6 9 317	0 14 172	12 0 168	8 0 245	5 2 240	2 1 225	
7 10 186	L = 2	7 7 186	0 1 174	6 3 210	4 3 281	
3 12 180	12 1 212	0 9 207	7 2 187	9 3 243	5 4 207	
L = 1	2 6 302	L = 4	0 7 289	1 4 203	3 5 215	

$2.0 \times F_{MIN} \le |F(\mathrm{CALC})| < 3.0 \times F_{MIN}$

L = 0	2 11 378	3 8 350	6 6 324	L = 4	L = 6	1 7 351
0 9 383	L = 1	0 11 329	1 7 357	5 1 375	2 2 375	
1 10 424	11 1 331	L = 3	3 9 436	8 4 338	0 3 329	

$3.0 \times F_{MIN} \le |F(\mathrm{CALC})|$

L = 0	5 5 628	0 2 679	L = 3	L = 4	0 4 492
0 3 745	3 6 530	0 5 759	0 0 574	1 3 502	L = 6
1 4 570	L = 1	L = 2	0 31044	0 8 552	3 0 592
2 5 586	1 0 976	8 0 568	0 6 640	L = 5	

[a] First column is h followed by k and $F_c = 10F_c$(absolute). $F_{\min} = 159$. The number of reflections less than $F_{\min}$ is 87. Unobserved reflections were not included in the refinement.

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[12] W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, a Fortran Crystallographic Least Squares Program," Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962. The version incorporates modifications by W. A. Spofford, III.

[13] $R = \Sigma\|F_o - F_c\|/\Sigma|F_o|$; weighted $R = \{(\Sigma w(F_o - F_c)^2]/\Sigma wF_o^2\}^{1/2}$; standard error $= \{[\Sigma w(F_o - F_c)^2]^{1/2}/S\}(N_O - N_V)$, where N_O is the number of observations, N_V is the number of variables, S is the scale factor 0.381, $w = 1/\sigma^2(F)$, $\sigma(F) = [K/F(Lp)][I(\text{scan}) + (T_1/T_2)(B) + D^2I(\text{scan})^2]^{1/2}$, where T_1 and T_2 are the total scan and total background times, respectively, $1/Lp$ is the Lorentz polarization correction, B is the background count, I(scan) is the number of scan counts, D is a constant, usually 0.03 to approximate instrumental error, K is a scale factor, to define convenient scale for weights; $N_O = 240$, $N_V = 42$.

[14] D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

[15] Anomalous dispersion corrections made to F_c, as suggested by J. A. Ibers and W. C. Hamilton, *ibid.*, **17**, 781 (1964).

[16] D. T. Cromer, *ibid.*, **18**, 17 (1965).

[17] W. C. Hamilton, *ibid.*, **18**, 502 (1965).

tional and thermal parameters are listed in Table I. Interatomic distances and angles, root-mean-square components of thermal displacement, and their errors were computed[18] with the parameters and variance–covariance matrix from the last cycle of least-squares refinement and are listed in Tables IV and V.

TABLE IV

INTERATOMIC DISTANCES (Å) ANGLES (DEG), AND ESD'S[a]

Bonded Distances	
Cu–Cl	2.406 (5)
Cu–S	2.360 (1)
C(1)–S	1.701 (9)
N(1)–C(1)	1.354 (4)
C(1)–N(2)	1.30 (1)
N(1)–C(2)	1.49 (2)
C(3)–N(2)	1.47 (1)

Angles	
S–Cu–S	106.4 (1)
Cu–S–C(1)	111.1 (3)
S–Cu–Cl	112.4 (1)
S–C(1)–N(1)	121.6 (9)
C(1)–N(2)–C(3)	123.0 (2)
C(1)–N(1)–C(2)	121.3 (9)
S–C(1)–N(2)	123.0 (2)
N(2)–C(1)–N(1)	115.3 (8)

Intermolecular Nonbonded Distances <4 Å	
C(2)–C(1)	3.555 (5)
C(2)–N(2)	3.80 (1)
S–N(1)	3.665 (7)
C(2)–C(3)	3.61 (2)

Intramolecular Nonbonded Distances, <4 Å	
S–Cl	3.960 (4)
Cu–C(1)	3.370 (1)
S–N(1)	2.673 (5)
Cu–N(2)	3.443 (4)
N(2)–Cl	3.157 (3)
S–N(2)	2.642 (9)
N(1)–N(2)	2.24 (1)
S–C(2)	3.025 (2)
C(1)–C(2)	2.48 (1)
C(2)–N(2)	3.63 (1)
C(1)–C(3)	2.46 (2)
C(3)–N(1)	2.74 (2)
S–S	3.779[b]

[a] The esd's are directly from ORFFE wherein some coordinates are invariant due to space group considerations. This makes some esd's larger or smaller than they might otherwise appear.
[b] Related by space group symmetry.

