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Preparation, Crystal Structure, and Bonding of the Dimers of Tris(thiourea)copper(I) Tetrafluoroborate and Tris(*s*-dimethylthiourea)copper(I) Tetrafluoroborate

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The crystal structures of the tetrafluoroborate salts of the dimers of tris(thiourea)copper(I) and tris(*s*-dimethylthiourea) copper(I) have been determined and refined by conventional techniques. The final R values were found to be 0.052 and 0.068, respectively. Both structures consist of sulfur-bridged dimeric cations $Cu_2L_6^{2+}$ (L = ligand) and BF_4^- anions with some hydrogen bonding (N-H· · ·F). The Cu_2S_2 bridging unit is a planar lozenge with its center on a crystallographic center of symmetry. Each Cu(I) is four-coordinate and the Cu-Cu distances are short, ~2.8 Å, whereas the Cu-S-Cu angle is sharp, ~72°. There are two different Cu-S distances in the lozenge. The orientation of the planar bridging thiourea group clearly specifies that the bridging sulfur atom contributes a $p\pi$ S-C MO and electron pair as well as a S sp^2 orbital and electron pair to the bridge bond. In spite of the relatively short Cu-Cu distance and sharp Cu-S-Cu bridge angle, the four-center bridge bond is composed of electron-pair bonds and not electron-deficient bonds. The terminal Cu-S distances are normal at ~2.3 Å and somewhat shorter than the bridge Cu-S distances. The terminal Cu-S bonds are made up from an sp^2 S orbital and electron pair with a copper(I) orbital. Crystal structure data are as follows: for the tris(thiourea)copper(I) tetrafluoroborate dimer, $a = 13.284$ (3) Å, $b = 11.470$ (4) Å, $c = 9.005$ (3) Å, $\beta = 95.11$ (1)°, space group $P2_1/c$, $Z = 4$, NO = 1256; $d_m = d_c = 1.68$ g cm^{-3}; for the tris(*s*-dimethylthiourea)copper(I) tetrafluoroborate dimer, $a = 19.382$ (1) Å, $b = 8.006$ (1) Å, $c = 13.582$ (1) Å, $\beta = 106.5$ (1)°, space group $P2_1/n$, $Z = 4$, NO = 2601, $d_m = 1.50$ g cm^{-3}, $d_c = 1.52$ g cm^{-3}.

Introduction

Cu(I) in compounds with soft donor ligands gives rise to an interesting array of stoichiometries and geometric configurations including polynuclear species. Traditionally, Cu(I) is viewed as most commonly found as two-coordinate linear[2] and four-coordinate tetrahedral.[3] However, recently a number of three-coordinate planar complexes have been isolated and their crystal structures solved.[4-7] A planar coordination number of 3 is to be expected with soft ligands, noncoordinating anions, and ligands with bulky substituents. For example, $Cu[SCN_2H_2(CH_2)_2]_3^+(SO_4^{2-})_{1/2}$,[7] $Cu[SCN_2(CH_3)_4]_3^+BF_4^-$,[7] $(Ph_3P)_3Cu_2Cl_2$,[8] $Cu(SPMe_3)_3^+ClO_4^-$,[5] and $Cu(C_6H_7N)_3^+ClO_4^-$ [6] are all three-coordinate planar entities. Two examples of Cu(I) participating in the formation of six-membered rings are $[Cu(Me_3PS)Cl]_3$[9] and $Cu_4(tu)_{10}(SiF_6)_2$.[10] In the former each Cu(I) is three-coordinate planar whereas in the latter each Cu(I) is four-coordinate, approximately tetrahedral. In addition, Cu(I) forms a multitude of polynuclear complexes such as $Cu_4I_4L_4$[11] (L = R_3P, R_3As), $[(C_2H_5)_2NCS_2Cu_4]$,[12] $Cu_4OCl_6(Ph_3PO)_4$,[13a,b] $Cu_4OCl_6(py)_4$,[13c] $[PPh_3CuCl]_4$,[14] $Cu_4(tu)_6(NO_3)_4$[15] [tu = $SC(NH_2)_2$], and $Cu_4(tu)_9(NO_3)_4$[15] all of which have a basic tetrahedral array of Cu(I) species. $[CuHP(Ph)_3]_6$[16,17] is an octahedron of copper atoms, $[Me_3SiCH_2Cu]_4$[18] is a square-planar polynuclear Cu(I) moiety, $[N_3(CH_3)_2Cu]_4$,[19] $[F_3C_2O_2Cu(C_6H_6)]_4$,[20] and $[(Ph_2PCH_2)_2]_2Cu_4I_4$[21] are planar parallelograms of Cu(I) whereas $\{Cu_8[S_2CC(CN)_2]_6\}^{4-}$ [22] is a cube of Cu(I) moieties. Some examples of "tetrahedral" Cu(I) complexes are K_2CuCl_3,[23] $Cu_5Cl_{16}^{11-}$,[24] $Cu_2Cl_3^-$,[25] $[Cu(CH_3CSNH_2)_4]^+Cl^-$,[26a] and $Cu_2Cl_2(PPh_3)_3$.[26b] An exhaustive discussion of the stereochemistry for some four-coordinate Cu(I) complexes has appeared.[27]

It is clear from the above that the stoichiometry frequently can be misleading as to the geometry about the Cu(I) species. We have been synthesizing and establishing the structures of a series of thiourea (tu)-copper(I) complexes not only because of the appearance of unusual stoichiometries but also because the planar thiourea molecule is an excellent geometric probe for the electrons used by this ligand in complex formation. Some of these are $Cu(tu)_2Cl$[4] which contains planar three-

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Table II[a]

A. Tris(thiourea)copper(I) Tetrafluoroborate

Atomic Positional and Thermal Parameters

Atom	x	y	z
Cu	0.4074 (1)	0.4518 (1)	0.4372 (1)
S(1)	0.5771 (2)	0.3901 (2)	0.3934 (3)
S(2)	0.3447 (2)	0.5406 (3)	0.2176 (3)
S(3)	0.3493 (2)	0.2789 (3)	0.5256 (4)
C(1)	0.5919 (7)	0.4264 (9)	0.2109 (11)
C(2)	0.2307 (8)	0.6016 (11)	0.2387 (12)
C(3)	0.2255 (10)	0.2805 (12)	0.5480 (15)
N(11)	0.6020 (8)	0.5362 (9)	0.1693 (11)
N(12)	0.5937 (8)	0.3426 (9)	0.1138 (9)
N(21)	0.2022 (7)	0.6273 (11)	0.3701 (11)
N(22)	0.1696 (8)	0.6268 (12)	0.1201 (11)
N(31)	0.1803 (12)	0.1960 (16)	0.5952 (36)
N(32)	0.1686 (11)	0.3650 (15)	0.5215 (28)
B	0.0640 (12)	0.5940 (16)	0.7431 (18)
F(1)	0.1624 (6)	0.5761 (9)	0.7896 (11)
F(2)	0.0294 (6)	0.6793 (10)	0.8323 (10)
F(3)	0.0089 (8)	0.4980 (11)	0.7488 (14)
F(4)	0.0542 (7)	0.6327 (11)	0.6016 (10)
H(1)	0.602 (9)	0.589 (11)	0.238 (14)
H(2)	0.617 (10)	0.551 (12)	0.072 (16)
H(3)	0.591 (8)	0.268 (9)	0.142 (12)
H(4)	0.610 (7)	0.355 (9)	0.011 (11)
H(5)	0.249 (9)	0.649 (10)	0.458 (14)
H(6)	0.136 (11)	0.662 (14)	0.383 (17)
H(7)	0.104 (10)	0.660 (11)	0.087 (15)
H(8)	0.190 (7)	0.606 (8)	0.019 (11)
H(9)	0.219 (12)	0.140 (14)	0.630 (17)
H(10)	0.108 (13)	0.192 (14)	0.612 (17)
H(11)	0.101 (12)	0.366 (14)	0.534 (17)
H(12)	0.192 (12)	0.439 (14)	0.477 (17)

