Table 9 (*cont.*)

	B_i	q_i	q_i	q_i
C(2)	2·54	−0·035	−0·999	0·014
	1·94	0·724	−0·016	0·690
	1·49	−0·689	0·035	0·724
C(3)	2·99	0·011	0·980	0·200
	2·24	0·307	−0·194	0·932
	1·55	−0·952	−0·051	0·303
C(4)	4·04	0·022	0·892	0·451
	2·35	0·580	−0·379	0·721
	1·91	−0·815	−0·246	0·525
C(5)	2·92	0·172	0·609	0·775
	2·66	0·596	−0·691	0·410
	1·53	−0·784	−0·391	0·482
N	3·11	0·071	−0·924	0·376
	1·90	−0·244	0·349	0·905
	1·73	0·967	0·156	0·200
O(1)	3·44	−0·144	−0·605	0·783
	2·03	−0·757	0·577	0·307
	1·60	0·638	0·548	0·541
O(2)	2·82	−0·719	−0·550	0·426
	2·20	0·685	−0·667	0·294
	1·77	0·123	0·503	0·856
O(3)	3·88	0·005	0·908	0·420
	2·31	0·820	−0·244	0·518
	1·87	−0·572	−0·342	0·745
O(4)	4·46	−0·065	0·906	0·418
	2·65	0·362	−0·369	0·856
	1·87	−0·930	−0·207	0·304
O(5)	5·37	−0·913	0·085	0·399
	2·48	0·376	0·553	0·744
	1·94	0·157	−0·829	0·536
O(6)	3·59	0·385	0·737	0·556
	2·78	−0·567	−0·287	0·772
	2·21	0·728	−0·612	0·307

The apparent magnitudes and orientations of the principal axes of the temperature-factor ellipsoids are given in Table 9. With very few exceptions, the thermal motions are slightly higher in the zinc compound than in the copper compound; this effect could of course be caused by differences in the sizes or perfections of the crystals chosen for intensity measurements. Not surprisingly, one of the exceptions to the trend is O(2), the apical ligand that is bonded more closely to the zinc atom than to the copper atom. The shapes and orientations of the ellipsoids are strikingly similar in the two compounds; and, as discussed by GM, the patterns of the more pronounced anisotropies are readily interpretable from a structural standpoint. It should be mentioned that in neither compound is there evidence of significant rigid-body motion of the glutamate group as a whole – which is hardly surprising, since this group is tied down in several places by relatively strong bonds to two different metal atoms.

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The Crystal Structure of Tetrasodium Tetramminecopper (II) Di-catena-di-μ-thiosulphato-cuprate (I)

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The crystal structure of tetrasodium tetramminecopper(II) di-catena-di-μ-thiosulphato-cuprate(I), $Na_{4n}[Cu(NH_3)_4]_n[Cu_n(S_2O_3)_{2n}]_2$, has been determined and refined by differential syntheses, three-dimensional data being used (final $R = 11·5$ %). The crystals are tetragonal, space group $I4/m$, $a = 13·814$ and $c = 5·759$ Å. Two formula units are contained in the unit cell.

The crystal structure consists of cations Na^+ and $[Cu^{II}(NH_3)_4]^{2+}$ and of catena-anions, $[Cu_n(S_2O_3)_{2n}]^{3n-}$. The coordination around Cu^{II} is purely square planar, no other atom completing the coordination polyhedron to give any pyramidal or bipyramidal arrangement.

The anion is formed by Cu^I atoms tetrahedrally coordinated by four thiosulphato groups S(1)–S(2)O_3. Each S(1) bridges two Cu^I atoms giving rise to chains parallel to [001].

The thiosulphato group has nearly tetrahedral structure.

Introduction

Thiosulphato complexes of univalent silver or univalent copper are known either in the solid state or in solution. The equilibria involved in solution are important in connexion with the photographic process.

Also, in the solid state, the thiosulphato complexes of univalent silver and copper are very similar and very often isostructural; some of these had been prepared in this laboratory and had been found to belong to two sets, each comprising several isostructural compounds. The first set is formed by the compounds $Na_4[Cu^{II}(NH_3)_4][Cu^{I}(S_2O_3)_2]_2$, pale violet crystals, $Na_4[Cu^{II}(NH_3)_4]\,[Ag(S_2O_3)_2]_2$, pale violet crystals (Ferrari, Cavalca & Coghi, 1952*a*) and the compound $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2$, yellow crystals (Ferrari, Cavalca & Coghi, 1952*b*); the second set comprises compounds such as $(NH_4)Ag(S_2O_3)_4Cl_2$ and others where, alternatively or together, NH_4 is replaced by K, Ag is replaced by Cu^I and Cl is replaced by Br or I (Ferrari, Cavalca & Nardelli, 1952).