Description and Discussion

The structure may be described as Cu(dmt)$_3$Cl molecules separated by ordinary van der Waals distances (Figures 1 and 2). Although Figure 2 superficially looks as though the structure contains holes, these are in fact filled by the methyl groups which probably dominate the molecular packing. In this regard it is interesting to note that chlorotris(monomethylthiourea)silver(I)[19] has essentially the same molecular configuration but crystallizes in an orthorhomic space group with a significantly different packing arrangement. The molecule has symmetry $3m$ (C_{3v}), and all atoms are constrained to at least a mirror plane. The copper and chlorine atoms lie on the intersection of the threefold axis and vertical mirrors while the sulfur, carbon, and nitrogen atoms lie only on the mirrors. The three sulfur and chlorine atoms bound to the copper describe a trigonal pyramid with the chlorine at the apex. The copper atom is 0.88 Å above the base of the pyramid and 2.42 Å from the apex. The configuration of the chlorine and sulfur atoms around the copper could also be described as tetrahedral with a strong trigonal distortion along the copper–chlorine axis. The sulfur–copper–sulfur angle of 106.4 (1)° shows the sulfur atoms to be pulled away from the copper–chlorine direction.

TABLE V

RMS COMPONENTS OF THERMAL DISPLACEMENT ALONG PRINCIPAL AXES AND THE ANGLES THE PRINCIPAL AXES MAKE WITH THE CARTESIAN COORDINATE SYSTEM DEFINED BY (I) $(\overline{\text{Cu–Cl}})$, (II) $((\overline{\text{Cu–Cl}}) \times (\overline{\text{Cu–S}}))$, AND (III) $\overline{\text{I}} \times \overline{\text{II}}$

Atom	Axis	Displacement, Å	Angle (in deg) axis makes with I	II	III
Cu	1	0.181 (1)	90[a]	0[a]	90[a]
	2	0.181 (1)	90[a]	90[a]	0[a]
	3	0.202 (4)	0[a]	90[a]	90[a]
Cl	1	0.187 (1)	90[a]	0[a]	90[a]
	2	0.187 (1)	90[a]	90[a]	0[a]
	3	0.200 (8)	0[a]	90[a]	90[a]
S	1	0.155 (5)	87 (4)	90 (2)	3 (4)
	2	0.206 (4)	3 (4)	90 (7)	87 (4)
	3	0.221 (4)	90 (7)	0 (7)	90 (2)
C(1)	1	0.18 (2)	84 (13)	90 (6)	6 (13)
	2	0.23 (2)	6 (13)	90 (10)	84 (13)
	3	0.26 (2)	90 (10)	0 (11)	90 (6)
N(1)	1	0.13 (2)	75 (5)	90 (1)	15 (5)
	2	0.29 (2)	15 (5)	90 (2)	75 (5)
	3	0.44 (2)	90 (2)	0 (2)	90 (1)
N(2)	1	0.10 (3)	55 (6)	90 (1)	35 (6)
	2	0.23 (2)	35 (6)	90 (1)	55 (6)
	3	0.44 (2)	90 (1)	0 (1)	90 (1)
C(2)	1	0.14 (3)	55 (10)	90 (1)	35 (10)
	2	0.25 (2)	35 (10)	90 (1)	55 (10)
	3	0.56 (3)	90 (1)	0 (1)	90 (1)
C(3)	1	0.16 (2)	37 (12)	90 (1)	63 (12)
	2	0.25 (3)	53 (12)	90 (1)	37 (12)
	3	0.56 (3)	90 (1)	0 (1)	90 (1)

[a] With this Cartesian coordinate system these angles are demanded by symmetry.

The sulfur atoms bonded to a particular copper entity are separated by 3.779 Å (van der Waals distance 3.70 Å) and there is no evidence for any abnormal S–S interaction being responsible for the observed Cu(I) environment. The methyl groups on the dmt ligand are oriented such that no symmetry exists about the carbon–sulfur bond (Figure 1). The unsymmetrical configuration of the methyl groups allows the close approach [3.157 (3) Å] of intramolecular nitrogen and chlorine atoms, suggesting the possibility of N–H · · · Cl hydrogen bonding.