Anisotropic Temperature Factors of the Form
$[\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl))] \times 10^4$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	50 (1)	68 (1)	82 (2)	−1 (1)	6 (1)	8 (1)
S(1)	50 (2)	43 (2)	50 (3)	4 (2)	12 (2)	4 (2)
S(2)	58 (2)	98 (3)	61 (3)	23 (3)	8 (2)	15 (3)
S(3)	48 (2)	51 (2)	158 (5)	−2 (2)	33 (2)	−3 (3)
C(1)	29 (6)	71 (10)	75 (13)	−4 (6)	5 (7)	−5 (9)
C(2)	41 (7)	82 (11)	100 (15)	−1 (7)	−10 (8)	16 (11)
C(3)	65 (9)	60 (11)	203 (24)	11 (9)	26 (12)	26 (14)
N(11)	93 (9)	63 (9)	76 (12)	−4 (8)	26 (9)	13 (10)
N(12)	90 (9)	87 (10)	53 (11)	−20 (7)	27 (8)	−22 (9)
N(21)	46 (7)	160 (14)	124 (16)	25 (8)	17 (8)	−31 (12)
N(22)	60 (8)	176 (15)	122 (16)	24 (9)	−30 (9)	15 (13)
N(31)	105 (15)	164 (23)	1375 (118)	17 (15)	277 (35)	260 (44)
N(32)	81 (11)	146 (20)	837 (78)	20 (13)	73 (24)	96 (33)
B	69 (12)	117 (18)	122 (22)	−20 (12)	21 (14)	−34 (17)
F(1)	60 (5)	208 (14)	327 (20)	24 (7)	−13 (9)	−92 (14)
F(2)	69 (6)	245 (15)	247 (16)	20 (8)	10 (8)	−110 (13)
F(3)	127 (8)	194 (14)	388 (24)	−83 (10)	18 (12)	39 (15)
F(4)	122 (9)	265 (16)	174 (14)	−43 (10)	20 (9)	20 (13)

Isotropic Temperature Factors for Hydrogen[b]

Atom	B, Å^2	Atom	B, Å^2	Atom	B, Å^2	Atom	B, Å^2
H(1)	5.0	H(4)	2.0	H(7)	6.0	H(10)	9.0
H(2)	9.0	H(5)	4.0	H(8)	1.5	H(11)	7.5
H(3)	2.0	H(6)	10.0	H(9)	15.0	H(12)	15.0

[a] Estimated standard deviations of last figures in this and the following tables are in parentheses. [b] $\sigma(B) \simeq B$ for halogens; scale = 0.1840 (4).

coordinate Cu(I), Cu(*s*-dmtu)$_3$Cl[28] (dmtu = dimethylthiourea) which contains tetrahedral four-coordinate Cu(I), Cu$_4$(tu)$_9$(NO$_3$)$_4$[29] which contains a planar rectangle of Cu(I) as well as those mentioned above. We wish to report here on the preparation, structure, and bonding of Cu(*s*-dmtu)$_3$BF$_4$ and Cu(tu)$_3$BF$_4$. A preliminary report on the bonding appeared elsewhere.[30]

Experimental Section

***Tris(thiourea)copper(I) Tetrafluoroborate*, Cu(tu)$_3$BF$_4$.** Preparation of this compound in a pure form is beset by a number of compli-

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B. Tris(*s*-dimethylthiourea)copper(I) Tetrafluoroborate

Final Atomic Positional and Thermal Parameters

Atom	*x*	*y*	*z*
Cu	0.0390 (1)	0.1268 (2)	0.0649 (1)
S(1)	0.0835 (1)	−0.1422 (3)	0.0198 (2)
S(2)	0.0782 (1)	0.0981 (3)	0.2425 (2)
S(3)	0.0834 (2)	0.3513 (4)	−0.0037 (2)
C(1)	0.1334 (5)	−0.0791 (12)	−0.0610 (7)
N(1)	0.2054 (5)	−0.0906 (13)	−0.0300 (8)
N(2)	0.1016 (4)	−0.0204 (11)	−0.1520 (6)
C(4)	0.2459 (6)	−0.1632 (19)	0.0720 (10)
C(5)	0.1383 (7)	0.0354 (16)	−0.2285 (9)
C(2)	0.0584 (4)	0.2830 (13)	0.2928 (7)
N(3)	0.0578 (4)	0.2929 (12)	0.3906 (6)
N(4)	0.0441 (4)	0.4190 (11)	0.2340 (6)
C(6)	0.0688 (7)	0.1493 (18)	0.4612 (9)
C(7)	0.0254 (6)	0.5847 (14)	0.2677 (9)
C(3)	0.1743 (6)	0.3390 (14)	0.0383 (10)
N(5)	0.2064 (5)	0.2601 (12)	0.1291 (7)
N(6)	0.2188 (6)	0.3974 (14)	−0.0138 (9)
C(8)	0.2841 (6)	0.2447 (20)	0.1737 (4)
C(9′)	0.1894 (8)	0.4817 (18)	−0.1151 (11)
B	0.3623 (9)	0.1256 (30)	−0.0912 (12)
F(1)	0.3185 (6)	0.0127 (22)	−0.1033 (15)
F(2)	0.4306 (6)	0.0671 (20)	−0.0410 (11)
F(3)	0.3789 (7)	0.1699 (16)	−0.1754 (8)
F(4)	0.3503 (8)	0.2543 (22)	−0.0425 (13)
	Theoretical Calculated Hydrogen Positions (Only on Nitrogen Atoms)		
H(1)	0.2340	−0.0542	−0.0770
H(2)	0.0480	−0.0100	−0.1753
H(3)	0.0458	0.4011	0.4187
H(4)	0.0456	0.4137	0.1611
H(5)	0.1761	0.2132	0.1712
H(6)	0.2721	0.3852	0.0155

