

## The Structure of Tetrakis(thiourea)copper(I) Hexafluorosilicate

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**Abstract.**  $\{\text{Cu}[\text{C}(\text{NH}_2)_2\text{S}]_4\}_2\text{SiF}_6 \cdot 2\text{C}_4\text{H}_{16}\text{CuN}_8\text{S}_4^+ \cdot \text{SiF}_6^{2-}$ , orthorhombic,  $P2_12_12_1$ ,  $a = 13.133$  (3),  $b = 21.186$  (8),  $c = 12.303$  (5) Å,  $Z = 4$ ,  $D_m = 1.71$  (2),  $D_c = 1.71$  Mg m<sup>-3</sup>. Diffractometer data were used to solve and refine the structure by standard techniques to an  $R$  of 0.067. The structure consists of isolated  $\text{Cu}[\text{C}(\text{NH}_2)_2\text{S}]_4^+$  and  $\text{SiF}_6^{2-}$  ions. The Cu<sup>I</sup> is bonded to the S atoms of the thiourea groups producing a  $D_{2d}$  ( $42m$ ) distorted-tetrahedral  $\text{CuS}_4$  geometry. The Cu–S distances range from 2.319 (5) to 2.362 (6) Å.

**Introduction.** The reaction between  $\text{Cu}^{2+}$  and thiourea is an interesting oxidation–reduction reaction that generates a variety of Cu<sup>I</sup>–thiourea metal polynuclear species (Griffith, Spofford & Amma, 1978, and references therein) in which the degree of complexity is anion dependent. In the preparation of the dimer  $\text{Cu}_2[\text{C}(\text{NH}_2)_2\text{S}]_6^{2+} \cdot 2\text{BF}_4^-$  (Taylor, Weininger & Amma, 1974), upon long standing in glass two other products are formed, one of which is a polymeric cluster

$\text{Cu}_4[\text{C}(\text{NH}_2)_2\text{S}]_{10}^{4+}$  (Gash, Griffith, Spofford & Amma, 1973) and the other is the title compound. Details of this preparation will be published elsewhere (Gash, Griffith & Amma, 1979).

The data were collected by routine methods on a Picker diffractometer at room temperature by a  $\theta$ – $2\theta$  scan out to a maximum  $2\theta$  of  $55^\circ$  with Mo  $K\alpha$  radiation,  $\lambda = 0.71068$  Å. The scan time for each reflection was 102 s at  $0.5^\circ \text{ min}^{-1}$  and 40 s for background counting at the extremes of the scan. 3667 total reflections were measured and, of these, 2075 were retained as non-zero (two standard deviations above background). The structure was solved by straightforward Patterson and Fourier techniques and refined by a full-matrix least-squares procedure with weights based upon counting statistics (for details of computer programs, scattering factors, weighting scheme, etc., see Griffith *et al.*, 1978; Hunt, Griffith & Amma, 1976). The linear absorption coefficient is  $1.865 \text{ mm}^{-1}$ . The crystal used for data collection was  $0.10 \times 0.15 \times 0.25$  mm and bounded by the faces  $\{110\}$ ,  $\{001\}$ ,  $\{100\}$ ,  $\{120\}$ , which gave minimum and