The crystal structure of the compound

$$Na_4[Cu^{II}(NH_3)_4]\,[Cu^{I}(S_2O_3)_2]_2\,,$$

belonging to the first set, has now been investigated; because of the particular chain structure resulting from the present determination the salt can be called tetrasodium tetrammine-copper(II) di-catenadi-μ-thiosulphato-cuprate(I). The different valence state of the copper atoms, as determined by magnetic measurements ($\mu = 1{\cdot}78$ Bohr magnetons) (Ferrari, Cavalca & Coghi, 1952*a*) and as inferred from the isostructurality with the tetramminenickel compound (Ferrari, Cavalca & Coghi, 1952*b*), is confirmed by the present research.

Experimental

Preparation

Crystals of the compound have been prepared by evaporation of a mixture containing sodium thiosulphate, copper(II) sulphate and tetramminecopper(II) sulphate. Clusters of pale violet needles are obtained.

Crystal data

One crystal was rotated around the elongation axis, [001] and around [$\bar{1}$10].

Cu $K\alpha$ radiation was used ($\lambda = 1{\cdot}5418$ Å).

Tetrasodium tetramminecopper(II) di-catena-di-μ-thiosulphatocuprate(I) $Na_{4n}[Cu^{II}(NH_3)_4]_n\ [Cu^{I}_n(S_2O_3)_{2n}]_2$.

F.W. ($n = 1$): 799·240.

Tetragonal bipyramidal

$a = 13{\cdot}814 \pm 0{\cdot}003 \qquad c = 5{\cdot}759 \pm 0{\cdot}002$ Å

$U = 1099{\cdot}0$ Å^3

$D_m = 2{\cdot}45$ g.cm^{-3} (by flotation); $\quad D_x = 2{\cdot}41$ g.cm^{-3}

$Z = 2 \qquad F(000) = 790$

$\mu = 117{\cdot}55$ cm^{-1} (Cu $K\alpha$).

Possible space groups: $I4/m$ (no.87), $I\bar{4}$ (no.83) and $I4$ (no.79), from systematic absences.

The crystals do not exhibit piezoelectricity; the space group $I4/m$ has therefore been assumed. The determination of the structure has confirmed that the assumption was correct.

Intensity measurements

Integrated reflexions $hk0$, $hk1$, $hk2$, $hk3$, $hk4$ by rotation around [001], and hhl by rotation around [$\bar{1}$10], were measured by means of a microphotometer on photographs taken by the equi-inclination Weissenberg method, using the multiple-film technique. The intensities were corrected for absorption as for cylindrical specimens ($\mu R = 0{\cdot}65$) and for Lorentz and polarization factors.

Structure factors have been calculated with the use of atomic form factors obtained by the Forsyth & Wells (1959) formula with the improved constants given by Moore (1963).

Determination of the structure

The Patterson function $P(UV)$ and Fourier functions $\varrho_0(xy)$ were first calculated. The (x,y) projection is well resolved. The z coordinates of the heavy atoms were derived from the $P(UVW)$ function and the complete structure was solved by three-dimensional Fourier functions $\varrho_0(xyz)$. Refinement was carried out by differential syntheses; the anisotropic thermal parameters were derived following Nardelli & Fava (1960). (Final disagreement index $R = 11{\cdot}5\%$; observed reflexions only.) Table 1 gives the final atomic coordinates with their e.s.d.'s; anisotropic thermal parameters are listed in Table 2. Structure factors based on the final parameters are compared with the observed structure factors in Table 3. The observed and calculated values of electron density and the second derivatives at the atomic peaks are compared in Table 4.

Table 1. *Final atomic coordinates* × 10⁴ (*with e.s.d.'s*)

	x/a	y/b	z/c
Cu^{II}	0000	0000	0000
Cu^{I}	0000	5000	2500
S(1)	1074 (2)	4180 (2)	5000
S(2)	0891 (2)	2710 (2)	5000
O(1)	1377 (7)	2349 (6)	2892 (23)
O(2)	−0137 (9)	2456 (5)	5000
Na	2061 (4)	3319 (3)	0000
N	1381 (4)	0421 (6)	0000

Discussion of the structure

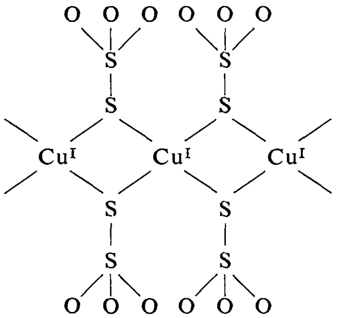
The main bond lengths and angles are quoted in Table 5. The whole structure, projected on (001) is represented in Fig. 1; a clinographic projection of it is shown in Fig. 2.