Anisotropic Temperature Factors of the Form $[\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl))] \times 10^4$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	35 (0)	240 (3)	69 (1)	−17 (1)	18 (0)	−23 (1)
S(1)	31 (1)	196 (5)	72 (2)	5 (2)	14 (1)	−4 (2)
S(2)	35 (1)	210 (5)	62 (2)	10 (2)	13 (1)	−13 (2)
S(3)	43 (1)	221 (6)	90 (2)	−11 (2)	22 (1)	11 (3)
C(1)	36 (4)	184 (18)	77 (7)	2 (6)	15 (4)	−36 (9)
N(1)	28 (3)	308 (22)	138 (8)	−1 (6)	25 (4)	−50 (11)
N(2)	41 (3)	280 (19)	77 (6)	−12 (6)	25 (4)	−29 (9)
C(4)	41 (1)	420 (37)	120 (11)	−29 (11)	−3 (6)	−13 (17)
C(5)	69 (6)	352 (30)	115 (10)	−24 (10)	63 (6)	−18 (14)
C(2)	23 (3)	220 (20)	62 (6)	4 (6)	13 (3)	−14 (9)
N(3)	36 (3)	281 (21)	64 (6)	9 (6)	16 (3)	−6 (9)
N(4)	42 (3)	222 (18)	72 (6)	11 (6)	9 (3)	−4 (8)
C(6)	78 (6)	320 (31)	91 (9)	15 (11)	43 (6)	31 (14)
C(7)	57 (5)	203 (22)	113 (10)	27 (8)	9 (6)	−28 (12)
C(3)	54 (5)	180 (20)	111 (10)	−28 (8)	34 (6)	−41 (12)
N(5)	38 (3)	293 (21)	99 (7)	−23 (7)	17 (4)	−25 (11)
N(6)	75 (5)	268 (22)	154 (11)	−49 (9)	68 (6)	−35 (13)
C(8)	26 (4)	454 (38)	180 (15)	−13 (10)	3 (6)	−35 (20)
C(9)	95 (8)	326 (33)	124 (12)	−47 (13)	55 (8)	26 (17)
B	54 (7)	711 (62)	121 (13)	10 (10)	60 (8)	50 (25)
F(1)	77 (6)	1113 (61)	478 (32)	−123 (15)	131 (12)	−42 (35)
F(2)	71 (4)	960 (55)	293 (15)	34 (13)	53 (7)	289 (25)
F(3)	189 (9)	592 (33)	170 (10)	41 (14)	84 (8)	79 (15)
F(4)	145 (9)	996 (63)	395 (23)	55 (19)	141 (13)	−232 (31)

cations such as the formation of $Cu_4[SC(NH_2)_2]_{10}(SiF_6)_2$[9] or $Cu[SC(NH_2)_2]_4 \cdot {}^1/_2 SiF_6$[31] when the impure compound is crystallized in glass containers. In addition, seed crystals appear to be required for the formation of diffraction-quality crystals.

In a total volume of 100 ml of aqueous solution 4.9 g of $Cu(BF_4)_2 \cdot 6H_2O$[31b] (0.02 mol), 4.5 g of thiourea (0.06 mol), and 10 g of $NaBF_4$ were mixed and allowed to stand for 3 days. After filtration to remove the sulfur formed, the solvent was rapidly removed in a vacuum desiccator until precipitation of platelike crystals occurred. This impure material was then used for seeding the following solution. A solution as above without the $NaBF_4$ was mixed in a plastic system (to prevent the formation of SiF_6^{2-}). The sulfur was removed. After slow evaporation of the solution to 10 ml, the seed crystals were added. Good diffraction-quality crystals of $Cu(tu)_3BF_4$ were isolated after several days. *Anal.* Calcd for $Cu(tu)_3BF_4$: Cu, 16.78; Found: Cu, 16.72.

Tris(*s*-dimethylthiourea)copper(I) Tetrafluoroborate, $Cu(s\text{-dmtu})_3BF_4$. Clear polyhedral crystals of this compound were readily obtained

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(31) (a) G. W. Hunt and E. L. Amma, *Cryst. Struct. Commun.*, 3, 523 (1974). (b) These experiments were repeated a number of times with different samples of cupric tetrafluoroborate from Alfa Products, Ventron. Initially we thought the SF_6^{2-} was an impurity but we are now convinced that it arises from the reaction of BF_4^- with glass.

Table III^{a}

A. Tris(thiourea)copper(I) Tetrafluoroborate

Bond Lengths, Å

Cu-S(1)	2.429 (3)	C(1)-N(11)	1.33 (1)
Cu-S(1)'	2.367 (3)	C(1)-N(12)	1.30 (1)
Cu-S(2)	2.313 (3)	C(2)-N(21)	1.31 (1)
Cu-S(3)	2.295 (3)	C(2)-N(22)	1.32 (1)
		C(3)-N(31)	1.24 (2)
S(1)-C(1)	1.72 (1)	C(3)-N(32)	1.24 (2)
S(2)-C(2)	1.69 (1)		
S(3)-C(3)	1.68 (1)	B-F(2)	1.37 (2)
		B-F(3)	1.33 (2)
B-F(1)	1.35 (2)	B-F(4)	1.34 (2)
C(3)-N(31)^{b}	1.46 (3)	N-H(av)	0.9 (1)
C(3)-N(32)^{b}	1.36 (2)		

Hydrogen-Bonded Distances, Å

H bond	N-F	F-H
N(21)-H(6)-F(4)	2.99 (1)	2.3 (2)
N(22)-H(7)-F(2)^{z}	3.12 (1)	2.4 (1)
N(22)-H(8)-F(1)^{z}	3.03 (2)	2.1 (1)
N(32)-H(11)-F(4)''	3.07 (2)	2.3 (2)

Nonbonded Distances, Å

Cu-Cu'	2.840 (3)	S(1)-S(3)	3.583 (4)
		S(1)'-S(2)	3.652 (4)
S(1)-S(1)'	3.865 (5)	S(1)'-S(3)	3.971 (4)
S(1)-S(2)	3.761 (4)	S(2)-S(3)	4.083 (4)

Angles, Deg

Cu-S(1)-Cu'	72.6 (1)	S(3)-C(3)-N(31)	123 (1)
S(1)-Cu-S(1)'	107.4 (1)	S(3)-C(3)-N(32)	125 (1)
S(2)-Cu-S(3)	124.8 (1)	N(31)-C(3)-N(32)	112 (2)
S(3)-Cu-S(1)	98.6 (1)		
S(2)-Cu-S(1)	105.0 (1)	F(1)-B-F(2)	107 (1)
S(3)-Cu-S(1)'	116.8 (1)	F(2)-B-F(3)	111 (1)
S(2)-Cu-S(1)'	102.6 (1)	F(2)-B-F(4)	108 (2)
		F(3)-B-F(4)	108 (1)
Cu-S(1)-C(1)	105.7 (3)	F(1)-B-F(3)	113 (2)
Cu'-S(1)-C(1)	114.7 (4)	F(1)-B-F(4)	111 (1)
Cu-S(2)-C(2)	110.1 (4)		
Cu-S(3)-C(3)	113.4 (5)	H(1)-N(11)-H(2)	125 (13)
		H(3)-N(12)-H(4)	113 (9)
S(1)-C(1)-N(11)	121.5 (8)	H(5)-N(21)-H(6)	109 (11)
S(1)-C(1)-N(12)	118.2 (8)	H(7)-N(22)-H(8)	97 (9)
N(11)-C(1)-N(12)	120 (1)	H(9)-N(31)-H(10)	115 (10)
		H(11)-N(32)-H(12)	110 (11)
S(2)-C(2)-N(21)	121.9 (8)		
S(2)-C(2)-N(22)	119.5 (9)		
N(21)-C(2)-N(22)	119 (1)		

