The Crystal Structure of Diethyl-disulfide Copper (I) Chloride

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The crystal structure of diethyl-disulfide copper(I) chloride has been determined and refined from three-dimensional X-ray data. The crystals are orthorhombic (space group $C222_1$) with eight formula units $CuCl \cdot (C_2H_5)_2S_2$ in a unit cell with the dimensions $a = 11.04$ Å, $b = 12.64$ Å and $c = 12.54$ Å. The structure has continuous $-Cu-Cl$-chains in which the Cu-atoms may be grouped into pairs. Each pair of Cu-atoms binds two disulfide molecules through covalent copper-sulfur bonds. The copper atoms are tetrahedrally coordinated to two chlorine atoms and two sulfur atoms, one from each of the disulfide groups. The bond lengths are: $Cu-Cl = 2.29$ and 2.34 Å, $Cu-S = 2.34$ and 2.40 Å, and $S-S = 2.04$ Å. The structure is discussed in relation to possible interaction between copper and disulfide groups in copper-containing enzymes.

The present structure determination was undertaken in connection with the problem of copper binding in the copper-containing oxidases cytochrome c oxidase, fungal laccase and ceruloplasmin. In cytochrome c oxidase there are two different kinds of copper atoms; one that is detectable by electron paramagnetic resonance and one that is not. Beinert [1] suggests in a recent discussion that the latter type, which functions as an electron acceptor, may involve a Cu^+-disulfide system. Electron spin resonance [2] and magnetic susceptibility measurements [3] of ceruloplasmin have shown that half the copper exists as Cu^+ and that the remaining half changes its valence during enzyme action. It has been suggested [1] that these copper atoms are arranged in clusters of two or four, possibly bridged by ligands which may involve a disulfide group. In a very interesting article, Hemmerich [1] has recently discussed copper disulfide complexes as model compounds for the active site of copper-containing enzymes, but no precise stereochemical knowledge of the interaction between Cu(I) and disulfide groups has so far been available.

EXPERIMENTAL

The complex between copper(I) chloride and diethyldisulfide was prepared by dissolving freshly purified CuCl in an excess of diethyldisulfide. (I am very much indebted to Professor G. Bergson who provided me with freshly prepared diethyldisulfide). Single crystals of the complex were obtained by slow evaporation of this solution. Since the crystals very easily loose diethyldisulfide and since the compound is oxidized on exposure to air, the evaporation was done in a capillary tube until a small number of white crystals had been formed. The remaining solution was then withdrawn from the capillary tube and the tube was sealed. The crystal used for the X-ray work was stable during the time of exposure.

Crystals prepared by evaporation were analyzed for copper, chloride, and sulfur. It was not possible, however, to obtain consistent values for the Cu:S ratio, probably due to difficulties in washing the crystals without loosing diethyldisulfide. Before this analytical problem was solved it was abandoned because the structure determination was completed and this showed that the formula of the complex investigated was CuCl·$(C_2H_5)_2S_2$.

The unit-cell dimensions of the orthorhombic crystals were determined from quartz-calibrated Weissenberg and oscillation photographs. Equi-inclination Weissenberg photographs for the nine zones $0 \leq l \leq 8$ were recorded using $CuK\alpha$-radiation. 466 independent intensities were estimated visually using the multiple-film technique and comparison with a calibrated intensity scale. The data were corrected for Lorentz and polarization effects. In order to obtain the extinction conditions for the $00l$ reflexions a 26° precession photograph of $h0l$ reflexions was recorded using the same crystal.

STRUCTURE DATA

Cell symmetry: Orthorhombic; space group $C222_1$
Dimensions: $a = 11.04 \pm 0.02$ Å, $b = 12.64 \pm 0.03$ Å, $c = 12.54 \pm 0.03$ Å
Volume of the unit cell: 1750 Å³
Density (observed by the flotation method): 1.6 g/cm³
Density: (calculated) 1.68 g/cm³ for a cell content of eight formula units CuCl·$(C_2H_5)_2S_2$.

DETERMINATION AND REFINEMENT OF ATOMIC PARAMETERS

A very careful analysis of the three-dimensional Pattersson synthesis was carried out since the exact composition of the compound was not known. An inspection of the general distribution of Pattersson peaks immediately excluded the possibility that the extinction condition $00l$ for $l = 2n + 1$ was accidental.