The copper–chlorine distance of 2.406 (5) Å is within experimental error of Pauling's covalent radii[20] sum for a single copper–chlorine bond of 2.41 Å, as is the copper–sulfur distance, 2.360 (1) Å, compared to Pauling's predicted value of 2.39 Å. This Cu–S distance falls in the 2.22–2.48 Å range of Cu–S distances found in other thiourea structures.[2–7] The metal–sulfur–carbon angle of 111.1 (3)° is distorted from the 120° inherent in the sp^2 hybridization formally affixed to the sulfur. However, we have come to accept some closing down of this angle as a property of metal–tu complexes. The S–C(1), C(1)–N(1), N(2)–C(3), and N(1)–C(2) distances are normal and not significantly different from those of free thiourea.[21–23] However, the C(1)–N(2) is four

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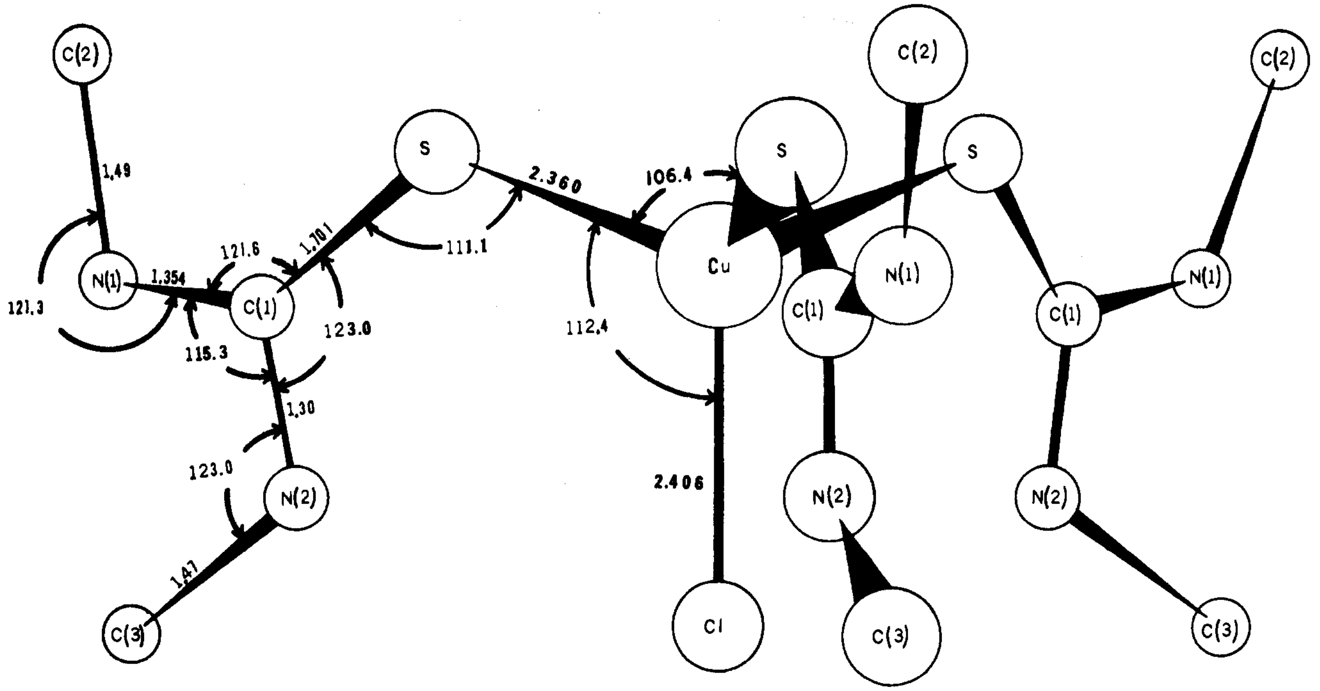

Figure 1.—A perspective view of the Cu(dmt)$_3$Cl molecule with pertinent distances and angles. It is to be noted that N(2) is well situated for a good hydrogen bond with Cl.