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Table 1. Final atomic positional parameters with estimated standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
Cu(1)	–0.2887 (2)	0.1751 (1)	0.0325 (2)	N(141)	–0.2364 (16)	0.0217 (7)	0.0688 (16)
S(11)	–0.4416 (4)	0.1389 (3)	–0.0460 (4)	N(142)	–0.2848 (21)	0.0016 (8)	0.2412 (12)
S(12)	–0.2818 (4)	0.2801 (2)	0.0897 (4)	C(21)	0.2260 (16)	0.1806 (12)	0.5751 (17)
S(13)	–0.1890 (4)	0.1476 (3)	–0.1201 (4)	N(211)	0.2308 (16)	0.1732 (8)	0.4709 (15)
S(14)	–0.2469 (4)	0.1222 (3)	0.1934 (4)	N(212)	0.2322 (18)	0.1358 (8)	0.6478 (15)
Cu(2)	0.2011 (2)	0.3324 (1)	0.4890 (2)	C(22)	0.0119 (16)	0.4368 (11)	0.4676 (20)
S(21)	0.2097 (5)	0.2572 (2)	0.6261 (4)	N(221)	–0.0694 (15)	0.4669 (10)	0.5009 (15)
S(22)	0.0899 (4)	0.4062 (3)	0.5654 (4)	N(222)	0.0262 (13)	0.4325 (9)	0.3633 (12)
S(23)	0.3570 (4)	0.3718 (3)	0.4219 (4)	C(23)	0.4393 (15)	0.4079 (10)	0.5091 (17)
S(24)	0.1385 (4)	0.2942 (3)	0.3234 (4)	N(231)	0.5180 (14)	0.4396 (11)	0.4684 (15)
Si	0.2201 (5)	0.0211 (3)	0.2849 (4)	N(232)	0.4310 (14)	0.4044 (9)	0.6152 (13)
C(11)	–0.5230 (16)	0.1126 (10)	0.0560 (18)	C(24)	0.0168 (17)	0.2699 (11)	0.3519 (18)
N(111)	–0.6076 (13)	0.0806 (9)	0.0232 (13)	N(241)	–0.0494 (14)	0.2676 (11)	0.2655 (15)
N(112)	–0.5064 (13)	0.1202 (8)	0.1585 (8)	N(242)	–0.0188 (13)	0.2566 (9)	0.4460 (13)
C(12)	–0.3130 (14)	0.3269 (11)	–0.0241 (15)	F(1)	–0.2285 (10)	0.5061 (5)	0.3482 (8)
N(121)	–0.3444 (14)	0.3858 (7)	–0.0082 (13)	F(2)	0.2088 (9)	0.0372 (5)	0.4177 (7)
N(122)	–0.3074 (16)	0.3057 (7)	–0.1225 (11)	F(3)	–0.3030 (18)	0.4642 (8)	0.1862 (9)
C(13)	–0.0719 (16)	0.1889 (9)	–0.1193 (17)	F(4)	0.3166 (10)	0.0704 (10)	0.2770 (9)
N(131)	–0.0528 (13)	0.2211 (8)	–0.0288 (15)	F(5)	0.1387 (11)	0.0783 (7)	0.2562 (11)
N(132)	–0.0122 (12)	0.1834 (12)	–0.2005 (14)	F(6)	–0.1212 (15)	0.4713 (9)	0.2070 (10)
C(14)	–0.2626 (17)	0.0420 (10)	0.1675 (17)				

Table 2. *Interatomic distances (Å) and angles (°) with e.s.d.'s in parentheses*

Cu(1)—S(11)	2.357 (6)	S(11)—Cu(1)—S(12)	117.8 (2)
Cu(1)—S(12)	2.335 (6)	S(11)—Cu(1)—S(13)	93.8 (2)
Cu(1)—S(13)	2.362 (6)	S(11)—Cu(1)—S(14)	113.0 (2)
Cu(1)—S(14)	2.340 (5)	S(12)—Cu(1)—S(13)	116.9 (2)
Cu(2)—S(21)	2.323 (5)	S(12)—Cu(1)—S(14)	101.1 (2)
Cu(2)—S(22)	2.337 (6)	S(13)—Cu(1)—S(14)	115.1 (2)
Cu(2)—S(23)	2.359 (6)	S(21)—Cu(2)—S(22)	101.4 (2)
Cu(2)—S(24)	2.340 (5)	S(21)—Cu(2)—S(23)	116.5 (2)
		S(21)—Cu(2)—S(24)	114.3 (2)
		S(22)—Cu(2)—S(23)	117.0 (2)
		S(22)—Cu(2)—S(24)	111.2 (2)
		S(23)—Cu(2)—S(24)	97.0 (2)

maximum transmission factors of 0.954–0.969. The structure was refined to a final conventional  $R$  of 0.067 and weighted  $R_w$  of 0.059. The H atom positions were calculated and an isotropic  $B$  factor of  $5.5 \text{ \AA}^2$  was assigned to each, but neither the coordinates nor the  $B$  factors were permitted to refine. The final non-hydrogen positional and thermal parameters are given in Table 1. Table 2 contains the bond distances and angles involving non-hydrogen atoms.\*