Table 1. Final atomic coordinates and their estimated standard deviations.

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B Å²	$\sigma(B)$ Å²
Cu(1)	0.0373	0.0005	0.0702	0.0004	0.1072	0.0005	6.2	0.2
S(2)	0.1799	0.0011	0.1428	0.0008	0.9901	0.0010	7.5	0.3
S(3)	0.3900	0.0010	0.3974	0.0008	0.3448	0.0009	7.6	0.3
Cl(4)	0.0000	—	0.1787	0.0010	0.2500	—	4.8	0.3
Cl(5)	0.1170	0.0012	0.0000	—	0.5000	—	4.5	0.3
C(6)	0.3220	0.0061	0.2001	0.0045	0.4778	0.0055	9.5	1.5
C(7)	0.4486	0.0052	0.1735	0.0049	0.4838	0.0057	10.0	1.6
C(8)	0.2659	0.0045	0.3898	0.0033	0.2655	0.0043	7.4	1.3
C(9)	0.1706	0.0051	0.4664	0.0039	0.2693	0.0048	9.5	1.4

The distribution of peaks was not consistent with a structure belonging to spacegroups $C222$, $Cmm2$, or $Cmmm$ but only with $C222_1$. The highest peaks of the Pattersson function formed a vector set consistent with the Harker-vectors of one Cu-atom in general position $8c$ of this spacegroup. Since it was not possible to form another similar vector set from the remaining high peaks it was concluded that there was only one Cu-atom in the asymmetric unit. All the remaining main features of the Pattersson function could then be

Table 2. Observed and calculated structure-factors.