The examination of the structure shows that the Cu atom at (0,0,0) has properties typical of bivalent copper. The symmetry of the complex $[Cu^{II}(NH_3)_4]^{2+}$ is, in fact, purely square planar. Four N atoms of NH_3 groups are in the same plane as Cu^{II}, and no other group enters the coordination sphere of the copper atom. The vacancy in the apical positions of the bipyramid has been found also in disodium glycylglycylglycylglycinocuprate(II) decahydrate (Freeman & Taylor, 1965). This situation, however, is different, for certain aspects, from those more commonly found in cupric compounds, where the square planar coordination around $\mathrm{Cu^{II}}$ is generally completed, along the normal to the square, by one ligand or by two ligands, more weakly bound than those in the square. Sometimes the coordination polyhedron is completed by Cu···Cu bonds as those in bis-*N*-methylsalicylaldiminatocopper (Cu···Cu = 3·33 Å, Lingafelter, Simmons, Morosin, Scheringer & Freiburg, 1961), or in cupric acetate dihydrate (Cu···Cu = 2·64 Å, van Niekerk & Schoening, 1953), or in monopyridinecopper(II) acetate (Cu···Cu = 2·63 Å, Barclay & Kennard, 1961). Even these bonds can be excluded in the present compound because the next Cu atom along the normal to the plane of the four N atoms is at 5·76 Å.

It is interesting to observe that a square planar coordination around copper(II) is in perfect agreement with the coordination around nickel in the isomorphous compound $\mathrm{Na_4[Ni(NH_3)_4]\ [Cu(S_2O_3)_2]_2}$, whose yellow color, according to Pauling (1960), is strictly related to planar coordination.

The distance $\mathrm{Cu^{II}}$–N, 1·994 Å, is in agreement with similar distances: 2·05 Å in tetramminecopper(II) sulphate (Mazzi, 1955); 1·99 Å in copper(II) proline dihydrate (Mathieson & Welsh, 1952); 1·997 Å in sodium glycylglycylglycinocuprate(II) monohydrate (Freeman, Schoone & Sime, 1965); 1·99 Å in bissemicarbazidecopper(II) chloride (Nardelli, Gasparri, Boldrini & Battistini, 1965); therefore the bonds in the square complex are not stronger than in pyramidal or bipyramidal complexes, thus suggesting that only steric hindrances let the apices of the bipyramid free.

The anions



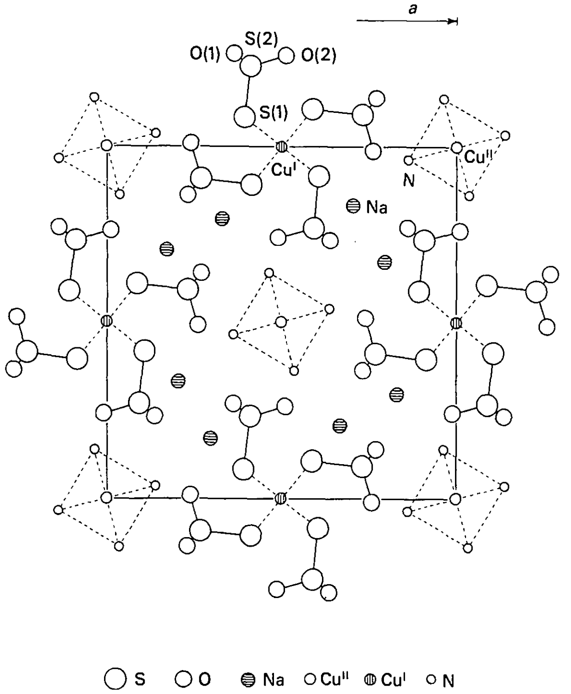


Fig. 1. Projection of the structure on (001).

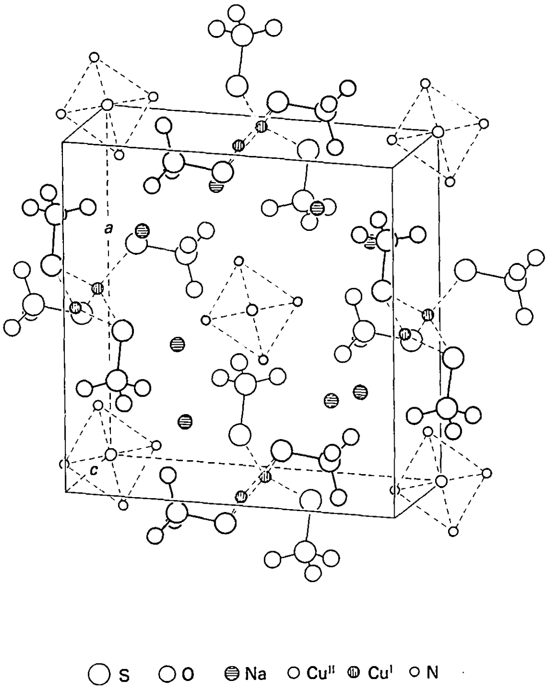


Fig. 2. Clinographic projection of the whole structure.