**Discussion.** The structure consists of isolated  $\text{Cu}[\text{C}(\text{NH}_2)_2\text{S}]_4^+$  and  $\text{SiF}_6^{2-}$  ions with only van der Waals contacts between them, see Fig. 1. The local environment about each Cu atom ( $\text{CuS}_4$ ) is best described as a  $D_{2d}$  ( $\bar{4}2m$ ) distortion of the idealized  $T_d$  ( $43m$ ) (Muetterties & Alegranti, 1970; Lippard & Palenik, 1971) tetrahedral geometry of the closed-shell  $d^{10}$  metal ion, see Table 2. The Cu—S distances [2.319 (5) to 2.362 (6) Å] are those expected for this type of coordination,  $\sim 0.07$ – $0.10 \text{ \AA}$  longer than in the three-coordinate planar case (Weininger, Hunt & Amma, 1972). A glance at the S—Cu—S angles shows this distortion as a compression of the  $\text{CuS}_4$  tetra-

\* Lists of structure factors, anisotropic thermal parameters, H atom positions and additional bond distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34262 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

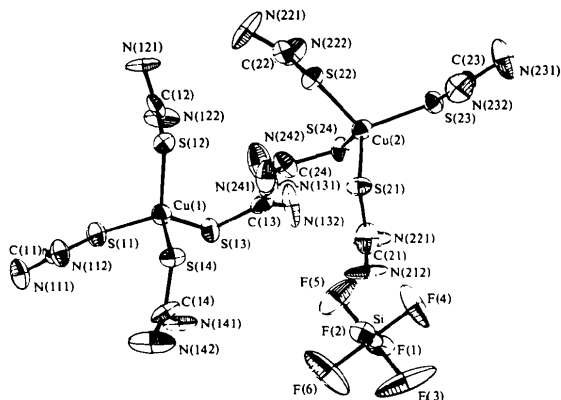


Fig. 1. An ORTEP drawing (Johnson, 1965) of the asymmetric unit of  $\{\text{Cu}[\text{C}(\text{NH}_2)_2\text{S}]_4\}\text{SiF}_6$ . The orientation of the thiourea groups is probably determined by packing considerations. Thermal ellipsoids are drawn at the 50% probability level.

hedron. The Cu—S—C angles of  $104.6$ – $112.4 (8)^\circ$  are normal for thiourea to  $\text{Cu}^I$   $\sigma$  donor–acceptor bonds. The S—C, C—N bonds and S—C—N, N—C—N angles are normal although the total variation is somewhat larger than expected.  $\text{SiF}_6^{2-}$  shows rotational motion about a F—Si—F axis as one might expect.

#### References

- GASH, A. G., GRIFFITH, E. A. H. & AMMA, E. L. (1979). To be published.
- GASH, A. G., GRIFFITH, E. A. H., SPOFFORD, W. A. III & AMMA, E. L. (1973). *J. Chem. Soc. Chem. Commun.* pp. 256–257.
- GRIFFITH, E. A. H., SPOFFORD, W. A. III & AMMA, E. L. (1978). *Inorg. Chem.* **17**, 1913–1917.
- HUNT, G. W., GRIFFITH, E. A. H. & AMMA, E. L. (1976). *Inorg. Chem.* **15**, 2993–2997.
- JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- LIPPARD, S. J. & PALENIK, G. J. (1971). *Inorg. Chem.* **10**, 1322–1324.
- MUETTERTIES, E. L. & ALEGRANTI, C. W. (1970). *J. Am. Chem. Soc.* **92**, 4114–4115.
- TAYLOR, I. F. JR, WEININGER, M. S. & AMMA, E. L. (1974). *Inorg. Chem.* **13**, 2835–2842.
- WEININGER, M. S., HUNT, G. W. & AMMA, E. L. (1972). *J. Chem. Soc. Chem. Commun.* pp. 1140–1141.