333. *The Crystal Structure of Tetrakisthioacetamidecopper*(I) *Chloride.*

By Mary R. Truter and K. W. Rutherford.

Three-dimensional *X*-ray crystal-structure analysis of the complex, $Cu(S{:}CMe{\cdot}NH_2)_4{}^+Cl^-$, has confirmed the tetragonal bisphenoidal ($\bar{4}$) arrangement of the sulphur atoms about the copper ion. After anistropic refinement the following bond lengths were obtained: Cu–S = 2·343 + 0·005, S–C = 1·71 ± 0·02, C–C = 1·50 ± 0·02, and C–N = 1·31 ± 0·02 Å. The thioacetamide unit is planar. The bond angles round the copper ion are distorted from those of a regular tetrahedron, the angle bisected by the $\bar{4}$ axis being 103°40′ ± 5′.

In 1936 Cox, Wardlaw, and Webster[1] demonstrated the approximately tetrahedral configuration of the cuprous ion by investigation of the crystal structure of tetrakisthioacetamidecopper(I) chloride. They found that there were two molecules in the tetragonal unit cell (a = 12·43 Å, c = 5·52 Å, space group $I\bar{4}$), so that the arrangement of the sulphur atoms about the copper ion must be square or tetrahedral. Consideration of a few intensities showed that the square arrangement was impossible.

This paper describes a three-dimensional determination of the structure to measure the lengths of the metal–ligand bonds and of the bonds within the ligand for comparison with those in thioacetamide itself.[2]

Methods and Results

Crystal Data.—$C_8H_{20}N_4S_4CuCl$, M = 399·54. Tetragonal, a = 12·449 ± 0·005 Å, c = 5·469 ± 0·005 Å, U = 847·6 Å^3, D_m = 1·56 (by flotation), Z = 2, D_c = 1·56, $F(000)$ = 412. Space group. $I\bar{4}$ ($S_4{}^2$, No. 82). Cu-K_α radiation, single crystal oscillation and Weissenberg photographs, absorption coefficient μ = 76 cm.$^{-1}$. Molecular symmetry required, $\bar{4}$ about copper and chlorine.

Determination of an Approximate Structure.—The two copper atoms in the unit cell can be assigned to one of the pairs of special positions with $\bar{4}$ symmetry; we chose these to be (0,0,0) and ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$). A Fourier synthesis was calculated with phases given by the copper atoms only for $F(hk0)$ and in the resulting projection of the electron density, peaks appeared at $x/a = \frac{1}{2}$, $y/b = 0$ (and $x/a = 0$, $y/b = \frac{1}{2}$), and at x/a = 0·071, y/b = 0·129 (and seven symmetry-related positions); these confirmed the conclusion by Cox *et al.*[1] that the chloride ions occupy the

---

[1] Cox, Wardlaw, and Webster, *J.*, 1936, 775.

[2] Truter, *J.*, 1960, 997.

positions ($\frac{1}{2}$,0,$\frac{1}{4}$) and 0,$\frac{1}{2}$,$\frac{3}{4}$) and that the sulphur atoms are in general positions. It was not possible to distinguish the light atoms from the spurious peaks until we had calculated the next synthesis based on the signs given by the copper and chloride ions and the sulphur atoms. Another set of structure factors was calculated for all the atoms except hydrogen, and a third Fourier synthesis was computed; the corresponding electron-density map is shown in Fig. 1. The atoms of one asymmetric unit are shown joined by lines; the following discussion refers to one asymmetric unit. One of the atoms in the overlapping pair which are close enough to be bonded to sulphur must be C(1) and the other, (3), could then be CH_3 or NH_2, while (2) is NH_2 or CH_3. Refinement by successive Fourier difference syntheses reduced $R(hk0)$ to 0·19 but did not resolve the overlapping atoms.

To determine the z-co-ordinates the $(0kl)$ projection was solved. This gave further refinement of both x- and y-co-ordinates because of the tetragonal symmetry, but as the structure is non-centrosymmetrical the phases could not be determined from the copper atom alone. An approximate z-co-ordinate was obtained for the sulphur atom by assuming that the Cu–S bonds were arranged in a regular tetrahedron; this led to a value $z/c = \pm 0{\cdot}237$ and gave a reasonable value, 2·29 Å, for the Cu–S bond length. Preliminary calculation of structure factors showed that the sulphur atom at $x/a = 0{\cdot}077$ and $y/b = 0{\cdot}127$ should have $z/c = +0{\cdot}237$. For the other atoms z-co-ordinates were derived from reasonable assumptions about the bond lengths and angles. Structure factors were calculated and gave an R value of 0·23; this was reduced to 0·11 after refinement by Fourier and difference Fourier syntheses. Fig. 2 shows a drawing of the structure in this projection, in which atom (2) overlapped another related to it by symmetry. Comparison of the interatomic distance C(1)–(3) = 1·405 Å and C(1)–(2) = 1·520 Å with the single bond values for C–C and C–N bonds suggested that (2) was the CH_3 group and (3) was the NH_2 group. These assumptions were used for the first three-dimensional structure factor calculation [$R(hkl) = 0{\cdot}157$] and subsequent refinement showed that they were correct. Fig. 3 is a drawing of the structure projected along the c-axis.