Table 2. *Anisotropic temperature factors* (Å^2) (*with shifts of the last cycle* $\times 10^3$)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
$\mathrm{Cu^{II}}$	1·760 (−65)	1·760 (−65)	3·595 (221)	0·000	0·000	0·000
$\mathrm{Cu^{I}}$	2·405 (−52)	2·405 (−52)	3·437 (110)	0·000	0·000	0·000
S(1)	0·961 (−21)	0·841 (−48)	1·777 (103)	−0·117 (−17)	0·000	0·000
S(2)	0·706 (−42)	0·732 (−38)	1·503 (90)	0·032 (2)	0·000	0·000
O(1)	2·255 (−29)	2·131 (−46)	2·915 (70)	−0·291 (−48)	0·987 (116)	−0·327 (−47)
O(2)	1·800 (−92)	0·957 (−77)	2·085 (130)	−0·091 (−11)	0·000	0·000
Na	2·248 (−6)	1·552 (−59)	2·785 (69)	−0·666 (−69)	0·000	0·000
N	0·649 (−72)	1·542 (−30)	2·892 (220)	−0·513 (−53)	0·000	0·000

Table 3. *Observed and calculated structure factors*

h	k	l	$10F_o$	$10F_c$
2	0	0	745	746
4	0	0	1217	1276
6	0	0	163	106
8	0	0	1508	1576
10	0	0	969	968
12	0	0	1066	1059
14	0	0	534	482
16	0	0	< 103	26-
1	1	0	804	1221-
3	1	0	983	1144-
5	1	0	1099	856
7	1	0	826	726
9	1	0	334	365-
11	1	0	940	981-
13	1	0	< 121	97-
15	1	0	112	132
17	1	0	< 81	90-
0	2	0	771	746
2	2	0	967	1121
4	2	0	1583	1919
6	2	0	738	733
8	2	0	981	1086
10	2	0	933	934
12	2	0	832	872
14	2	0	< 118	27-
16	2	0	379	300
1	3	0	905	855
3	3	0	992	1066-
5	3	0	542	386
7	3	0	1067	1130-
9	3	0	494	507-
11	3	0	273	286-
13	3	0	< 121	97-
15	3	0	499	481
17	3	0	161	137-
0	4	0	1212	1276
2	4	0	1479	1823
4	4	0	591	591
6	4	0	1104	1132
8	4	0	1602	1750
10	4	0	469	422
12	4	0	1140	1120
14	4	0	249	182
16	4	0	175	152
1	5	0	798	898-
3	5	0	1112	1280-
5	5	0	771	876-
7	5	0	350	287
9	5	0	220	124
11	5	0	120	190-
13	5	0	< 120	80-
15	5	0	218	200-
17	5	0	< 50	83
0	6	0	178	106
2	6	0	399	434
4	6	0	2103	2659
6	6	0	1323	1424
8	6	0	329	262-
10	6	0	< 118	61-
12	6	0	485	463
14	6	0	662	606
16	6	0	863	766
1	7	0	136	213-
3	7	0	< 90	24-
5	7	0	1100	1186-
7	7	0	792	763-
9	7	0	305	209
11	7	0	< 121	33
13	7	0	242	194
15	7	0	1003	885-
0	8	0	1498	1576
2	8	0	1314	1414
4	8	0	499	520
6	8	0	1084	1125
8	8	0	796	773
10	8	0	591	557
12	8	0	242	216
14	8	0	711	583
1	9	0	941	972-
3	9	0	< 103	84-
5	9	0	554	488
7	9	0	220	142
9	9	0	< 121	96-
11	9	0	< 118	103-
13	9	0	362	331-
15	9	0	128	125-
0	10	0	967	968
2	10	0	237	253
4	10	0	855	820
6	10	0	638	608
8	10	0	347	305
10	10	0	586	500
12	10	0	577	455
14	10	0	507	516
1	11	0	155	143-
3	11	0	667	609
5	11	0	566	562-
7	11	0	185	166-
9	11	0	930	926-
11	11	0	496	451
13	11	0	110	84-
0	12	0	1033	1059
2	12	0	< 120	14-
4	12	0	350	308
6	12	0	< 118	33
8	12	0	1302	1253
10	12	0	925	842
12	12	0	192	123
1	13	0	434	449-
3	13	0	225	122
5	13	0	279	228
7	13	0	< 113	1
9	13	0	576	539-
11	13	0	215	224-
0	14	0	547	482
2	14	0	651	629
4	14	0	775	697
6	14	0	208	105
8	14	0	400	290
10	14	0	< 76	62-
1	15	0	225	167
3	15	0	616	594-
5	15	0	185	150-
7	15	0	497	450-
9	15	0	382	391
0	16	0	< 103	26-
2	16	0	825	705
4	16	0	723	630
6	16	0	327	297
1	17	0	< 81	59-
3	17	0	347	340-
5	17	0	< 50	77
1	0	1	59	91
3	0	1	402	568
5	0	1	853	1024
7	0	1	471	366-
9	0	1	198	286
11	0	1	449	407-
13	0	1	457	461
15	0	1	504	432
17	0	1	< 72	59
0	1	1	72	91
2	1	1	1421	2146
4	1	1	414	539
6	1	1	584	646
8	1	1	446	336-
10	1	1	265	297
12	1	1	123	90-
14	1	1	185	199
16	1	1	204	150
1	2	1	460	677
3	2	1	532	341-
5	2	1	146	39-
7	2	1	1339	1515
9	2	1	341	370
11	2	1	543	483
13	2	1	441	419
15	2	1	260	204-
17	2	1	< 66	5-
0	3	1	410	568
2	3	1	636	863
4	3	1	382	445
6	3	1	661	702
8	3	1	< 149	26-