H	K	L	$|Fo|$	$|Fc|$	H	K	L	$|Fo|$	$|Fc|$	H	K	L	$|Fo|$	$|Fc|$
2	0	0	132.2	149.4	2	6	1	70.0	66.2	0	14	2	29.4	28.7
4	0	0	22.2	27.1	4	6	1	71.6	85.5	2	0	3	43.0	60.2
6	0	0	67.2	58.3	1	7	1	63.4	64.9	4	0	3	144.1	141.3
10	0	0	12.4	10.8	3	7	1	78.2	80.1	6	0	3	48.2	53.3
3	1	0	46.7	48.8	5	7	1	55.1	58.5	8	0	3	15.9	19.9
13	1	0	19.7	18.7	9	7	1	39.8	36.7	10	0	3	35.1	47.5
0	2	0	134.0	151.2	0	8	1	30.3	20.1	1	1	3	88.3	76.7
2	2	0	70.1	76.7	2	8	1	26.3	25.2	3	1	3	139.4	138.0
4	2	0	40.1	26.7	4	8	1	60.5	58.7	5	1	3	73.5	36.4
6	2	0	28.8	31.2	8	8	1	30.9	22.4	7	1	3	39.4	44.7
8	2	0	16.0	11.5	1	9	1	30.6	32.9	9	1	3	25.1	31.4
10	2	0	13.5	12.5	3	9	1	37.9	39.5	11	1	3	20.2	28.5
12	2	0	19.3	21.1	5	9	1	27.4	25.9	13	1	3	10.4	6.1
3	3	0	74.0	52.1	0	10	1	55.7	54.4	0	2	3	96.6	104.1
5	3	0	78.2	68.5	2	10	1	51.4	40.9	2	2	3	127.3	125.2
11	3	0	24.2	25.7	4	10	1	31.0	26.7	4	2	3	66.9	60.8
0	4	0	150.9	150.0	1	11	1	38.0	39.9	8	2	3	21.0	21.8
4	4	0	20.2	19.2	3	11	1	24.1	12.4	10	2	3	21.7	30.4
6	4	0	10.1	14.4	5	11	1	23.7	12.8	1	3	3	152.4	145.2
8	4	0	26.9	15.7	9	11	1	15.3	3.7	3	3	3	111.3	110.7
1	5	0	122.2	106.4	3	13	1	20.1	5.8	5	3	3	58.9	59.8
3	5	0	10.5	9.9	2	14	1	18.3	1.7	7	3	3	25.0	26.1
5	5	0	26.1	25.0	4	0	2	61.1	63.4	0	4	3	159.4	175.5
7	5	0	12.4	15.6	6	0	2	35.5	29.1	2	4	3	119.9	129.4
9	5	0	11.2	9.0	8	0	2	51.3	52.3	4	4	3	119.0	105.0
0	6	0	33.1	40.8	10	0	2	19.3	9.2	6	4	3	35.2	38.1
2	6	0	76.4	76.3	1	1	2	83.2	70.9	8	4	3	18.3	13.3
4	6	0	36.4	29.1	3	1	2	105.9	76.7	10	4	3	15.1	14.0
6	6	0	34.7	37.1	5	1	2	50.7	39.3	1	5	3	115.9	112.9
10	6	0	13.0	19.5	7	1	2	41.5	48.1	3	5	3	100.2	85.4
12	6	0	8.8	12.4	9	1	2	19.0	25.0	5	5	3	53.7	45.5
1	7	0	57.9	63.2	13	1	2	13.7	10.8	0	6	3	53.2	51.2
3	7	0	108.8	125.9	0	2	2	37.2	6.8	2	6	3	75.5	63.8
7	7	0	13.3	6.8	2	2	2	96.7	92.2	4	6	3	10.8	11.1
11	7	0	20.4	17.0	4	2	2	77.1	72.1	6	6	3	22.4	33.0
0	8	0	48.5	34.3	6	2	2	89.2	103.3	8	6	3	18.0	19.1
2	8	0	96.1	100.5	8	2	2	54.1	67.8	1	7	3	57.2	46.0
4	8	0	89.2	80.0	12	2	2	16.6	6.2	3	7	3	22.6	14.7
6	8	0	21.6	20.1	1	3	2	134.7	120.3	5	7	3	26.7	28.6