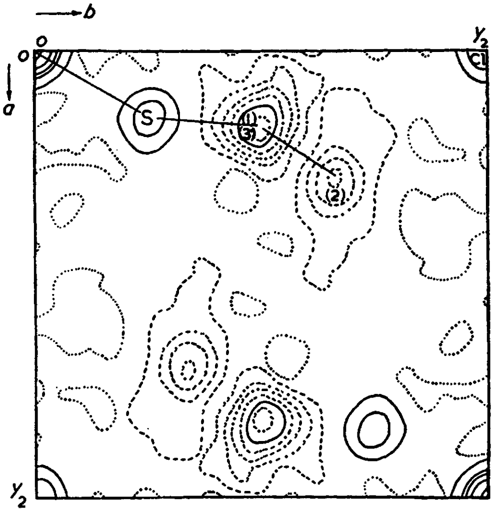

FIG. 1. The electron density projected down [001]. The zero contour is dotted, the intervals of 2e/Å^2 are shown by broken lines, and those of 10e/Å^2 by full lines. One quarter of the unit cell is shown.

Three-dimensional Refinement.—Four successive refinements by the method of differential syntheses, with allowance for individual isotropic temperature factors, for each atom, reduced R to 0·108. It was evident from the curvatures of the electron density in different directions that an allowance for anisotropic thermal motion was required. The isotropic thermal parameter for copper, $B = 3{\cdot}3$ Å^2, was larger than that for the lighter chlorine and sulphur ($B = 3{\cdot}2$ and 3·1 Å^2, respectively), not smaller as would be expected from the difference in atomic masses; this suggested that the scattering power of the copper was probably being reduced by the effect of anomalous dispersion. Accordingly anisotropic refinement was carried out by the method of least squares, the scattering factor curve for copper now being corrected for the real part of the anomalous dispersion.[3] Even in the most unfavourable cases correction for the imaginary

[3] Dauben and Templeton, *Acta Cryst.*, 1955, **8**, 841.

part of the anomalous dispersion would introduce a difference between the intensities of (*hkl*) and ($\overline{hkl}$) of less than 10% and not be detectable by our experimental technique. Six cycles of anisotropic refinement led to no more significant changes in the parameters and *R* was reduced to 0·088.

Results.—The observed structure amplitudes and the components of the final calculated structure factors are given in Table 1.

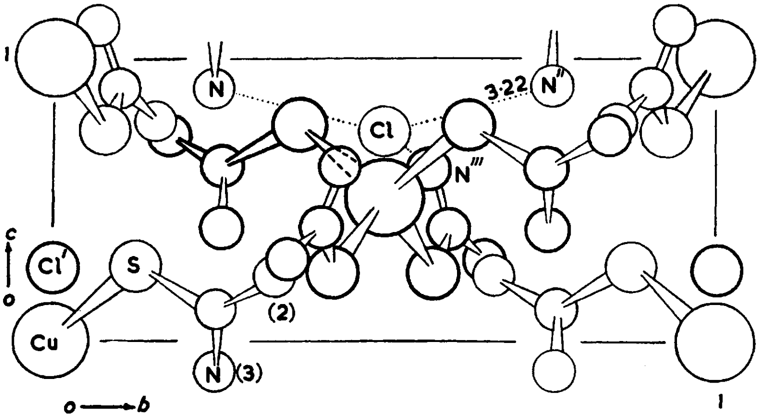

FIG. 2. The structure projected along [100]. The complex ion centred on the copper atom at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) and the chloride ion at ($\frac{1}{2}$,0,$\frac{1}{4}$) are shown by thick circles. Three of the four hydrogen bonds reaching the chloride ion are shown by dotted lines; the fourth is from a nitrogen atom in the unit cell beneath the one shown.

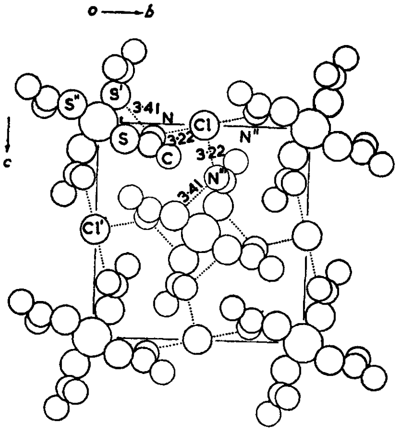

FIG. 3. The structure projected along [001]. The hydrogen bonds are shown by dotted lines, on some of which the distances in Å are marked.