10	3	1	755	764
12	3	1	< 130	31-
14	3	1	760	725
16	3	1	243	222-
1	4	1	1587	1817-
3	4	1	213	364
5	4	1	416	458
7	4	1	922	994
9	4	1	204	226
11	4	1	232	187-
13	4	1	325	262-
15	4	1	326	274
17	4	1	450	516
0	5	1	851	1024
2	5	1	634	745
4	5	1	84	113
6	5	1	111	79
8	5	1	919	824-
10	5	1	237	213
12	5	1	825	791
14	5	1	638	630
16	5	1	304	284-
1	6	1	1260	1402
3	6	1	147	48-
5	6	1	87	108
7	6	1	573	543
9	6	1	389	379
11	6	1	403	351
13	6	1	309	246-
15	6	1	259	193
0	7	1	483	366-
2	7	1	653	586-
4	7	1	797	859
6	7	1	480	487
8	7	1	950	940
10	7	1	136	92-
12	7	1	< 110	34
14	7	1	< 100	74
16	7	1	< 50	85
1	8	1	1076	1160
3	8	1	573	585
5	8	1	646	669
7	8	1	499	426-
9	8	1	512	461-
11	8	1	567	509
13	8	1	265	256
15	8	1	312	250
0	9	1	215	286
2	9	1	< 97	9-
4	9	1	< 102	200
6	9	1	502	486
8	9	1	408	397
10	9	1	< 111	22-
12	9	1	125	95
14	9	1	< 81	118-
1	10	1	501	485
3	10	1	263	272
5	10	1	127	123
7	10	1	320	277-
9	10	1	875	841
11	10	1	317	273
13	10	1	608	540
0	11	1	465	407-
2	11	1	435	389
4	11	1	130	128
6	11	1	900	885
8	11	1	187	158
10	11	1	167	108
12	11	1	163	133-
1	12	1	< 110	54-
3	12	1	< 113	44-
5	12	1	722	666
7	12	1	279	258-
9	12	1	125	62
11	12	1	< 91	21-
13	12	1	429	495
0	13	1	457	461
2	13	1	909	899
4	13	1	426	370-
6	13	1	438	423-
8	13	1	292	236-
10	13	1	618	556
12	13	1	139	165
1	14	1	494	469-
3	14	1	248	198
5	14	1	311	293
7	14	1	793	703
9	14	1	99	130
0	15	1	502	432
2	15	1	358	253
4	15	1	343	297
6	15	1	< 92	139
8	15	1	201	192-
1	16	1	226	170
3	16	1	538	467
5	16	1	76	61-
7	16	1	76	234
0	17	1	< 72	59
2	17	1	86	113-
4	17	1	< 50	121
0	0	2	1807	2061
2	0	2	117	230-
4	0	2	476	524-
6	0	2	959	1043-
8	0	2	455	452-
10	0	2	460	386
12	0	2	341	303
14	0	2	193	186-
16	0	2	531	457-
1	1	2	557	706
3	1	2	1422	1911
5	1	2	857	914
7	1	2	1818	2135
9	1	2	652	644
11	1	2	219	173
13	1	2	173	88
15	1	2	796	703
17	1	2	245	259
0	2	2	127	230-
2	2	2	774	961-
4	2	2	243	312-
6	2	2	848	919-
8	2	2	563	551
10	2	2	504	504-
12	2	2	199	156
14	2	2	586	568-
16	2	2	114	89
1	3	2	1195	1518
3	3	2	376	358
5	3	2	1675	2071
7	3	2	302	357
9	3	2	279	252
11	3	2	331	288
13	3	2	821	782
15	3	2	803	733
0	4	2	476	524-
2	4	2	682	758-
4	4	2	241	152
6	4	2	593	615-
8	4	2	356	291
10	4	2	381	401-
12	4	2	615	588
14	4	2	451	420-
16	4	2	341	317-
1	5	2	1442	1575
3	5	2	221	241
5	5	2	652	637
7	5	2	612	627
9	5	2	1445	1517
11	5	2	426	396
13	5	2	446	369
15	5	2	162	103
0	6	2	953	1043-
2	6	2	318	356-
4	6	2	321	205
6	6	2	544	486
8	6	2	1051	1090-
10	6	2	593	617-
12	6	2	567	515-
14	6	2	410	338
16	6	2	340	382
1	7	2	962	1017
3	7	2	669	701
5	7	2	119	107
7	7	2	586	595
9	7	2	542	601
11	7	2	672	633
13	7	2	718	646
15	7	2	309	335-
0	8	2	476	452-
2	8	2	266	173
4	8	2	460	441-
6	8	2	339	303
8	8	2	417	411-
10	8	2	164	95-
12	8	2	98	101-
14	8	2	107	82
1	9	2	317	237-
3	9	2	1445	1545
5	9	2	867	876
7	9	2	847	843
9	9	2	586	492
11	9	2	659	603
13	9	2	101	94-
0	10	2	477	386
2	10	2	675	666-
4	10	2	143	86-
6	10	2	532	533-
8	10	2	116	58
10	10	2	192	176-
12	10	2	120	25-
14	10	2	< 26	97
1	11	2	749	729
3	11	2	918	934
5	11	2	365	309
7	11	2	561	497
9	11	2	317	313-
11	11	2	644	569
13	11	2	445	411
0	12	2	339	303
2	12	2	975	1000-
4	12	2	240	161-
6	12	2	470	426-
8	12	2	566	496
10	12	2	360	344
12	12	2	83	131-
1	13	2	339	298
3	13	2	742	686
5	13	2	906	859
7	13	2	235	188
9	13	2	96	25-
11	13	2	145	185
0	14	2	141	186-
2	14	2	428	380
4	14	2	129	70-
6	14	2	336	322-
8	14	2	84	109-