8	8	0	12.3	7.8	3	3	2	66.9	69.8	7	7	3	42.2	47.1
10	8	0	24.3	11.7	5	3	2	98.1	110.9	11	7	3	10.2	5.1
1	9	0	25.2	17.8	7	3	2	78.8	98.5	0	8	3	43.3	33.5
3	9	0	46.1	57.4	9	3	2	43.3	50.2	2	8	3	30.5	22.4
5	9	0	50.5	55.1	0	4	2	12.5	13.3	4	8	3	37.3	27.7
9	9	0	26.9	18.6	2	4	2	42.4	40.4	6	8	3	40.7	40.2
0	10	0	16.7	13.4	4	4	2	85.9	79.0	8	8	3	21.4	19.7
4	10	0	28.1	29.6	6	4	2	94.6	102.9	1	9	3	43.9	41.3
6	10	0	27.5	23.8	8	4	2	63.1	72.8	3	9	3	28.8	21.1
8	10	0	25.6	26.5	1	5	2	49.2	39.0	5	9	3	29.6	26.9
1	11	0	28.2	28.4	3	5	2	96.8	82.6	7	9	3	27.4	27.5
9	11	0	8.7	17.7	5	5	2	88.9	88.9	0	10	3	28.3	24.1
0	12	0	29.1	28.6	7	5	2	43.9	44.6	2	10	3	49.5	52.5
2	12	0	27.4	25.9	0	6	2	51.0	51.5	6	10	3	25.3	18.2
1	13	0	24.6	18.8	2	6	2	91.6	86.9	8	10	3	12.6	14.1
0	14	0	11.6	13.9	6	6	2	88.5	72.5	1	11	3	44.2	43.2
2	0	1	183.9	199.4	1	7	2	40.5	35.7	3	11	3	25.5	24.0
4	0	1	19.2	34.6	3	7	2	97.1	82.3	0	12	3	23.4	23.3
6	0	1	108.7	122.5	5	7	2	20.6	7.2	2	12	3	31.9	32.0
8	0	1	48.0	56.9	7	7	2	21.4	20.7	1	13	3	12.3	16.2
1	1	1	103.4	100.4	0	8	2	39.8	27.8	3	13	3	11.8	14.8
3	1	1	113.6	120.2	2	8	2	26.8	17.0	5	13	3	9.7	6.8
5	1	1	90.6	92.9	4	8	2	14.0	13.8	1	15	3	10.1	6.9
7	1	1	75.3	82.7	6	8	2	30.4	38.8	2	0	4	144.8	160.6
2	2	1	196.6	160.9	3	9	2	25.8	17.9	4	0	4	25.4	26.6
4	2	1	136.6	129.4	5	9	2	38.5	28.0	6	0	4	40.0	56.5
6	2	1	81.1	76.3	7	9	2	26.4	29.9	1	1	4	115.2	110.6
1	3	1	92.9	95.0	0	10	2	23.8	24.3	3	1	4	106.9	108.7
3	3	1	116.2	83.9	2	10	2	32.0	25.3	5	1	4	19.1	19.3
5	3	1	102.1	91.1	4	10	2	40.5	29.6	0	2	4	108.4	111.8
7	3	1	19.0	17.0	6	10	2	31.8	25.1	2	2	4	125.6	117.8
9	3	1	36.4	39.9	8	10	2	15.0	16.5	4	2	4	90.3	96.4
2	4	1	153.1	147.0	1	11	2	22.7	22.7	6	2	4	33.6	31.3
4	4	1	34.0	35.9	3	11	2	37.0	29.1	1	3	4	65.7	63.1
8	4	1	21.0	32.9	5	11	2	34.2	30.7	3	3	4	67.3	65.5
1	5	1	126.3	116.2	2	12	2	19.1	20.7	5	3	4	97.6	101.1
3	5	1	93.6	91.8	4	12	2	21.7	21.4	0	4	4	36.5	26.7
5	5	1	19.1	15.1	1	13	2	20.4	19.5	2	4	4	73.7	69.4
0	6	1	101.7	90.5	3	13	2	16.4	14.4	4	4	4	64.5	65.8