B. Tris(*s*-dimethylthiourea)copper(I) Tetrafluoroborate

Interatomic Distances, Å, and Angles, Deg

Bonded Distances

Cu(1)-S(1)	2.461 (3)	N(3)-C(6)	1.47 (1)
Cu(1)-S(2)	2.325 (3)	N(4)-C(7)	1.48 (1)
Cu(1)-S(3)	2.301 (3)	S(3)-C(3)	1.69 (1)
Cu(1)-S(1)$^{\mathrm{II}}$	2.328 (3)	C(3)-N(5)	1.37 (1)
S(1)-C(1)	1.73 (1)	C(3)-N(6)	1.35 (1)
C(1)-N(1)	1.34 (1)	N(5)-C(8)	1.46 (1)
C(1)-N(2)	1.30 (1)	N(6)-C(9)	1.49 (2)
N(1)-C(4)	1.50 (2)	B-F(1)	1.22 (2)
N(2)-C(5)	1.49 (2)	B-F(2)	1.35 (2)
S(2)-C(2)	1.72 (1)	B-F(3)	1.31 (2)
C(2)-N(3)	1.33 (1)	B-F(4)	1.29 (3)
C(2)-N(4)	1.33 (1)		

Nonbonded Distances

Cu(1)· · ·Cu(1)$^{\mathrm{II}}$	2.828 (3)	F(2)· · ·F(4)	2.16 (2)
S(1)· · ·S(1)$^{\mathrm{II}}$	3.868 (5)	F(3)· · ·F(4)	2.14 (2)
N(1)· · ·F(1)	2.78 (1)	S(1)· · ·S(3)$^{\mathrm{II}}$	3.594 (5)
N(3)· · ·F(2)$^{\mathrm{III}}$	2.96 (2)	S(1)· · ·S(3)	3.964 (4)
N(6)· · ·F(4)	2.92 (2)	S(1)· · ·S(2)	3.610 (4)
F(1)· · ·F(2)	2.14 (2)	S(2)· · ·S(3)	3.935 (4)
F(1)· · ·F(3)	2.14 (2)	N(1)· · ·N(2)	2.28 (1)
F(1)· · ·F(4)	2.12 (2)	N(3)· · ·N(4)	2.30 (1)
F(2)· · ·F(3)	2.00 (2)	N(5)· · ·N(6)	2.30 (20)

Angles

S(1)-Cu(1)-S(1)$^{\mathrm{II}}$	107.7 (1)	S(2)-C(2)-N(3)	120.8 (7)
Cu(1)-S(1)-Cu(1)$^{\mathrm{II}}$	72.3 (1)	S(2)-C(2)-N(4)	119.4 (9)
S(1)-Cu(1)-S(2)	97.8 (1)	N(3)-C(2)-N(4)	119.4 (9)
S(1)$^{\mathrm{II}}$-Cu(1)-S(2)	120.3 (1)	C(2)-N(3)-C(6)	124.5 (9)
S(1)-Cu(1)-S(3)	112.7 (1)	C(2)-N(4)-C(7)	125.1 (8)
S(1)$^{\mathrm{II}}$-Cu(1)-S(3)	101.8 (1)	S(3)-C(3)-N(5)	119.2 (8)
S(2)-Cu(1)-S(3)	116.6 (1)	S(3)-C(3)-N(6)	124.6 (11)
Cu(1)-S(1)-C(1)	101.5 (3)	N(5)-C(3)-N(6)	116 (1)
Cu(1)$^{\mathrm{II}}$-S(1)-C(1)	110.2 (3)	C(3)-N(5)-C(8)	124 (1)
Cu(1)-S(2)-C(2)	106.4 (3)	C(3)-N(6)-C(9)	120 (1)
Cu(1)-S(3)-C(3)	107.1 (4)	F(1)-B-F(2)	110 (1)
S(1)-C(1)-N(1)	120.1 (8)	F(1)-B-F(3)	114 (1)
S(1)-C(1)-N(2)	120.6 (8)	F(1)-B-F(4)	116 (1)
N(1)-C(1)-N(2)	119.3 (9)	F(2)-B-F(3)	95 (1)
C(1)-N(1)-C(4)	122 (1)	F(2)-B-F(4)	108 (1)
C(1)-N(2)-C(5)	126 (1)	F(3)-B-F(4)	111 (1)

Theoretical Hydrogen-Bond Angles

N(1)-H(1)· · ·F(1)	152.7	N(6)-H(6)· · ·F(4)	130.7
N(3)-H(3)· · ·F(2)$^{\mathrm{III}}$	147.1		

^{a} Superscripts correspond to the following transformations: prime, centering; double prime, translation plus centering; z, translation in the *c* direction; (I) x, y, z; (II) $-x, -y, -z$; (III) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (IV) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$. ^{b} Distances calculated with a riding motion correction.

by slow evaporation from a solution of equal volumes of 0.0025 *M* $Cu(BF_4)_2 \cdot 6H_2O$ and 0.01 *M N,N'*-dimethylthiourea (*s*-dmtu).

Tris(*u*-dimethylthiourea)copper(I) Tetrafluoroborate, Cu(*u*-dmtu)$_3$BF$_4$. Preparation similar to Cu(*s*-dmtu)$_3$BF$_4$ above.

X-Ray Data

Cu(tu)$_3$BF$_4$. The clear, colorless air-stable crystals were mounted on glass fibers and preliminary Weissenberg and precession photographs showed the crystals to be monoclinic with 0*k*0 absences of $k = 2n + 1$ and *h*0*l* absences of $l = 2n + 1$, corresponding to space group $P2_1/c$.[32] A crystal 0.08 × 0.08 × 0.24 mm was mounted along the *c* direction and aligned on a Picker automated diffractometer by variations of well-known techniques.[33] Twelve reflections were accurately centered and from these χ, ϕ, and 2θ values a least-squares fit of lattice constants was made.[34] With Mo Kα (λ 0.71068 Å) the cell constants were found to be $a = 13.284$ (3) Å, $b = 11.470$ (4) Å, $c = 9.005$ (3) Å, $\beta = 95.11$ (1)°, $\rho_o = 1.68$ g cm^{-3} from CCl$_4$–CBr$_3$H mixtures, and $\rho_o = 1.68$ g cm^{-3} with $Z = 4$. With Mo Kα $\mu = 21.3$ cm^{-1}, no absorption corrections were made.

A total of 2500 independent *hkl* reflections were measured by the θ-2θ scan technique to 2θ = 60° using Zr-filtered Mo Kα radiation at room temperature. The peaks were scanned for 102 sec and backgrounds were estimated by stationary counting at ±0.425° 2θ of peak maximum for 20 sec. Integrated intensities were calculated assuming a linear variation in background from the function $I(\text{net}) = I(\text{scan}) - 2.55(B_1 + B_2)$ where B_1 and B_2 are background counts. Reflections were considered absent if the integrated intensity was less than $1.5[(2.55)^2(B_1 + B_2)]^{1/2}$ (1.5σ of background); 1256 nonzero intensities were found by this criterion. A standard reflection was measured every ten reflections to ensure stability of operation and to monitor any crystal decomposition. Maximum variation in standard peak was 3σ although, in general, the variation between standard peaks was σ or less. The takeoff angle, source-to-crystal, and crystal-to-counter values were 3.7°, 18 cm, and 23 cm, respectively. The peak width at half-peak height for an average reflection was 0.3° 2θ indicating a mosaic spread such that all the reflection was counted during the scan. The counting rate never exceeded 5000 counts/sec and no attenuators were used. Lorentz-polarization corrections were made and the intensities were reduced to structure factors.

(32) "International Tables for X-Ray Crystallography," Vol. I, N. F. M. Henry and K. Lonsdale, Ed., Kynoch Press, Birmingham, England, 1952, p 99.

(33) (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.

(34) The least-squares fit to compute the lattice dimensions is a program based upon ref 33 by W. A. Spofford, III, for the IBM 1620.