10	14	2	226	218-
1	15	2	689	594
3	15	2	215	199-
5	15	2	173	112
7	15	2	195	148
0	16	2	522	457-
2	16	2	177	164
4	16	2	301	269
6	16	2	< 40	41
1	17	2	< 45	87
1	0	3	127	239
3	0	3	71	66
5	0	3	707	775
7	0	3	269	223-
9	0	3	279	280
11	0	3	577	552-
13	0	3	524	509
15	0	3	350	317
0	1	3	127	239
2	1	3	661	898
4	1	3	443	513
6	1	3	537	589
8	1	3	467	430-
10	1	3	181	185
12	1	3	< 98	51-
14	1	3	285	225
16	1	3	< 50	16
1	2	3	336	472
3	2	3	294	257-
5	2	3	131	173
7	2	3	683	767
9	2	3	336	351
11	2	3	470	441
13	2	3	312	301
15	2	3	237	234-
0	3	3	71	66
2	3	3	860	1068
4	3	3	< 69	58
6	3	3	434	459
8	3	3	174	145-
10	3	3	750	773
12	3	3	203	179-
14	3	3	637	573
16	3	3	137	166-
1	4	3	986	1085-
3	4	3	317	301
5	4	3	< 79	42
7	4	3	992	1078
9	4	3	< 97	49
11	4	3	199	184-
13	4	3	367	317-
15	4	3	348	334
0	5	3	707	775
2	5	3	279	343
4	5	3	132	135
6	5	3	88	89
8	5	3	630	628-
10	5	3	< 111	8-
12	5	3	787	753
14	5	3	514	517
1	6	3	533	617
3	6	3	149	157
5	6	3	171	72
7	6	3	345	340
9	6	3	256	222
11	6	3	373	366
13	6	3	237	207-
15	6	3	< 45	61
0	7	3	269	223-
2	7	3	548	540-
4	7	3	780	815
6	7	3	147	111
8	7	3	847	843
10	7	3	106	66-
12	7	3	< 91	5
14	7	3	< 74	22-
1	8	3	1063	1185
3	8	3	279	278
5	8	3	501	495
7	8	3	458	427-
9	8	3	265	227-
11	8	3	282	247
13	8	3	221	238
0	9	3	279	280
2	9	3	147	94-
4	9	3	< 97	4
6	9	3	560	529
8	9	3	280	264
10	9	3	< 94	60-
12	9	3	< 79	38
1	10	3	292	319
3	10	3	159	118
5	10	3	189	188
7	10	3	302	293-
9	10	3	601	583
11	10	3	330	309
0	11	3	577	552-
2	11	3	475	453
4	11	3	112	74
6	11	3	703	679
8	11	3	< 93	72
10	11	3	187	145
12	11	3	137	142-
1	12	3	< 98	78-
3	12	3	147	83
5	12	3	370	355
7	12	3	150	135-
9	12	3	< 79	46
11	12	3	< 37	37-
0	13	3	524	509
2	13	3	667	638
4	13	3	367	338-
6	13	3	386	361-
8	13	3	136	137-
1	14	3	539	495-
3	14	3	166	105
5	14	3	355	319
7	14	3	492	555
0	15	3	350	317
2	15	3	163	183
4	15	3	309	313
6	15	3	< 45	54
1	16	3	250	228
3	16	3	337	358
0	0	4	2231	2759
2	0	4	373	452
4	0	4	482	511
6	0	4	139	112-
8	0	4	677	692
10	0	4	670	658
12	0	4	672	636
14	0	4	257	229
1	1	4	434	599-
3	1	4	308	319-
5	1	4	184	210
7	1	4	504	521
9	1	4	247	232-
11	1	4	568	541-
13	1	4	205	183-
15	1	4	128	162
0	2	4	374	452
2	2	4	384	457
4	2	4	770	839
6	2	4	252	238
8	2	4	696	714
10	2	4	394	361
12	2	4	571	535
14	2	4	62	84-
1	3	4	332	332
3	3	4	497	526-
5	3	4	342	328
7	3	4	664	648-
9	3	4	344	345-
11	3	4	257	220-
13	3	4	77	48
0	4	4	481	511
2	4	4	658	750
4	4	4	387	418
6	4	4	452	448
8	4	4	850	863
10	4	4	327	263
12	4	4	772	687
14	4	4	< 79	13
1	5	4	237	218-
3	5	4	683	720-
5	5	4	416	422-
7	5	4	164	49
9	5	4	299	295
11	5	4	194	158-
13	5	4	118	68-
0	6	4	138	112-
2	6	4	441	420
4	6	4	1118	1227
6	6	4	899	919
8	6	4	275	266-
10	6	4	130	152-
12	6	4	209	169
1	7	4	114	76-
3	7	4	106	60-
5	7	4	732	715-
7	7	4	425	390-
9	7	4	121	119
11	7	4	109	96
13	7	4	128	148
0	8	4	679	692
2	8	4	666	687
4	8	4	210	217
6	8	4	646	628
8	8	4	381	327
10	8	4	397	327
12	8	4	144	118
1	9	4	672	684-
3	9	4	156	137
5	9	4	226	208
7	9	4	170	159
9	9	4	< 83	55-
11	9	4	< 63	46-
0	10	4	671	658
2	10	4	135	78
4	10	4	297	421
6	10	4	286	236
8	10	4	259	202
10	10	4	141	256
1	11	4	< 88	17-
3	11	4	361	361
5	11	4	348	284-
7	11	4	143	117-
9	11	4	566	608-
0	12	4	678	636
2	12	4	195	174-
4	12	4	174	116
6	12	4	< 77	5-
8	12	4	745	780
1	13	4	296	243-
3	13	4	119	100
5	13	4	200	209
7	13	4	< 45	15-
0	14	4	257	229
2	14	4	441	434
4	14	4	412	404
1	15	4	128	126