H	K	L	$|F_o|$	$|F_c|$
6	4	4	36.2	40.3
8	4	4	28.1	34.1
1	5	4	116.1	117.8
3	5	4	59.3	52.9
5	5	4	36.4	33.0
7	5	4	30.2	34.2
0	6	4	192.6	190.5
2	6	4	100.7	85.3
6	6	4	33.7	34.1
1	7	4	110.8	110.9
3	7	4	25.9	19.3
5	7	4	29.6	24.6
7	7	4	19.7	14.2
9	7	4	15.0	8.1
0	8	4	62.0	65.9
2	8	4	36.5	33.5
1	9	4	31.3	21.7
3	9	4	23.0	20.2
7	9	4	15.4	8.6
2	10	4	25.7	19.4
6	10	4	16.4	12.4
7	11	4	12.3	13.1
3	13	4	19.9	22.3
2	14	4	16.3	16.3
4	14	4	15.0	20.1
2	0	5	24.2	27.6
4	0	5	131.1	132.6
6	0	5	27.9	29.9
8	0	5	22.2	30.0
10	0	5	25.3	36.4
1	1	5	38.3	33.0
3	1	5	108.2	109.9
5	1	5	71.5	81.4
7	1	5	32.9	31.6
9	1	5	26.7	43.9
11	1	5	15.0	17.1
0	2	5	46.7	37.0
2	2	5	120.4	106.1
4	2	5	57.9	55.9
6	2	5	25.5	33.3
8	2	5	32.9	39.3
10	2	5	24.2	24.0
1	3	5	88.7	65.0
3	3	5	62.4	51.0
5	3	5	54.1	53.2
7	3	5	11.2	13.8
9	3	5	12.1	14.9
11	3	5	10.7	9.5
0	4	5	43.2	44.3
2	4	5	88.6	76.4
4	4	5	80.3	70.7
6	4	5	23.5	30.4
8	4	5	12.9	8.1
12	4	5	8.4	7.7
1	5	5	48.3	39.7
3	5	5	58.1	41.8
5	5	5	42.9	45.5
7	5	5	29.9	35.5
0	6	5	14.2	8.0
2	6	5	38.7	30.3
4	6	5	33.8	37.0
6	6	5	63.7	65.5
8	6	5	26.5	33.5
1	7	5	41.5	37.8
3	7	5	29.0	31.0
5	7	5	56.5	51.5
7	7	5	55.1	58.1
0	8	5	30.6	21.5
2	8	5	18.6	20.6
4	8	5	36.1	36.1
6	8	5	51.9	42.5
8	8	5	12.4	21.1
1	9	5	11.6	11.8
3	9	5	11.8	11.0
5	9	5	33.5	28.6
7	9	5	11.6	17.4
2	10	5	12.0	15.6
4	10	5	22.0	19.1
6	10	5	11.5	11.7
8	10	5	11.3	5.4
1	11	5	24.6	23.4
7	11	5	10.5	3.9
0	12	5	24.6	23.8
4	12	5	11.7	6.3
6	12	5	9.4	4.0
8	12	5	6.9	4.5
1	13	5	17.8	14.3
4	14	5	8.6	12.9
2	0	6	82.2	94.7
4	0	6	123.4	134.7
6	0	6	19.0	14.7
10	0	6	19.4	18.3
1	1	6	33.8	35.1
3	1	6	138.3	121.9
5	1	6	45.6	58.7
7	1	6	35.2	34.0
9	1	6	19.1	18.2
0	2	6	9.8	15.5
2	2	6	22.9	15.9
4	2	6	45.7	42.2
6	2	6	47.6	52.2
8	2	6	46.7	42.6
1	3	6	29.4	24.6
3	3	6	50.6	42.6
5	3	6	50.9	52.9
7	3	6	41.8	47.7
9	3	6	26.2	29.2
0	4	6	26.4	27.8
2	4	6	38.3	33.3
4	4	6	58.2	55.5
6	4	6	44.7	46.7
8	4	6	32.5	30.7
10	4	6	17.6	11.1
1	5	6	13.5	7.6
3	5	6	44.3	36.4
5	5	6	41.6	33.8
0	6	6	47.5	48.1
4	6	6	40.8	33.2
6	6	6	13.2	6.2
1	7	6	59.0	59.5
3	7	6	23.8	18.8
5	7	6	22.0	19.6
0	8	6	80.0	77.6
2	8	6	39.0	34.4
4	8	6	20.5	12.4
6	8	6	17.0	18.4
8	8	6	15.7	9.7
1	9	6	43.0	48.5
3	9	6	19.9	16.1
5	9	6	24.8	22.1
0	10	6	19.0	14.7
4	10	6	26.0	25.9
6	10	6	20.1	17.5
3	11	6	21.8	16.7
5	11	6	18.0	27.3
2	0	7	51.6	57.2
4	0	7	27.4	26.7
6	0	7	13.4	9.3
12	0	7	7.5	6.0
1	1	7	77.8	92.4
3	1	7	28.1	25.9
5	1	7	27.9	29.2
9	1	7	15.9	9.9
0	2	7	80.8	116.7
2	2	7	86.5	84.0
4	2	7	21.1	23.2
6	2	7	25.5	25.3
1	3	7	103.7	108.8
3	3	7	51.4	42.6
5	3	7	30.5	31.6
0	4	7	53.1	66.1
2	4	7	91.6	89.5
4	4	7	9.3	13.1
6	4	7	19.8	23.1
8	4	7	11.3	14.8
1	5	7	55.7	52.7
3	5	7	57.1	55.6
5	5	7	23.9	20.1
7	5	7	21.4	19.2
11	5	7	11.7	15.1
0	6	7	21.1	13.2
2	6	7	50.2	39.5
4	6	7	37.3	39.9
6	6	7	36.6	28.4
8	6	7	12.1	11.6
1	7	7	15.7	14.6
3	7	7	30.8	28.0
5	7	7	31.6	23.9
7	7	7	25.4	23.5
0	8	7	11.8	11.7
2	8	7	21.9	17.7
6	8	7	16.6	11.0
10	8	7	9.9	6.5
1	9	7	42.0	32.0
3	9	7	27.7	27.6
0	10	7	41.3	31.5
2	10	7	42.6	30.0
4	10	7	25.5	24.1
1	11	7	23.5	21.2
3	11	7	19.0	15.4
5	11	7	18.4	11.8
7	11	7	9.8	3.3
2	12	7	10.9	7.5
6	12	7	12.2	3.9
2	14	7	7.0	4.7
2	0	8	25.1	37.9
4	0	8	18.7	19.5
6	0	8	22.1	29.9
10	0	8	9.9	4.8
1	1	8	71.4	85.4
3	1	8	32.9	36.0
5	1	8	15.4	15.9
7	1	8	13.7	13.0
0	2	8	27.1	31.3
2	2	8	73.9	65.6
4	2	8	20.6	28.9
6	2	8	15.5	15.7
10	2	8	9.6	8.0
12	2	8	8.3	11.4
1	3	8	39.1	31.4
3	3	8	59.8	59.5
5	3	8	44.8	45.4
11	3	8	9.0	14.5
0	4	8	28.0	25.6
2	4	8	49.7	40.3
4	4	8	45.0	44.8
6	4	8	18.8	24.1
8	4	8	22.7	19.2
3	5	8	21.0	19.0
5	5	8	33.9	30.6
7	5	8	18.2	16.1
9	5	8	16.0	18.5
0	6	8	19.8	16.5
2	6	8	28.2	21.9
4	6	8	29.9	21.5
6	6	8	20.8	20.0
8	6	8	19.1	12.6
1	7	8	18.9	11.7
3	7	8	34.0	46.4
5	7	8	14.7	9.6
7	7	8	10.4	11.1
0	8	8	10.6	6.7
2	8	8	51.6	36.5
4	8	8	36.4	34.1
1	9	8	20.8	11.2
3	9	8	31.0	24.2
6	10	8	12.2	11.4
8	10	8	9.9	10.8
1	11	8	10.1	10.4
7	11	8	10.0	11.2
0	12	8	9.2	12.1