Cu(*s*-dmtu)$_3$BF$_4$. The air-stable crystals were mounted on glass fibers and preliminary Weissenberg and precession film data showed the following systematic extinctions: for $h0l$, $h + l = 2n + 1$; for $0k0$, $k = 2n + 1$; indicating the centric space group $P2_1/n$ (from ref 32, with appropriate transformations). A crystal with dimensions 0.35 × 0.54 × 0.75 mm was mounted along the [001] direction and aligned on a card-operated, full-circle Picker-automated diffractometer by a local variation of well-known methods.[33] The cell constants were determined by a least-squares refinement of the angles χ, ϕ, and 2θ for 14 general khl reflections:[34] $a = 19.382$ (1) Å, $b = 8.006$ (1) Å, $c = 13.582$ (1) Å, and $\beta = 106.55$ (1)°. With four molecules per unit cell the calculated density is 1.52 g cm^{-3} while the observed density in 1,2-dibromoethylene and benzene is 1.50 g cm^{-3}. A total of 5078 independent hkl intensities were measured by the usual θ-2θ scan technique with Zr-filtered Mo Kα radiation. Backgrounds were measured for 20 sec at ±0.60° 2θ from the peak maximum and for the broadest peaks at ±0.75° 2θ, and the peaks were scanned for 71.50 sec (1.2° 2θ) and 89.90 sec (1.5° 2θ). A standard reflection ($hkl = -9,3,5$) was measured every ten reflections to monitor the stability of the operation. The variation in the standard reflection from one standard to another was less than 3σ. However, from the beginning to the end of the data collection the standard peak showed a total loss in intensity from decomposition of approximately 6%. The width of an average reflection at half-peak height was found to be 0.3° 2θ. All instrumental constants were the same as above.

The net integrated intensity was calculated assuming a linear variation in background from the function $I(\text{net}) = I(\text{scan}) - A(B_1 + B_2)$ where B_1 and B_2 are the background counts and $A = 1.7875$ or 2.2475 for scan times of 71.50 and 89.9 sec, respectively. The standard reflection was used to scale the data on an absolute basis for each section of ten reflections. Reflections were considered absent if their I(net) was less than $2.5[A^2(B_1 + B_2)]^{1/2}$. Based on this criterion 2601 nonzero reflections remained. With a linear absorption coefficient, μ, of 14.49 cm^{-1}, the minimum and maximum transmission coefficients for a crystal, bound by the (001), (100), (00$\bar{1}$), ($\bar{1}$00), (101), (1$\bar{1}$1), (111), ($\bar{1}$1$\bar{1}$), and ($\bar{1}\bar{1}\bar{1}$) planes, were 0.356 and 0.674, respectively.[35] Lorentz-polarization corrections were made and the intensities reduced to structure factors.

Cu(*u*-dmtu)$_3$BF$_4$. The air-stable crystals were mounted on glass fibers in air. Preliminary Weissenberg and precession photographs showed the crystals to be monoclinic, $P2_1/n$, with $a = 19.26$ (1) Å, $b = 8.72$ (1) Å, $c = 12.76$ (1) Å, $\beta = 113.2$ (1)° (MoKα, λ 0.71068 Å), and $\rho_o = \rho_c = 1.55$ g cm^{-3} with four molecules per cell.

Structure Solutions and Refinements

The solutions of the crystal structures of Cu(tu)$_3$BF$_4$ and Cu(*s*-dmtu)$_3$BF$_4$ were carried out by routine heavy-atom methods in which the Cu and S atoms were located from the three-dimensional Patterson function[36] and the remaining nonhydrogen atoms were located from three-dimensional electron density maps. Hydrogen atom positions were found in difference maps for Cu(tu)$_3$BF$_4$ and they were included in the final refinement. Difference maps of Cu(dmtu)$_3$BF$_4$ indicated almost complete disorder of the methyl group hydrogens and it was decided to neglect all methyl hydrogen atom contributions. The function minimized in the least-squares refinement[37] for each case was $\Sigma(F_o - F_c)^2$ (unit weights). Scattering factors for Cu, S, C, N, B, and H were from Cromer and Waber.[38] The effects of anomalous dispersion (Cu, S) were included by addition to F_c.[39] The values of $\Delta f'$ and $\Delta f''$ for Cu and S were those given by Cromer.[40] The final R and weighted R were 0.052, 0.059 and 0.068, 0.072 for Cu(tu)$_3$BF$_4$ and Cu(dmtu)$_3$BF$_4$, respectively. Final observed and calculated structure factors are listed in Table Ia. Unobserved data were not used in the refinement but are listed in Table Ib.[41] Final atomic po-

Table IV. Rms Displacements along Principal Axes of Thermal Ellipsoids (Å)

Atom	Axis 1	Axis 2	Axis 3
A. Tris(thiourea)copper(I) Tetrafluoroborate			
Cu	0.178 (2)	0.210 (2)	0.217 (2)
S(1)	0.138 (4)	0.168 (4)	0.214 (4)
S(2)	0.154 (4)	0.199 (4)	0.279 (4)
S(3)	0.181 (5)	0.185 (4)	0.266 (4)
C(1)	0.159 (16)	0.174 (15)	0.219 (16)
C(2)	0.170 (17)	0.211 (17)	0.245 (16)
C(3)	0.187 (19)	0.232 (18)	0.299 (17)
N(11)	0.157 (16)	0.213 (15)	0.290 (14)
N(12)	0.129 (17)	0.226 (14)	0.300 (14)
N(21)	0.170 (16)	0.229 (14)	0.340 (15)
N(22)	0.165 (17)	0.274 (15)	0.350 (15)
N(31)	0.160 (25)	0.301 (24)	0.788 (33)
N(32)	0.242 (19)	0.300 (22)	0.593 (28)
B	0.203 (21)	0.228 (22)	0.307 (23)
F(1)	0.223 (11)	0.297 (12)	0.436 (13)
F(2)	0.232 (12)	0.268 (11)	0.447 (13)
F(3)	0.232 (14)	0.389 (12)	0.443 (14)
F(4)	0.259 (11)	0.312 (12)	0.437 (13)
Tris(*s*-dimethylthiourea)copper(I) Tetrafluoroborate			
Cu(1)	0.230 (2)	0.233 (2)	0.297 (2)
S(1)	0.228 (3)	0.247 (3)	0.258 (3)
S(2)	0.223 (3)	0.241 (3)	0.278 (3)
S(3)	0.243 (4)	0.285 (3)	0.287 (4)
C(1)	0.21 (1)	0.25 (1)	0.29 (1)
N(1)	0.21 (1)	0.28 (1)	0.37 (1)
N(2)	0.26 (1)	0.26 (1)	0.32 (1)
C(4)	0.24 (2)	0.36 (2)	0.38 (2)
C(5)	0.21 (1)	0.33 (2)	0.40 (2)
C(2)	0.20 (1)	0.23 (1)	0.27 (1)
N(3)	0.23 (1)	0.25 (1)	0.31 (1)
N(4)	0.25 (1)	0.26 (1)	0.30 (1)
C(6)	0.25 (1)	0.32 (2)	0.38 (2)
C(7)	0.23 (1)	0.29 (1)	0.37 (2)
C(3)	0.22 (1)	0.27 (1)	0.34 (2)
N(5)	0.24 (1)	0.29 (1)	0.33 (1)
N(6)	0.24 (1)	0.29 (1)	0.43 (1)
C(8)	0.21 (2)	0.38 (2)	0.42 (2)
C(9)	0.24 (2)	0.37 (2)	0.43 (2)
B	0.20 (2)	0.34 (2)	0.51 (3)
F(1)	0.23 (1)	0.60 (2)	0.69 (2)
F(2)	0.34 (1)	0.36 (1)	0.66 (2)
F(3)	0.33 (1)	0.46 (1)	0.58 (2)
F(4)	0.30 (1)	0.55 (2)	0.68 (2)