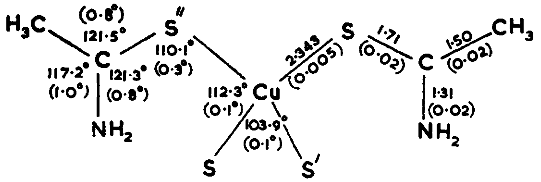

FIG. 4. The bond lengths, in Å, and angles in the tetrakisthioacetamidecopper(I) ion with the standard deviations in parentheses.

Table 2 shows the co-ordinates of the atoms in Å and their standard deviations, σ. Table 3 gives the thermal vibration parameters and their standard deviations; U_{11}, U_{22}, and U_{33} are the mean-square amplitudes of vibration parallel to the crystallographic a^*, b^*, and c^* axes, respectively, and with the values of U_{12}, U_{23}, and U_{13} they define the magnitude and direction of the ellipsoid of vibration.

As shown in Table 3, the motion of the copper atom along the *c*-axis is greater than that for the sulphur atom; this effect is not consistent with motion of the complex ion as a rigid body, so it is not possible to apply a simple correction for systematic errors caused by rotational

TABLE 1.

Observed structure amplitudes and calculated structure factors ($F_c = A + iB$) × 10.

l	$\lvert F_o\rvert$	*A*	*B*
00*l*			
2	803	−784	0
4	540	514	0
6	220	−209	0
10*l*			
1	749	678	−24
3	312	321	−23
5	84	−64	−10
7	109	100	2
20*l*			
0	731	744	0
2	214	29	−136
4	435	392	31
6	39	−1	−34
30*l*			
1	599	482	−185
3	212	213	−16
5	139	131	28
40*l*			
0	37	70	0
2	763	740	−92
4	112	−98	41
6	119	124	−15
50*l*			
1	329	259	−221
3	184	170	46
5	216	210	−34
60*l*			
0	24	23	0
2	186	176	47
4	277	258	−64
6	86	94	41
70*l*			
1	438	198	−428
3	483	203	391
5	226	104	−188
80*l*			
0	484	543	0
2	127	37	123
4	184	155	−73
6	58	−10	52
90*l*			
1	402	183	−365
3	308	127	281
5	132	47	−125
10,0,*l*			
0	126	111	0
2	115	122	62
4	94	110	21
11,0,*l*			
1	244	170	152
3	75	63	−35
5	45	46	37
12,0,*l*			
0	252	255	0
2	74	65	−38
4	37	26	46
13,0,*l*			
1	135	96	99
3	114	56	−114
14,0,*l*			
0	160	171	0
2	42	−57	−20
15,0,*l*			
1	112	41	−97
16,0,*l*			
0	129	156	0
11*l*			
0	730	769	0
2	177	163	−7
4	328	311	−31
6	67	−5	38
21*l*			
1	118	−103	−18
3	548	462	−11
5	187	190	−18
7	44	36	18
−21*l*			
1	1160	435	1091
3	614	273	−571
5	317	88	243
7	121	46	−99
31*l*			
0	649	−701	0
2	620	716	74
4	69	79	−7
6	194	183	7
−31*l*			
0	894	886	0
2	517	520	−118
4	160	−53	128
6	130	54	−92
41*l*			
1	555	485	388
3	149	80	−102
5	232	211	62
−41*l*			
1	928	767	821
3	560	100	−513
5	241	3	228
51*l*			
0	527	−587	0
2	811	980	52
4	277	−246	−12
6	225	217	10
−51*l*			
0	185	35	0
2	571	529	−150