explained on the basis of two sulfur atoms in general position 8c, and one chlorine atom in each of the special positions 4a and 4b.

It was thus assumed that the formula of the complex was $CuCl \cdot (C_2H_5)_2S_2$. The atomic coordinates obtained so far were then refined by the method of least-squares using a diagonal approximation. These refined coordinates were used to compute phase angles for a three-dimensional difference Fourier summation, from which the remaining four carbon atoms were located. There were only four main peaks in this function. The atomic coordinates (hydrogen atoms excluded), individual isotropic temperature factors, and nine scale-

factors, one for each set of Weissenberg multiple-films, were then refined by the method of full matrix least-squares. After four cycles of refinement the conventional R-value was 0.135 and all shifts were less than one tenth of their estimated standard deviations. A final three-dimensional difference synthesis showed no peak higher than one third of the height of a carbon atom. Final atomic parameters are listed in Table 1, and a comparison of $|F_{obs}|$ and $|F_{calc}|$ is made in Table 2.

All the calculations were made in Uppsala on the computer CD 3600 using a set of programmes adapted to this computer by R. Liminga and J. O. Lundgren at the Institute of Chemistry, Uppsala. The basic routines of these programmes were devised by Zalkin, Berkeley, Calif., U.S.A.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure has continuous $-Cu-Cl-Cu-Cl$ chains running in the a-direction. The copper atoms of these chains may be grouped into pairs with a
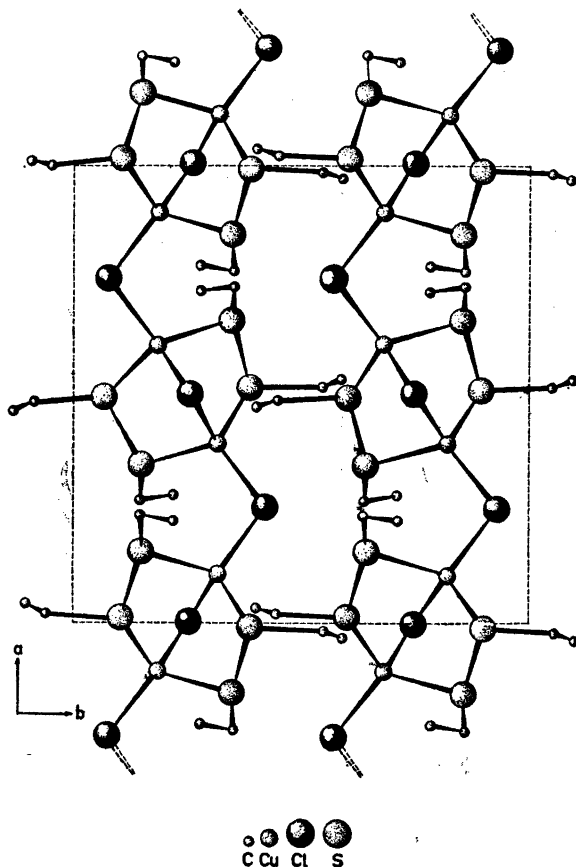
Fig. 1. Projection of the structure along the c-axis.

fairly chort Cu—Cu distance of 3.22 Å between paired Cu-atoms compared to a distance of 3.68 Å between adjacent non-paired Cu-atoms. Each such pair of copper atoms binds two disulfide molecules through covalent copper-sulfur bonds in the way shown in Fig. 1.