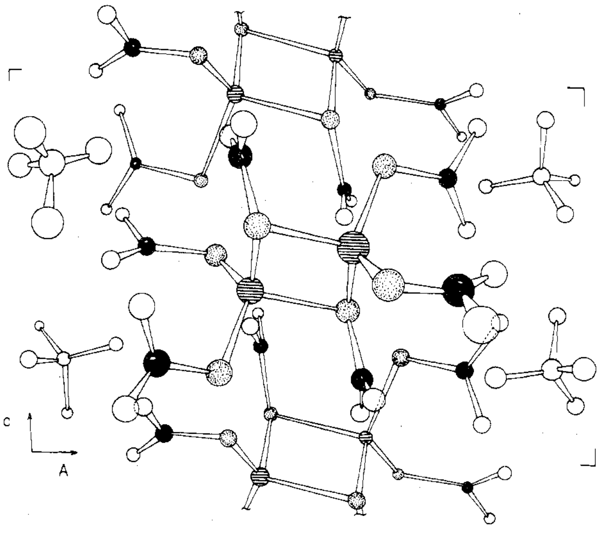

Figure 1. Packing diagram of Cu$_2$[SC(NH$_2$)$_2$]$_6$$^{2+}$(BF$_4$$^-$)$_2$ down the *b* axis. The centers of the Cu$_2$[SC(NH$_2$)$_2$]$_6$$^{2+}$ dimeric ion are on centers of symmetry at $^1/_2$, 0, 0 and $^1/_2$, $^1/_2$, $^1/_2$. The striped circles are Cu atoms, the dotted circles are S atoms, the solid circles are C atoms, and the open circles are nitrogen atoms. The hydrogen atoms are not shown for reasons of simplicity.

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(35) Absorption corrections were made with local variations of program GONO 9, originally written by W. C. Hamilton, Brookhaven National Laboratory, Upton, N. Y.

(36) Patterson and electron density syntheses were calculated using "ERFE-3, a Three-Dimensional Fourier Summation Program Adapted for the IBM 7040 from ERFR-2 of Sly, Shoemaker, and van den Hende," by D. R. Harris.

(37) 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.

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

(39) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).

(40) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(41) See paragraph at end of paper regarding supplementary material.

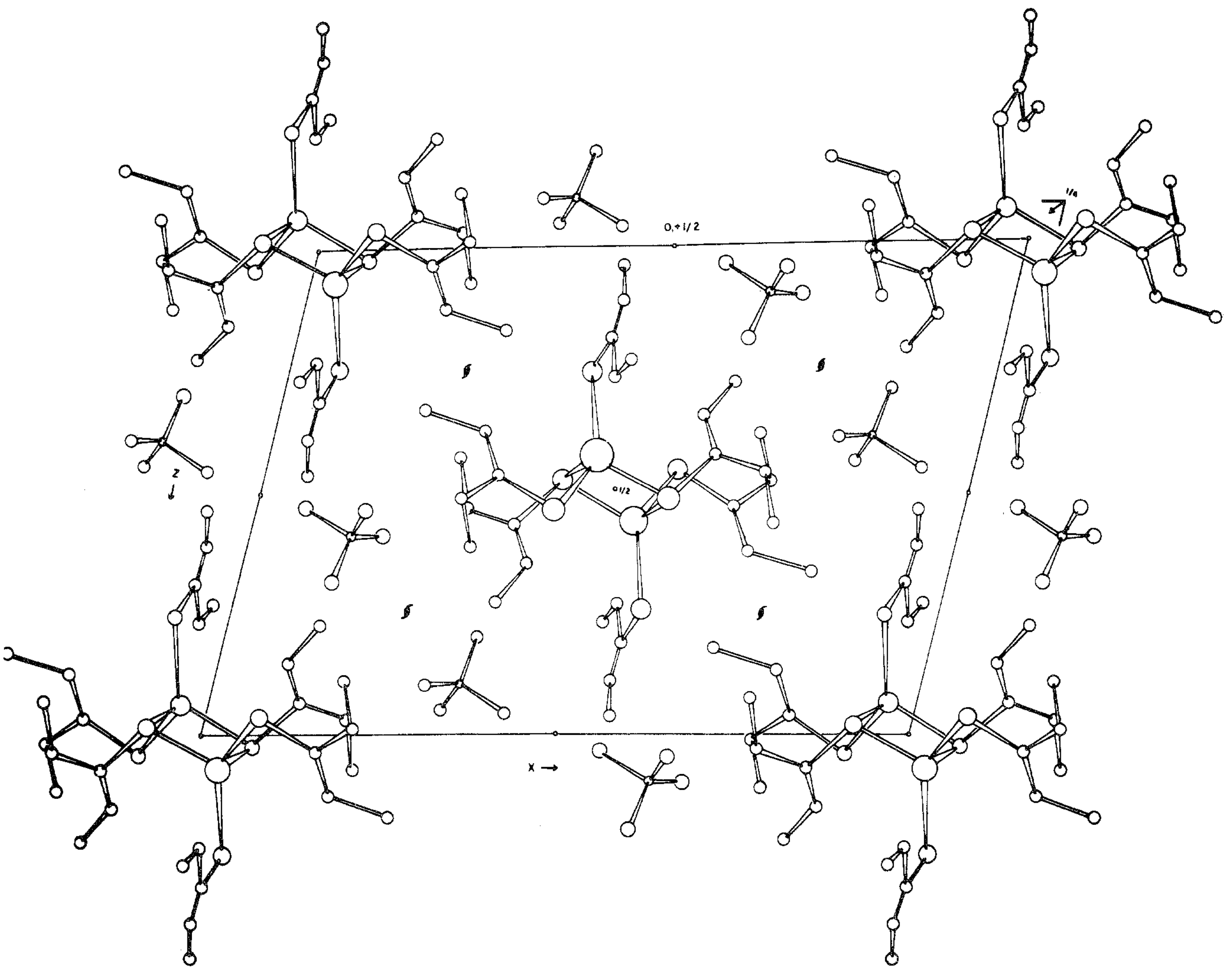

Figure 2. Packing diagram of $Cu_2(s\text{-dmtu})_6{}^{2+}(BF_4{}^-)_2$. The centers of the dimers are at centers of symmetry at 0, 0, 0 and $^1/_2$, $^1/_2$, $^1/_2$. It is seen that all the ligands are in the C_s symmetry conformation rather than either of the C_{2v} conformations.

sitional and thermal parameters are found in Table II.

Interatomic distances, angles, dihedral angles between normals to planes, and their errors[42] were computed using the parameters and variance-covariance matrix from the last cycle of least squares and are found in Table III. Root-mean-square components of thermal displacement are listed in Table IV.