4	47	26	20
6	113	97	−9
61*l*			
1	186	196	12
3	162	159	52
5	207	192	−16
−61*l*			
1	390	189	−327
3	309	261	108
5	157	110	−77
71*l*			
0	48	50	0
2	447	388	141
4	49	37	−16
6	54	72	1
−71*l*			
0	139	156	0
2	453	371	39
4	133	49	−121
6	112	49	89
81*l*			
1	365	348	−79
3	214	137	136
5	90	−43	−61
−81*l*			
1	472	280	−338
3	224	114	165
5	133	63	−103
91*l*			
0	478	510	0
2	53	23	−12
4	124	118	−30
−91*l*			
0	81	−93	0
2	328	296	14
4	78	51	−59
10,1,*l*			
1	190	130	128
3	185	139	−120
5	55	36	55
−10,1,*l*			
1	220	96	192
3	155	114	−78
11,1,*l*			
0	87	86	0
2	163	148	−24
4	78	68	31
−11,1,*l*			
0	90	−93	0
2	368	346	21
12,1,*l*			
1	328	149	256
3	218	55	−232
−12,1,*l*			
1	251	162	180
3	111	31	−100
13,1,*l*			
0	34	6	0
2	183	163	−96
−13,1,*l*			
2	112	123	19
14,1,*l*			
1	107	39	85
3	129	73	−85
−14,1,*l*			
1	71	48	51
3	80	76	13
15,1,*l*			
0	51	42	0
2	49	48	24
−15,1,*l*			
0	236	187	0
2	49	−38	21
22*l*			
0	359	367	0
2	137	88	109
4	459	355	−145
6	110	53	97
32*l*			
1	581	238	−505
3	552	244	391
5	313	204	−178
−32*l*			
1	919	597	767
3	430	171	−342
5	218	44	193
42*l*			
0	433	387	0
2	654	597	109
4	94	−99	20
6	115	108	−15
−42*l*			
0	1023	1097	0
2	30	29	27
4	237	210	105
6	72	−19	−78
52*l*			
1	633	641	−81
3	27	15	32
5	78	77	−8
−52*l*			
1	267	284	−29
3	257	246	45
5	55	57	−10
62*l*			
0	135	139	0
2	478	443	−87
4	18	−16	22
6	97	93	−17
−62*l*			
0	701	880	0
2	194	−146	37
4	355	334	−33
6	60	−61	16
72*l*			
1	315	267	−142
3	199	161	81
5	66	79	−32
−72*l*			
1	629	416	−463
3	326	153	271
5	147	−51	−132
82*l*			
0	756	788	0
2	131	−132	15
4	262	255	−29
6	76	−69	16
−82*l*			
0	473	492	0
2	101	97	−53
4	121	106	−43
6	41	6	48
92*l*			
1	262	223	−165
3	161	163	0
5	41	−38	−20
−92*l*			
1	276	138	−237
3	128	122	80
5	128	123	−56
10,2,*l*			
0	504	538	0
2	268	−234	−95
4	294	316	−4
−10,2,*l*			
0	137	−129	0
2	329	335	−35
4	44	−15	−16
11,2,*l*			
1	60	53	39
3	148	163	−31
5	29	43	17
−11,2,*l*			
1	209	195	−69
3	14	13	−2
12,2,*l*			
0	95	110	0
2	102	103	−15
4	49	51	36
−12,2,*l*			
0	88	73	0
2	142	141	−21
13,2,*l*			
1	121	122	20
3	41	21	−39
−13,2,*l*			
1	115	50	−83
3	91	83	74
14,2,*l*			
0	20	7	0
2	103	108	4
−14,2,*l*			
0	263	234	0
15,2,*l*			
1	65	48	−36
−15,2,*l*			
1	134	74	−55
33*l*			
0	244	−170	0
2	722	714	50
4	100	−24	−95
6	127	110	53
43*l*			
1	608	563	−6
3	118	117	44
5	68	73	−13
−43*l*			
1	530	183	470
3	442	307	−220
5	161	92	129