Table 4. *Atomic peak heights* (e.Å^{-3}), *curvatures* (e.Å^{-5}) *and e.s.d.'s*

		ϱ	$-A_{hh}$	$-A_{kk}$	$-A_{ll}$	A_{hk}	A_{hl}	A_{kl}
Cu^{II}	obs.	66·3	759	778	374	0	−6	0
	calc.	68·8	729	747	392	0	−5	0
Cu^{I}	obs.	63·1	674	692	421	0	−7	0
	calc.	65·9	653	672	434	0	−7	0
S(1)	obs.	41·0	481	555	245	−11	−5	0
	calc.	41·3	466	535	250	−9	−5	0
S(2)	obs.	42·6	517	561	264	6	−9	0
	calc.	43·1	500	543	269	6	−9	0
O(1)	obs.	12·7	128	143	65	15	−3	−9
	calc.	13·1	125	139	66	16	−5	−7
O(2)	obs.	13·7	93	163	75	4	1	0
	calc.	14·2	91	158	77	4	2	0
Na	obs.	22·2	218	262	124	−25	−2	0
	calc.	22·6	212	253	126	−21	−2	0
N	obs.	12·7	188	123	63	−20	0	0
	calc.	12·9	179	119	65	−18	0	0
e.s.d.		0·5	6	6	3	3	3	3

Table 5. *Main interatomic distances and angles* (*with e.s.d.'s*)

Anion	
Cu^{I}–S(1)	2·357 ± 0·012 Å
S(1)–S(2)	2·046 ± 0·003
S(2)–O(1)	1·474 ± 0·012
S(2)–O(2)	1·463 ± 0·013
O(1)–S(2)–O(1)($x, y, 1-z$)	110·9 ± 0·6°
O(1)–S(2)–O(2)	111·2 ± 0·4
O(1)–S(2)–S(1)	106·2 ± 0·4
O(2)–S(2)–S(1)	111·0 ± 0·3
Cu^{I}–S(1)–S(2)	113·5 ± 0·1
Coordination around Cu^{II}	
Cu^{II}–N	1·994 ± 0·006 Å
Coordination around Na	
Na–O(1)	2·337 ± 0·012 Å
Na–O(1)($x, y, \bar{z}$)	2·337 ± 0·012
Na–O(1)($\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$)	2·642 ± 0·012
Na–O(1)($\frac{1}{2}-x, \frac{1}{2}-y, z-\frac{1}{2}$)	2·642 ± 0·012
Na–O(2)($\frac{1}{2}-y, \frac{1}{2}+x, \frac{1}{2}-z$)	2·235 ± 0·013

are formed by Cu^{I} atoms tetrahedrally surrounded by four thiosulphato groups S(1)–S(2)O$_3$ [Fig. 3(*a*)]. Each S(1) atom is bound to two Cu^{I} atoms, distant $\frac{1}{2}c$ from one another, thus forming chains parallel to [001] [Fig. 3(*b*)]. Chains with S atoms bridging two Cu^{I} atoms have been found in tris(thiourea)copper(I) chloride (Knobler, Okaya & Pepinsky, 1959), where however, only two S atoms of the tetrahedron are shared; in this compound distances between copper(I) and sulphur are Cu^{I}–S = 2·33 Å, for unshared S, and Cu^{I}–S = 2·40 Å, for shared S. Surprisingly the distance Cu^{I}–S(1) = 2·357 Å found in our study is nearer to that corresponding to unshared atoms and it is almost equal to the distance Cu^{I}–S = 2·345 Å found in tetrakis(thioacetamide)cuprous chloride (Truter, 1957) with unbridged tetrahedral complexes Cu^{I}S$_4$.