Description and Discussion of Structures

The structures of $Cu(tu)_3BF_4$ and $Cu(s\text{-dmtu})_3BF_4$ consist of isolated $Cu_2(tu)_6{}^{2+}$ or $Cu_2(s\text{-dmtu})_6{}^{2+}$ molecular ions and $BF_4{}^-$ anions with only van der Waals and hydrogen-bond forces superposed on the ionic interaction. The similarity of the unit cell constants of $Cu(u\text{-dmtu})_3BF_4$ to those of the symmetric salt makes it very likely that this compound also exists as a $Cu_2L_6{}^{2+}$ dimer. As expected, $Cu(tu)_3ClO_4$[43] is also similar (Figures 1 and 2). The center of each dimer is a crystallographic center of symmetry which demands that the copper and bridging sulfur atoms form a planar Cu_2S_2 unit. However, in each structure this Cu_2S_2 unit is not square but lozenge shaped with alternating short and long Cu-S bridging distances. This distortion is intimately related to the nature of the bridging S orbitals and electrons; *vide infra.* Each

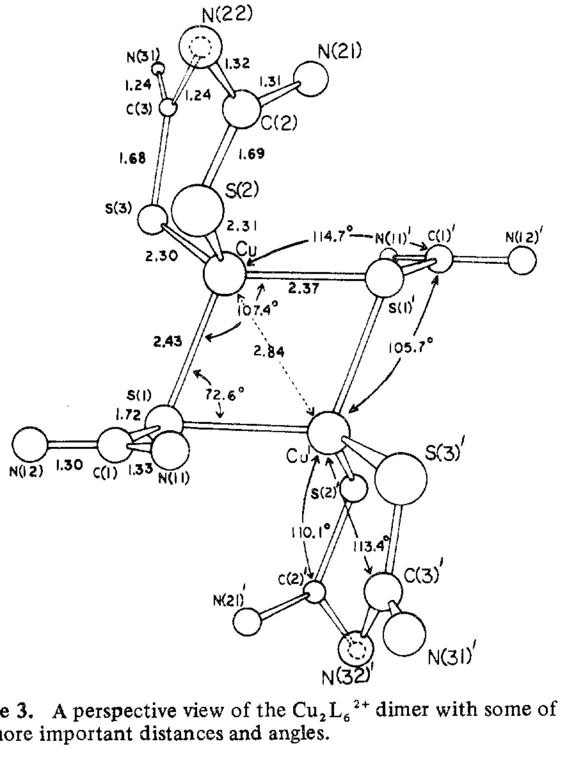

Figure 3. A perspective view of the $Cu_2L_6{}^{2+}$ dimer with some of the more important distances and angles.

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(42) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, a Fortran Crystallographic Function and Error Program," Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964. The version incorporates modifications by W. A. Spofford, III.

(43) F. Hanic and E. Durcanska, *Inorg. Chim. Acta*, 3, 293 (1969).

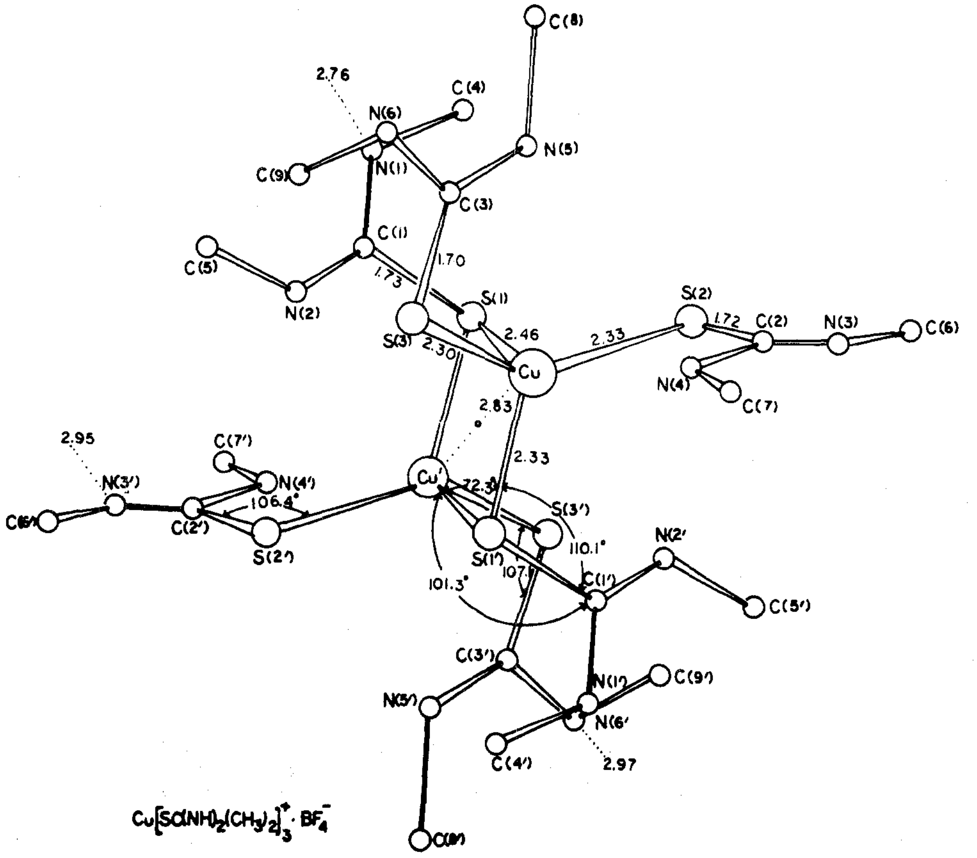

Figure 4. A perspective view of the $Cu_2L_6{}^{2+}$ dimer with some of the more important distances and angles.

copper atom in the dimer is four-coordinate (Cu-S) with approximately tetrahedral geometry although there are significant distortions from regular tetrahedral symmetry (Figures 3 and 4). The Cu-S distances are all 2.3 Å or greater, typical of "tetrahedral" Cu-S bonds which are at least 0.05 Å longer than three-coordinate planar Cu-S bonds. The Cu-S-C angles are all normal at 105° or greater. In addition, the tu and *s*-dmtu groups appear normal except for somewhat short C(3)-N(31) and C(3)-N(32) distances in $Cu(tu)_3BF_4$ which probably are simply reflections of the large thermal motions of these nitrogens, Table IV. The tu and *s*-dmtu groups are planar well within experimental error except for methyl hydrogens.

It is interesting to note (Figure 2) that in $Cu_2(s\text{-dmtu})_6{}^{2+}$ the methyl groups on the bridging ligands are ordered in such a way as to minimize steric repulsions in the bridge. Presumably in $Cu_2(u\text{-dmtu})_6{}^{2+}$ the methyl groups are on the nitrogen atom furthermost removed from the bridge. In this regard it is noteworthy that with tetramethylthiourea (tmtu) not more than three ligands can be bound to Cu(I), and $Cu(tmtu)_3BF_4$[7,8] has a planar three-coordinate CuS_3 entity. Only with unsubstituted thiourea can one get four ligands around Cu(I) and then only under special circumstances as in $[2(Cu(tu)_4)^+][SiF_6{}^{2-}]$.[31] Regardless of concentration or quantity of tu with $BF_4{}^-$ the largest tu:Cu ratio obtainable seems to be 3:1.