TABLE 1. (*Continued*)

l	$\lvert F_o \rvert$	*A*	*B*
53*l*			
0	237	242	0
2	673	638	−92
4	154	−160	33
6	92	−97	−23
−53*l*			
0	384	432	0
2	169	−127	58
4	480	438	27
6	30	−12	−33
63*l*			
1	617	299	586
3	587	138	−528
5	267	104	221
−63*l*			
1	405	221	305
3	321	278	−72
5	37	−19	34
73*l*			
0	119	135	0
2	206	148	−102
4	199	207	58
6	52	48	−37
−73*l*			
0	659	762	0
2	95	−9	82
4	164	152	13
6	26	−36	−8
83*l*			
1	326	139	288
3	304	232	−166
5	83	30	86
−83*l*			
1	277	248	149
3	125	121	−43
5	39	29	35
93*l*			
0	399	376	0
2	28	0	−21
4	168	176	−7
−93*l*			
0	246	−243	0
2	472	454	1
4	66	−69	27
10,3,*l*			
1	121	96	−78
3	149	161	15
5	25	8	−13
−10,3,*l*			
1	248	204	102
3	86	36	−89
5	105	86	49
11,3,*l*			
0	84	66	0
2	86	93	55
4	92	100	3
−11,3,*l*			
0	100	−77	0
2	406	365	−47
4	132	−126	−7
12,3,*l*			
1	197	113	163
3	46	56	−17
−12,3,*l*			
1	113	105	−30
3	58	55	−34
13,3,*l*			
0	15	−24	0
2	251	220	11
−13,3,*l*			
2	60	67	−2
14,3,*l*			
1	125	94	76
3	55	7	−66
−14,3,*l*			
1	122	57	−83
3	90	69	48
15,3,*l*			
0	81	−91	0
2	149	153	15
−15,3,*l*			
0	100	84	0
2	42	57	−2
44*l*			
0	613	677	0
2	158	−126	63
4	433	404	0
6	11	−21	−6
54*l*			
1	397	302	235
3	238	186	−148
5	104	77	87
−54*l*			
1	365	26	−328
3	426	385	119
5	93	60	−74
64*l*			
0	290	271	0
2	202	133	−155
4	209	182	88
6	51	34	−49
−64*l*			
0	701	769	0
2	252	−218	−24
4	397	389	−10
6	75	−73	11
74*l*			
1	279	72	231
3	307	225	−178
5	139	109	106
−74*l*			
1	246	242	−39
3	210	177	54
5	17	6	−9
84*l*			
0	327	323	0
2	55	−2	60
4	236	224	74
−84*l*			
0	316	299	0
4	215	208	46
94*l*			
1	215	201	−61
3	182	123	125
5	37	−7	−55
−94*l*			
1	278	122	276
3	147	109	−110
5	87	96	66
10,4,*l*			
0	440	470	0
2	89	−92	29
4	139	152	−46
−10,4,*l*			
0	207	213	0
2	152	138	14
4	40	16	56
11,4,l			
1	277	113	−222
3	187	78	179
−11,4,*l*			
1	204	178	−51
3	71	41	68
12,4,*l*			
0	100	94	0
2	109	94	62
−12,4,*l*			
0	119	100	0
2	69	69	25
13,4,*l*			
1	125	116	−75
3	36	23	46
−13,4,*l*			
1	326	51	−260
3	207	73	184
14,4,*l*			
0	14	−12	0
2	155	146	−60
−14,4,*l*			
0	162	136	0
2	42	14	7
15,4,*l*			
1	42	45	−25
−15,4,*l*			
1	131	69	−87
55*l*			
0	340	375	0
2	137	142	37
4	216	183	96
6	57	5	−68
65*l*			
1	518	297	448
3	373	122	−315
5	157	31	157
−65*l*			
1	365	320	−6
3	204	162	−110
5	32	−11	38
75*l*			
0	66	−48	0
2	459	390	−54
4	70	−39	55
6	74	91	−39
−75*l*			
0	306	291	0
2	207	153	−92
4	99	115	33
85*l*			
1	363	208	280
3	123	81	−103
5	88	81	67
−85*l*			
1	415	75	418
3	411	190	−332
5	166	86	153
95*l*			
0	143	157	0
2	268	234	67
4	16	−21	−14
−95*l*			
2	255	230	−77
4	51	51	62
10,5,*l*			
1	236	187	−141
3	64	68	43
5	28	−3	−42
−10,5,*l*			
1	313	170	238
3	166	65	−159
11,5,*l*			
0	90	76	0
2	108	126	−34
4	42	34	−45
−11,5,*l*			
0	146	117	0
2	112	118	41
12,5,*l*			
1	120	66	−113
3	96	81	83
−12,5,*l*			
1	66	61	−15
3	96	82	72
13,5,*l*			
0	55	−71	0
2	193	188	9
−13,5,*l*			
0	88	100	0
2	65	38	56
14,5,*l*			
1	82	82	48
−14,5,*l*			
1	122	85	−25
15,5,*l*			
0	43	−37	0
66*l*			
0	607	619	0
2	86	70	−26
4	73	68	14
6	20	−7	−19
76*l*			
1	302	269	42
3	127	43	−129
5	72	67	45
−76*l*			
1	274	241	67
3	87	92	−41
5	49	51	31
86*l*			
0	27	−10	0
2	327	283	−32
−86*l*			
0	72	81	0
2	180	160	−86
4	99	95	45
96*l*			
1	265	155	−194
3	173	75	151
5	86	75	−70
−96*l*			
1	154	145	55
3	156	92	−141
5	59	52	67
10,6,*l*			
0	95	89	0
2	145	153	−16
4	55	22	−55
−10,6,*l*			
0	343	315	0
2	63	−8	−76
4	91	111	12
11,6,*l*			
1	338	86	−315
3	154	72	143
−11,6,*l*			
1	96	73	−74
3	104	109	4
12,6,*l*			
0	171	167	0
2	32	−39	32
−12,6,*l*			
0	263	279	0
2	150	−140	7
13,6,*l*			
1	55	53	−5
3	59	60	54
−13,6,*l*			
1	131	62	−77
3	93	69	65
14,6,*l*			
0	112	120	0
2	9	13	−4
−14,6,*l*			
0	152	121	0
2	42	40	15