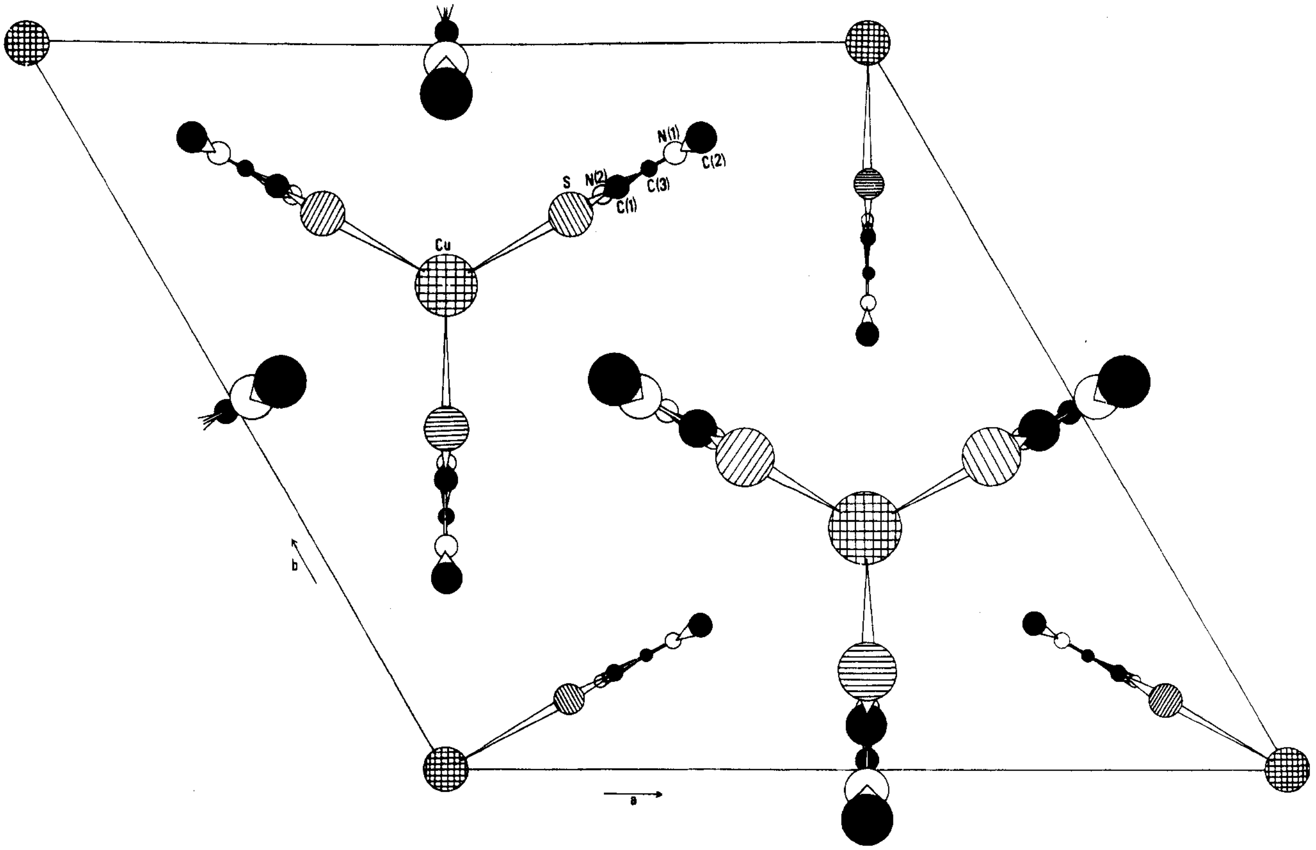

Figure 2.—A perspective view of the hexagonal unit cell of Cu(dmt)$_3$Cl down the "c" axis. The C_{3v} ($3m$) nature of the molecule is evident.

standard deviations shorter than the 1.340 (6)Å[22] found by Truter. There is no obvious reason why this bond should be shortened and more than likely our estimate of error is optimistic. The possible N(2)–H···Cl hydrogen bond should elongate this C–N distance rather than shorten it.

The thiourea complexes of the transition metals, in general, exhibit a dihedral angle between the M–S–C and S–C–N planes of 14–35°[24–28] in contrast to the coplanarity of these same planes in the present structure. This difference could be due to the hydrogen bonding or the closed d^{10} subshell of Cu(I) or to a combination of the two effects.