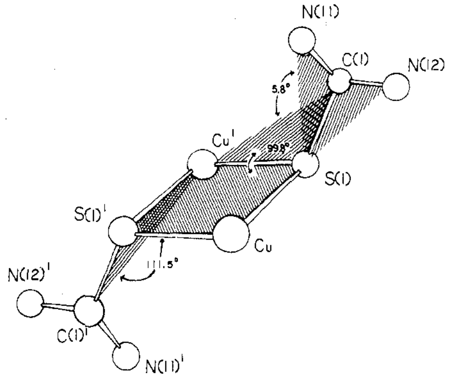

Figure 5. The important dihedral angles between planes of $Cu_2[SC(NH_2)_2]_6{}^{2+}$ which specify that the Cu′-S(1) bond includes an sp^2 orbital on S(1) and the Cu-S(1) bond includes a $p\pi$ MO from the S(1)-C(1) bond. The dihedral angle defined by CuS(1)C(1)-S(1)C(1)N(11) = 71.9 (6)° is not shown in the figure since it would create overlap of three sets of lines defining planes. The analogous dihedral angles (in degrees) for $Cu_2[s\text{-}SCN_2H_2(CH_3)_2]_6{}^{2+}$ and $Cu_4[SC(NH_2)_2]_{10}{}^{4+}$[10] are respectively as follows: Cu′S(1)C(1)-S(1)C(1)-N(11) = 5.7 (7), 10.8 (7); CuS(1)Cu′-CuS(1)C(1) = 107.8 (6), 108.6 (9); CuS(1)Cu′-Cu′S(1)C(1) = 96.0 (8), 96.9 (8); CuS(1)C(1)-S(1)C(1)N(11) = 70.1 (6), 85.9 (7).

Examination of the details of the orientation of the bridging tu ligands is informative. (We here refer to Figure 5 which is $Cu_2(tu)_6{}^{2+}$ but analogous details appear in the figure caption for $Cu_2(s\text{-dmtu})_6{}^{2+}$ as well as $Cu_4(tu)_{10}(SiF_6)_2$ and the arguments are parallel.) In Figure 5 the Cu′, S(1), C(1) and the S(1), C(1), N(12), N(11) planes seem to be almost coplanar [S(1), C(1), N(12), N(11) are coplanar], whereas the Cu, S(1), C(1) plane is essentially perpendicular to this plane. These facts coupled with the Cu-S(1)-C(1) angle of ~106° can only be interpreted such that the short Cu-S bridge bond is made up of a "tetrahedral" Cu orbital and a normally nonbonding sulfur sp^2 orbital and lone pair. However, the long Cu-S bridge bond is made up of a "tetrahedral" Cu(I) orbital and a $p\pi$ S-C MO with its electron pair. Hence, The Cu_2S_2 unit is bound together by four electron-pair bonds. It is to be noted in this case that sharp bridge angles (Cu-S-Cu′) of ~78° and short metal-metal distances (2.8 Å) do not give rise to electron-deficient sulfur-containing bridge bonds as has been found in $Cu(tu)_2Cl$[4] and $Cu_4(tu)_9(NO_3)_4$.[29] These examples illustrate the utility of the planar thiourea group as a probe in the nature of the metal–sulfur bonding and bridge bonding in particular.

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Registry No. $Cu(tu)_3BF_4$, 43096-99-7; Cu(*s*-dmtu)$_3$BF$_4$, 43097-00-3; Cu(*u*-dmtu)$_3$BF$_4$, 43097-01-4.

Supplementary Material Available. Table I, a listing of structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20X reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$5.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-2835.

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Structures of Metallocarboranes. IV.
Crystal and Molecular Structure of the Nido Metallocarborane Complex 8-η-Cyclopentadienyl-6,7-dicarba-8-cobalta-*nido*-nonaborane(11), 8-η-C_5H_5-8-Co-6,7-$C_2B_7H_{11}$, at −160°[1]

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The crystal and molecular structure of 8-η-C_5H_5-8-Co-6,7-$C_2B_7H_{11}$ has been determined by a complete three-dimensional X-ray diffraction study at −160°. The compound crystallizes in the monoclinic centrosymmetric space group $P2_1/n$ with $a = 6.811$ (2) Å, $b = 15.678$ (2) Å, $c = 10.949$ (5) Å, $\beta = 104.91$ (3)° at −160°, and $Z = 4$. Observed and calculated densities are 1.33 (2) and 1.348 g cm^{-3} at 25°. Diffraction data to $2\theta_{\max} = 50°$ (Mo Kα radiation) were collected on a Syntex $P\bar{1}$ automated diffractometer, and the structure was solved by conventional Patterson, Fourier, and full-matrix least-squares refinement techniques. The final discrepancy index is $R = 3.2\%$ for 1323 independent nonzero reflections. The molecule possesses a decaborane-like geometry, with the three heteroatoms occupying positions in the open face. The carbon atoms are adjacent to each other, one occupying a four-coordinate position and the other a five-coordinate position. The cobalt atom occupies another five-coordinate vertex, being bound to one carbon and three boron atoms and a π-bonded cyclopentadienyl ring. It is further coordinated by a hydrogen atom which bridges the bond between the cobalt atom and an adjacent boron atom occupying the other four-coordinate position. Another hydrogen atom bridges the bond between the four-coordinate boron atom and the adjacent boron atom on the open face. These bridging hydrogen atoms were unambiguously located in difference electron density maps and their coordinates and isotropic thermal parameters were successfully refined. Mechanistic aspects of the synthesis and chemistry of this compound are discussed in light of the atomic arrangement determined in this work.

Introduction

Three synthetic routes to the preparation of metallocarboranes have now been established.[2-4] Polyhedral expansion[5] involves the increase in the number of the vertices of a carborane or metallocarborane polyhedron through the incorporation of a new metallic vertex. The polyhedral subrogation reaction[6] involves the removal of a boron atom vertex from a carborane or metallocarborane by the action of strong base and replacement of this missing vertex with a transition metal ion; the product therefore has the same number of polyhedral vertices as did the starting material. The third synthetic method, termed polyhedral contraction,[7] involves the removal by strong base of a boron atom vertex from a metallocarborane followed by oxidation, which results in cage closure and the formation of a metallocarborane having one vertex less than its precursor. The first two synthetic methods have been widely applied and appear to be relatively general reactions of carboranes and metallocarboranes; polyhedral contraction has been examined to a lesser extent.

The actual mechanism of the polyhedral contraction process is more complex than described above. There is evidence that ligand-substituted metallocarboranes and nido metallocarboranes function as intermediates in this reaction.[7,8] In the polyhedral contraction of the complex 1-η-C_5H_5-1-Co-2,4-$C_2B_8H_{10}$, itself formed by polyhedral contraction of 3-η-C_5H_5-3-Co-1,2-$C_2B_9H_{11}$, a product formulated as $C_5H_5CoC_2B_7H_{11}$ was isolated.[8] Chemical and spectroscopic data indicated that this species possessed bridging hydrogen atoms, but it was impossible uniquely to assign the structure on the basis of these data alone. As a part of an effort to elucidate the mechanism of the polyhedral contraction reaction, a single-crystal X-ray structure determination of this compound was undertaken.

From a set of X-ray diffraction data collected at room temperature the structure was solved and refined to a discrepancy index of $R = 7.4\%$.[9] The overall geometry of the

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(9) $R = [\Sigma \| F_o| - |F_c\| / \Sigma |F_o|]$; $R_w = [\Sigma w \| F_o| - |F_c\|^2 / \Sigma w |F_o|^2]^{1/2}$; $w = 1/(\sigma(F))^2$.