TABLE 1. (*Continued*)

l	$\|F_o\|$	A	B
	$77l$		
0	268	−259	0
2	530	489	−97
4	116	−125	−18
	$87l$		
1	113	103	22
3	90	75	−60
5	125	130	27
	$-87l$		
1	303	154	237
3	140	47	−123
5	126	97	70
	$97l$		
0	237	−228	0
2	373	344	52
4	39	−44	3
	$-97l$		
0	144	146	0
2	165	158	−23
4	18	0	23
	$10,7,l$		
1	100	112	52
3	48	53	−6
	$-10,7,l$		
1	195	137	124
3	108	82	−98
	$11,7,l$		
0	91	123	0
2	55	59	2
4	57	48	−34
	$-11,7,l$		
0	198	190	0
2	39	−32	−25
	$12,7,l$		
1	61	59	−8
3	68	73	26
	$-12,7,l$		
1	53	26	−30
3	104	107	−17
	$13,7,l$		
0	104	101	0
2	46	16	49
	$-13,7,l$		
0	77	78	0
2	52	50	−32
	$14,7,l$		
1	93	57	83
	$-14,7,l$		
1	113	69	62
	$88l$		
0	12	−28	0
2	227	211	−10
	$98l$		
1	135	109	76
3	36	50	21
	$-98l$		
1	221	156	−112
3	111	41	120
	$10,8,l$		
0	160	167	0
2	62	51	41
	$-10,8,l$		
0	285	247	0
2	69	−5	71
	$11,8,l$		
1	100	102	−34
3	45	61	6
	$-11,8,l$		
1	125	59	−104
3	135	76	121
	$12,8,l$		
0	256	255	0
2	139	−75	−22
	$-12,8,l$		
0	224	218	0
2	91	−77	10
	$13,8,l$		
1	84	44	−46
	$-13,8,l$		
1	96	66	23
	$99l$		
0	81	−16	0
2	232	204	−13
	$10,9,l$		
1	248	95	179
3	104	55	−87
	$-10,9,l$		
1	143	79	−86
3	101	58	98
	$11,9,l$		
0	94	95	0
2	77	66	−31
	$-11,9,l$		
0	66	70	0
2	65	37	50
	$12,9,l$		
1	79	60	39
	$-12,9,l$		
1	103	65	60
	$13,9,l$		
0	125	119	0
	$-13,9,l$		
0	57	50	0
	$10,10,l$		
0	114	125	0
2	35	−9	−2
	$11,10,l$		
1	96	45	73
	$-11,10,l$		
1	204	34	−154
	$12,10,l$		
0	114	117	0
	$-12,10,l$		
0	33	25	0
	$11,11,$		
0	66	−50	0

TABLE 2.

Atomic co-ordinates.

	x/a	y/b	z/c	X	$\sigma(X)$	Y	$\sigma(Y)$	Z	$\sigma(Z)$
Cu ...	0·0000	0·0000	0·0000	0·000 Å	—	0·000 Å	—	0·000 Å	—
Cl ...	0·0000	0·5000	0·7500	0·000	—	6·2245	—	4·1018	—
S ...	0·0758	0·1273	0·2651	0·9435	0·0026 Å	1·5853	0·0023 Å	1·4496	0·0028 Å
C(1)	0·0979	0·2442	0·1137	1·219	0·009	3·040	0·008	0·622	0·010
C(2)	0·1506	0·3373	0·2348	1·875	0·011	4·199	0·010	1·284	0·015
N ...	0·0657	0·2575	−0·1094	0·818	0·010	3·205	0·011	−0·598	0·011

TABLE 3.

Thermal parameters (all units are 10^{-4} Å^2).

	U_{11}	σ	U_{22}	σ	U_{33}	σ	U_{12}	σ	U_{23}	σ	U_{13}	σ
Cu	379	7	379	7	523	16	0	—	0	—	0	—
Cl	413	12	413	12	625	31	0	—	0	—	0	—
S.........	563	13	378	10	405	11	−22	8	−3	10	−14	11
C(1) ...	416	41	322	35	383	44	60	34	−62	37	39	40
C(2) ...	588	53	385	43	743	79	−205	40	−56	54	−196	58
N	745	59	612	54	476	52	−20	38	60	49	−96	51

oscillation. Nevertheless, to render these results comparable with those for thioacetamide,[3] we carried out an analysis of the molecular vibration parameters for the thioacetamide group alone. Cruickshank's revised procedure [4] was used, the computation being carried out on the Pegasus computer with programmes written by Mr. A. Bujosa and Dr. D. W. J. Cruickshank.[5] From the internal consistency, the approximation that the thioacetamide group moved as a rigid body was as satisfactory as for the uncombined molecule and the calculated corrections were closely similar, being +0·018 Å for C–S, +0·015 Å for C–C, and +0·014 Å for C–N. The bond lengths and angles are shown in Fig. 4 together with an indication of their reliability;

---

[4] Cruickshank, *Acta Cryst.*, 1961, **14**, 896.