It is interesting to note that this is the first Cu(I) complex with thiourea or substituted thioureas that does not form a chain, polymer, or dimer structure but rather exists as a molecular entity. Moreover, this particular structure does not contain any of the delocalized three-center bonds as the others exhibit but only "normal" electron-pair bonds. We have also prepared the analogous $Ag(dmt)_3Cl$ complex. At first glance Weissenberg and oscillation photographs of $Ag(dmt)_3Cl$ appear to be isomorphous with $Cu(dmt)_3Cl$. A closer examination of the oscillation photographs of $Ag(dmt)_3Cl$ reveals approximately 10–20 weak reflections which make the *c* axis 6 times larger than the copper cell. Effectively, this places the molecular units in general positions removing all symmetry constraints. However, the two structures must be nearly isostructural since all but 10–20 reflections appear identical. Nevertheless, oscillation photographs of $Cu(dmt)_3Cl$ for 48-hr duration revealed no extraneous reflections.

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The Crystal Structure of $Ba_7Fe_6S_{14}$, a Trinuclear Iron Complex[1]

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The phase $Ba_7Fe_6S_{14}$ has been synthesized and is monoclinic, *C*2/*c*, $a = 25.490$ (2) Å, $b = 8.244$ (1) Å, $c = 14.949$ (2) Å, $\beta = 118.852$ (6)°, $Z = 4$ (temperature 25°). The structure consists of a trinuclear iron cluster in which a central FeS_4 tetrahedron shares two edges with other tetrahedra. The clusters link by corner sharing into infinite zigzag chains parallel to the *b* axis. The three iron atoms in a cluster form a straight line and are approximately 2.8 Å apart. The average Fe–S bond distance around each cation is 2.30 (3) Å, with no significant differences among them. The Ba–S distances of 3.3 Å are close to the sum of the ionic radii. Two barium ions are in eightfold, one is in sevenfold, and one is in sixfold coordination.

Introduction

In the course of an investigation of the system BaS–M–S (M = Mn,[2] Fe, Co, Ni[3]) we studied reactions of the type BaS + Fe + *x*S (*x* = 1–1.5). Mixtures corresponding to the compositions $BaFeS_2$, $Ba_4Fe_4S_9$, $Ba_5Fe_5S_{12}$, and $Ba_2Fe_2S_5$ were prepared and allowed to react under vacuum at temperatures ranging from 800 to 1100°. A compound having the composition $Ba_5Fe_5S_{12}$ had previously been reported.[4]

Each reaction product was highly crystalline, the crystals being in the form of large black shiny slabs, and all products gave nearly identical powder X-ray data. Each reaction mixture yielded predominantly the same compound and this was further verified by selecting single crystals from each of the products. Weissenberg and precession photographs were identical in every case, indicating a compound with monoclinic symmetry and unit cell parameters $a \simeq 25.4$ Å, $b \simeq 8.2$ Å, $c \simeq 14.9$ Å, and $\beta = 118°$. Using the resulting molecular volume and the measured density of the $Ba_5Fe_5S_{12}$ sample, an unreasonable number of molecules per unit cell was calculated ($Z = 5.5$). A single crystal was then selected for crystal structure analysis in order to elucidate its stoichiometry and structural parameters.

Experimental Section

Weissenberg and precession photographs of single crystals selected from the various reaction mixtures showed diffraction symmetry 2/*m* and the systematic absences were *hkl*, $h + k = 2n + 1$, and *h*0*l*, $l = 2n + 1$, consistent with the space groups *C*2/*c* and *Cc*. A small platelike crystal measuring 0.135 × 0.135 × 0.037 mm (0.037 mm = [010]) was selected from the BaS–Fe–S reaction product and mounted about the "*b*" axis on a GE single-crystal orienter. Twenty-four reflections were carefully centered on the $K\alpha_1$ and $K\alpha_2$ components of the molybdenum radiation (λ_1 0.70926 Å, λ_2 0.71354 Å) using a 1° takeoff angle and a 0.02° slit. The 2θ measurements, made at room temperature, 25 ± 0.5°, were used in a least-squares refinement for the determination of the lattice parameters $a = 25.490$ (2) Å, $b = 8.244$ (1) Å, $c = 14.949$ (2) Å, and $\beta = 118.852$ (6)°. Three-dimensional data to $(\sin\theta)/\lambda = 0.60$ were collected with Mo $K\alpha$ radiation using balanced filters and the stationary-crystal, stationary-counter method, a 5° takeoff angle, and the window of the pulse height analyzer set to accept 85% of the incident radiation. Peak heights were counted for 10 sec using a zirconium filter, and then background was counted for 10 sec using a yttrium

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