Each of the paired copper atoms is bonded to two sulfur atoms one from each of the two disulfide groups. Both disulfide groups of this dimeric structural unit thus form bridges between the paired Cu-atoms by the formation of Cu_1—S—S—Cu_2 bonds.

The copper atoms are thus tetrahedrally coordinated to two chlorine atoms and two sulfur atoms with bond angles S—Cu—S = 107°, Cl—Cu—Cl = 113°, and S—Cu—Cl = 106° (mean value). A tetrahedral coordination of copper(I) is fairly common [4] and has previously been found in for instance CuCl [5] and complexes between CuCl and thiourea [6] and thioacetamide.[7]

Table 3. Interatomic distances and angles.

Atoms	Distances (Å)	σ(Å)	Atoms	Distances (Å)	σ(Å)
Cu(1)— S(2)	2.34	0.01	S(2)—C(6)	1.99	0.06
Cu(1)— S(3)	2.40	0.01	S(3)—C(8)	1.70	0.05
Cu(1)—Cl(4)	2.29	0.01	C(6)—C(7)	1.44	0.09
Cu(1)—Cl(5)	2.35	0.01	C(8)—C(9)	1.43	0.07
S(2)— S(3)	2.04	0.02			

Atoms	Angles (°)	σ(°)	Atoms	Angles (°)	σ(°)
S(2)—Cu(1)— S(3)	106.8	0.5	S(3)— S(2)— C(6)	100.1	2.1
S(2)—Cu(1)—Cl(4)	112.1	0.4	Cu(1)— S(3)— S(2)	97.4	0.6
S(2)—Cu(1)—Cl(5)	106.1	0.5	Cu(1)— S(3)— C(8)	117.9	1.5
S(3)—Cu(1)—Cl(4)	114.1	0.5	S(2)— S(3)— C(8)	101.8	1.9
S(3)—Cu(1)—Cl(5)	92.4	0.4	Cu(1)—Cl(4)—Cu(1)	106.5	0.6
Cl(4)—Cu(1)—Cl(5)	112.9	0.4	Cu(1)—Cl(5)—Cu(1)	87.0	0.6
Cu(1)— S(2)— S(3)	102.0	0.6	S(2)— C(6)— C(7)	103.8	4.2
Cu(1)— S(2)— C(6)	115.6	2.0	S(3)— C(8)— C(9)	122.4	3.9

Continuous —Cu—Cl-chains is a structural feature that has been found in complexes of CuCl with cyclooctatetraene [8] and with azomethane.[9] The Cu—Cl bond lengths of 2.29 and 2.35 Å in this structure agree quite well with those of 2.28—2.34 Å found in the previously mentioned compounds and in several complex copper(I) chlorides.[4] The shorter distance of 2.29 Å is the Cu—Cl distance from the chlorine atom that bridges the paired Cu-atoms.

The copper-sulfur bond lengths of 2.34 and 2.40 Å are surprisingly short and are of the same order of magnitude as the Cu—S bond lengths in the thiourea [7] (2.33 Å) and thioacetamide [8] (2.345 Å) complexes of CuCl, indicating a comparatively strong Cu—S interaction.

The S—S bond of 2.04 Å in the disulfide group is of the same length as the S—S bond in N,N'-diglycyl-α-cystine dihydrate.[10] The dihedral angle CSS—SSC is 97.7°.

There are some aspects of this structure that might be of importance in relation to theories about the mode of binding of copper in copper-containing oxidases. If a disulfide group is involved in this interaction it seems most likely that the copper atom is coordinated by a localized σ-bond to only one of the sulfur atoms of the disulfide group. This of course includes the possibility that the copper atoms may be arranged in pairs with a disulfide bridge between the copper atoms arranged in a similar manner as one of the bridges in this structure. It seems less likely that there should be any kind of π-bond interaction between Cu^+ and the S—S bond since the length of this bond in N,N'-diglycyl-α-cystine dihydrate [10] strongly indicates that S—S bonds in cystine residues have a low π-bond order.[11] For stereochemical reasons it is also very unlikely that one copper atom is coordinated by σ-bonds to both sulfur atoms of the same disulfide group, since this would give a S—Cu—S bond angle of less than 60°.

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