[5] Cruickshank, Pilling, and (in part) Bujosa, Lovell, and Truter, "Computing Methods and the Phase Problem in X-ray Crystal Analysis," Pergamon Press, 1961, p. 32.

although the standard deviations calculated from those of the co-ordinates given in Table 2 are only 0·003 Å for Cu–S, 0·009 Å for C–S, 0·014 Å for C–C, and 0·015 Å for C–N, we have increased them to allow for the uncertainty in the correction for rotational oscillation. The Cu–S bond length corresponds to the corrected position for sulphur and is 0·003 Å shorter than the uncorrected one.

The plane through the thioacetamide group is defined by

$$0{\cdot}8852X - 0{\cdot}03388Y - 0{\cdot}3188Z + 0{\cdot}1646 = 0.$$

The deviations from this plane, +0·016Å for C(1) and −0·002 Å, −0·005 Å, and −0·005 Å for S, C, and N, respectively, are not statistically significant. The copper atom lies 0·165 Å from this plane so that the Cu–S bond makes an angle of 86° with the normal to the plane.

Each nitrogen atom has one contact at 3·22 Å to a chloride ion and one of 3·41 Å to a sulphur atom, and the angles subtended at the nitrogen are: C–N $\cdots$ Cl 115·0°, C–N $\cdots$ S′ 111·6° and Cl $\cdots$ N $\cdots$ S′ 112·6°.

Each chloride ion is surrounded by four NH_2 groups at 3·22 Å, forming a very flattened tetrahedron, the N $\cdots$ Cl $\cdots$ N″ angle which is bisected by the $\bar{4}$ axis being 152·4°; these contacts probably represent hydrogen bonds and are shown in Figs. 2 and 3. The only other interatomic distance of less than 3·5 Å between atoms not bonded to a common atom was 3·36 Å for Cu–N.

DISCUSSION

The structure consists of approximately tetrahedral complex cations and chloride anions held by electrostatic forces and by hydrogen bonds. The hydrogen bonding provides a probable explanation for the thermal motion of the chloride ions; the NH $\cdots$ Cl $\cdots$ HN bonds (Fig. 2) have a larger component in the *ab*-plane than parallel to the *c*-axis, so that the chloride ion is more restricted in its movement in the plane than perpendicular to it. The difference 0·021 Å between U_{11} and U_{33} for chlorine is statistically significant, being 6·5 times the corresponding standard deviation. The significant deviation of the S–Cu–S″ angle (which is bisected by the $\bar{4}$ axis) from that for a regular tetrahedron may also be attributable to a hydrogen bond from the NH_2 group to a neighbouring sulphur atom, as shown in Fig. 3. The $NH_2 \cdots S$ distance is comparable with those (3·40—3·50 Å) found for the corresponding bonds in thioacetamide.[2] While in thioacetamide the two N $\cdots$ S bonds and the N–C bond were approximately coplanar, supporting the postulate of sp^2-hybridisation for the nitrogen atom, in this complex the three bonds round nitrogen are far from coplanar, being disposed along three of the four tetrahedral directions.

FIG. 5. The bond lengths, in Å, and angles of thioacetamide, with the standard deviations in parentheses.

Within experimental error, the thioacetamide ligand has the same dimensions as in the uncomplexed molecule[2] (Fig. 5), so that, in spite of the apparently pyramidal environment of nitrogen, the simplest postulate is that the hybridisation of all the atoms is unchanged on complex formation. This implies that the sulphur is bonded to the copper by a lone pair of electrons in approximately the position they occupy in the free molecule. If we assume that in thioacetamide the sulphur atom is sp^2-hybridised, its six electrons can be disposed as 1 in a σ-bond to carbon, 1 in a p_z-orbital forming a π-bond with carbon, and 2 in each of the other two sp^2-orbitals as lone pairs. When one lone pair forms the S–Cu bond, this bond should lie in the plane of the thioacetamide molecule and the C–S–Cu angle should be less than 120° because the repulsion between the other lone pair and the copper or carbon atoms would be greater than that between these two atoms; in fact, the bond does not lie quite in the plane, it makes an angle to 86° to the normal, and the bond angle is less than 120°.

The arrangement of ligands round the copper supports the postulate that the orbitals used by this atom are formed by hybridisation of the 4*s*- and the three 4*p*-orbitals. Although the Cu–S distance has been determined very accurately, this may not represent a fixed bond length. The thermal vibration parameters suggest that, parallel to the *c*-axis, the copper and sulphur atoms are moving essentially independently.