The same distance Cu^{I}–S(1) = 2·357 Å is not very different from that Cu^{II}–S$_{av}$ = 2·317 Å (maximum value 2·339 Å) found by Bonamico, Dessy, Mugnoli, Vaciago & Zambonelli (1965) in diethyldithiocarbamatocopper(II) in spite of the divalence of the copper atom. On

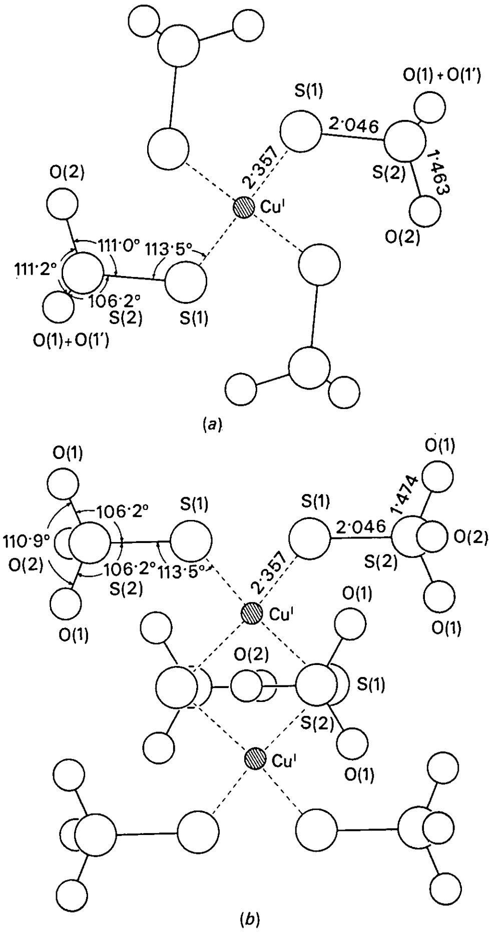


Fig. 3. Coordination around Cu^{I}: (*a*) viewed along [001], (*b*) viewed along [100].

the other hand, paramagnetism, oxidation numbers, distribution of chemically equivalent atoms over crystallographically equivalent points, isomorphism with the yellow nickel-copper(I) compound and with the violet copper(II)-silver(I) compound, all these facts permit an unequivocal individuation of divalent and univalent copper atoms in the structure.

The thiosulphato group has nearly tetrahedral symmetry, and the distances obtained, S(1)–S(2) 2·046, S(2)–O(1) 1·474, S(2)–O(2) 1·463 Å, are very close to those found in magnesium thiosulphate hexahydrate, which are 2·020, 1·484 and 1·479 Å respectively (Nardelli, Fava & Giraldi, 1962). They are only slightly different from those found in other compounds: S(1)–S(2) 1·961, S(2)–O(1) 1·568, S(2)–O(2) 1·519, and S(2)–O(3) 1·439 Å in $BaS_2O_3.H_2O$ (Nardelli & Fava, 1962); S(1)–S(2) 1·97 Å, S(2)–O(1) 1·59, S(2)–O(2) 1·46 and S(2)–O(3) 1·40 Å in $Na_2S_2O_3.5H_2O$ (Taylor & Beevers, 1952); S(1)–S(2) 2·01, S(2)–O(1) 1·52, S(2)–O(2) 1·46 and S(2)–O(3) 1·42 Å in $Na_2S_2O_3$ (Sándor & Csordás, 1961). It seems that in the last named compounds the sulphur–oxygen bonds are not all equivalent.

The Na^+ cation is surrounded by four O(1) and one O(2) atom, forming around the cation a distorted square pyramid. (Fig. 4).

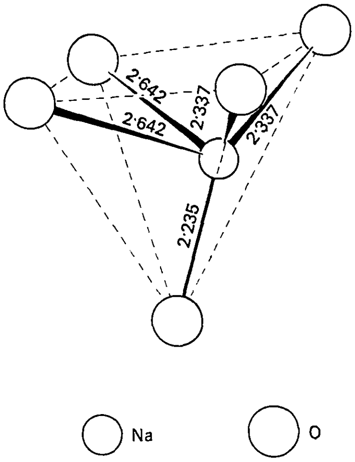


Fig. 4. Coordination around Na.

The shortest distance between cation $[Cu(NH_3)_4]^{2+}$ and anion $[Cu_n(S_2O_3)_{2n}]^{3n-}$ is $NH \cdots O(1) = 3{\cdot}141 \pm 0{\cdot}012$ Å corresponding to a weak hydrogen bond.

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