That the Cu–S distance may represent the average (either a time-average or a space-average) separation rather than a fixed bond length is supported by some interesting discrepancies in the literature. For example, in tristhioureacopper(I) chloride[6] considerable and significant variations (2·31—2·42 Å) were found between crystallographically independent Cu–S bond lengths. Even for cuprous sulphide, Cu_2S, the structure of the room-temperature form is complicated[7] and has not been solved, while the form stable above 105°, although the subject of controversy, is apparently deficient in copper and disordered. For cupric sulphide[8] the Cu–S distances vary from 2·19 to 2·35 Å and the arrangement cannot be simply attributed to the effect of the d^9-electron shell. These different distances may correspond to different amounts of ionic, covalent, and metallic character in the bonds; the thermal motion of the tetrakisthioacetamidecopper(I) ion suggests that this Cu–S bond also is not purely covalent.

EXPERIMENTAL

Tetrakisthioacetamidecopper(I) chloride, prepared by Kurnakow's method,[9] crystallised from water as pale yellow tetragonal needles.

The unit-cell dimensions were measured by the Straumanis method. For intensity measurement about the *c*-axis a needle 0·25 mm. in diameter was used, and for measurements about the *a*-axis a needle was cut to 0·25 mm. in length; no absorption correction was made.

Equi-inclination Weissenberg photographs were taken about the *a*- and *c*-axes up to 8*kl* and *hk*3; 509 independent reflections gave measurable intensities. A multiple-film technique was used and the intensities of the spots were estimated visually with the aid of a calibration strip. Lorentz and polarisation factors were applied by use of a Cochran chart. Approximately absolute values of F^2 were obtained by comparison with the absolute values quoted by Cox *et al.*[1] for (00*l*), (*hh*0), and (*h*00); during refinement the scale was one of the parameters. Extinction was corrected empirically from the relation $I = I_0 \exp(\alpha I_{\text{obs}})$; the values of I were those calculated during isotropic refinement. A plot of $\log I/I_{\text{obs}}$ against I_{obs} for reflections with $\sin^2 \theta \leqslant 0{\cdot}077$ gave two straight lines, one corresponding to $\alpha = 3{\cdot}54 \times 10^{-5}$ for values from the crystal set about the *c*-axis and the other with $\alpha = 2{\cdot}66 \times 10^{-5}$ for the other crystal.

Three-dimensional isotropic refinement was carried out on the Manchester University electronic computer with programmes devised by Dr. D. W. J. Cruickshank and Miss D. E. Pilling[5] modified for $I\bar{4}$ by Mr. R. Shiono; the method of differential synthesis was used, a back-shift correction applied for termination of series errors, and an "n" shift (determined empirically as $n = 1{\cdot}7$) to allow for the phase-angle effect in a non-centrosymmetrical structure. The scattering factors used were those of McWeeny[10] for C and N, of Berghuis *et al.*[11] for Cu^+ and Cl^-, and of James and Brindley[12] for S. Anisotropic refinement was carried out by the method of least squares on the Leeds University Ferranti Pegasus computer with programmes devised by Dr. D. W. J. Cruickshank and Miss D. E. Pilling.[5] The function minimised was $R' = \sum w(|F_o| - |F_c|)^2$ where the weighting factor, w, was $1/|F_o|$. The scattering factors of Berghuis *et al.*[11] were used for C, N, Cl^-, and Cu^+, with a correction[3] for the real part of the anomalous dispersion of copper; Tomiie and Stam's scattering factor[13] was used for sulphur.

---

[6] Knobler, Okaya, and Pepinsky, *Z. Krist.*, 1959, **111**, 385.
[7] Buerger and Buerger, *Amer. Min.*, 1944, **29**, 55.
[8] Oftedal, *Z. Krist.*, 1932, **83**, 9.
[9] Kurnakow, *Ber.*, 1894, **27**, 46.
[10] McWeeny, *Acta Cryst.*, 1951, **4**, 51.
[11] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.
[12] "International Tables for the Determination of Crystal Structures," Borntraeger, Berlin, 1935.
[13] Tomiie and Stam, *Acta Cryst.*, 1958, **11**, 126.

We thank our colleagues [5] for the use of their programmes, Mr. R. Shiono and Mr. J. F. P. Donovan for running the computations on the Manchester University electronic computer, and Miss M. Jowitt and Mrs. B. Hawkshaw for those on the Leeds University computer; we are grateful to the directors of the computing laboratories of Manchester and Leeds Universities for the use of their facilities. One of us (K. W. R.) is indebted to the University of Leeds for a Post-graduate research grant. Part of the cost of the computing was met by a grant from the D.S.I.R. and some of the equipment used was provided by the Royal Society and Imperial Chemical Industries Limited.

DEPARTMENT OF INORGANIC AND STRUCTURAL CHEMISTRY,
THE UNIVERSITY OF LEEDS.

[*Received, October* 19*th*, 1961.]