principal motion of O(5), a water molecule, is approximately perpendicular to the plane of the three atoms to which it is bonded – Cu, O(6), and O(6′). There is no indication of rigid-body motion of the glutamate group as a whole.

Further discussion of the details of the structure and its relationship to the nearly isostructural zinc compound is given in the following paper (Gramaccioli, 1966).

References

DUCHAMP, D. J. (1964). *Amer. Cryst. Assoc. Meeting*, Bozeman, Montana, paper B-14, p.29.

GRAMACCIOLI, C. M. (1963). *Acta Cryst.* **16**, A65.

GRAMACCIOLI, C. M. (1966). *Acta Cryst.* **19**, 600.

International Tables for X-ray Crystallography (1962). Vol. III, p.202–5, 214. Birmingham: Kynoch Press.

PAULING, L. (1960). *The Nature of the Chemical Bond.* 3rd ed. Ithaca: Cornell Univ. Press.

Acta Cryst. (1966). **21**, 600

The Crystal Structure of Zinc Glutamate Dihydrate*

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The crystal structure of zinc glutamate dihydrate, $ZnC_5H_7NO_4.2H_2O$, has been determined and refined by three-dimensional least-squares methods. The crystals are orthorhombic, space group $P2_12_12_1$, with $a=11{\cdot}190$, $b=10{\cdot}463$, and $c=7{\cdot}220$ Å. The final R index for 1035 reflections is 0·032; the standard deviations are about 0·004 Å for the light-atom positions.

Although the compound is nearly isostructural with the corresponding copper compound, the coordination about the zinc atom is a nearly regular square pyramid as compared with a square (with an additional ligand at a considerably greater distance) about the copper atom. The Zn–O and Zn–N distances range from 2·03 to 2·10 Å. This change in coordination has an appreciable effect upon the dimensions of one of the carboxyl groups; otherwise, the dimensions of the glutamate group are not significantly different from those found in copper glutamate. Hydrogen-bond lengths differ by as much as 0·05 Å between the two compounds.

Introduction

The determination of the structure of zinc glutamate (Zn.glu) was originally undertaken as a continuation of studies of the coordination of metal atoms with amino acids and peptides. Interest was further whetted when preliminary photographs showed that crystals of zinc glutamate dihydrate have the same space group, and very nearly the same cell dimensions, as the copper compound Cu.glu (Gramaccioli & Marsh, 1966; hereafter, GM) but that there are differences in intensity of corresponding reflections far greater than would be expected if the two compounds were truly isostructural. Very early in the analysis it became apparent that these differences in intensity were due primarily to differences in the coordinates of the metal atoms, rather than of the amino-acid or water molecules, and that as a result the coordination about zinc would be appreciably different from that about copper. In order to assure a good comparison between the two compounds, the same care has been taken with the present refinement as with that of the copper compound.

Experimental

White prismatic crystals of zinc glutamate dihydrate, $ZnC_5H_7NO_4.2H_2O$, form on slow evaporation of an aqueous solution of zinc oxide in glutamic acid; like the copper compound, they are elongated along **c** with principal faces {110} and {011}. Unit-cell dimensions were obtained as described by GM, based on measurements of 70 $0kl$ and $hk0$ reflections from two crystals; the results are summarized in Table 1. Once again, the difference between b values measured for the two crystals is much greater than the apparent experimental uncertainty, although the discrepancy is much less than that observed in Cu.glu. In view of this discrepancy, the e.s.d.'s of the final ('best') values include a lack-of-confidence factor of about 15.

The experimental density was not measured; that calculated on the basis of four molecules per unit cell is 1·937 g.cm^{-3}. Absence of reflections $h00$, $0k0$, and $00l$ with h, k or l odd indicates the space group $P2_12_12_1$.

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Table 1. *Unit-cell dimensions*

The values found for copper glutamate dihydrate are given for comparison. Estimated standard deviations are given in parentheses.

	Crystal No. 1	Crystal No. 2	'Best'	Cu.glu (GM)
a		11·1895 (1) Å	11·190 (2) Å	11·084 (6) Å
b	10·4637 (1) Å	10·4616 (2)	10·463 (1)	10·350 (3)
c	7·2202 (1)		7·220 (2)	7·238 (2)

[λ(Cu $K\alpha$) = 1·5418 Å]

Intensities were estimated visually from Weissenberg photographs of layers 0–6 about **c** and 0–9 about **a**, using copper radiation and crystals about 0·1 mm in diameter and approximately uniform in cross section. Of the 1101 reflections within the effective copper sphere, 21 were too weak to be observed. The data processing and correlation, including the assignment of standard deviations, were carried out on the CRYRM system as described by GM. In view of the relatively small value of μR (0·2), no absorption correction was applied.

Refinement of the structure

The starting parameters were those of Cu.glu (GM). Preliminary refinement was by Fourier methods based on the *hk*0 and 0*kl* data. Three-dimensional refinement was by full-matrix least squares; the quantity minimized was $\Sigma\, w(F_o^2-F_c^2)^2$ with weights w equal to the inverse of the squares of the standard deviations in F_o^2 as evaluated during the data-reduction process. As in Cu.glu, 163 parameters were refined: coordinates of all 24 atoms, anisotropic temperature parameters of the 13 heavier atoms, isotropic temperature factors of the hydrogen atoms, and a scale factor. Of 1101 measured intensities, 66 were omitted from the least squares: 21 which were too weak to be observed (and all of which, at the end, had values of F_c less than the threshold value of F_o) and 45 which apparently suffered from extinction or other observational errors. Near the end of the refinement the data were rescaled on the basis of a film factor of 3·8 rather than the empirical value of about 3·6; and, as in the case of Cu.glu, there was significant improvement in the agreement of the medium and strong reflections.

The final R index for 1035 reflections of non-zero weight is 0·032 and the goodness of fit,

$$(\Sigma\, w\,(F_o^2\text{-}F_c^2)^2/n-p)^{\frac{1}{2}},$$

0·93 (based on weights assigned on the basis of the empirical film factor of 3·6 rather than the final value of 3·8). During the last refinement cycle no parameter shift was as large as 5% of its standard deviation.

The final parameters of the heavier atoms are given in Table 2 and of the hydrogen atoms in Table 3; observed and calculated structure factors are given in Table 4. The electron density projected onto (001), calculated at the conclusion of the refinement, is shown in Fig. 1.

Table 3. *Parameters and standard deviations for the hydrogen atoms*

	x	*y*	*z*	*B*
H(1)	0·524 (3)	0·540 (4)	0·599 (7)	2·4 (10)
H(2)	0·426 (3)	0·497 (3)	0·871 (6)	0·6 (7)
H(3)	0·401 (4)	0·371 (4)	0·752 (7)	1·4 (9)
H(4)	0·573 (3)	0·368 (4)	1·050 (6)	0·8 (8)
H(5)	0·544 (3)	0·243 (3)	0·880 (6)	0·7 (8)
H(6)	0·621 (3)	0·368 (4)	0·451 (7)	1·1 (8)
H(7)	0·574 (4)	0·291 (4)	0·602 (7)	1·5 (9)
H(8)	0·795 (3)	0·084 (3)	0·586 (6)	0·1 (7)
H(9)	0·755 (6)	0·130 (6)	0·456 (10)	5·4 (15)
H(10)	0·701 (4)	0·130 (5)	0·167 (7)	2·2 (10)
H(11)	0·607 (7)	0·174 (7)	0·229 (11)	6·7 (18)

As in Cu.glu the coordinates of the hydrogen atoms, and particularly of those of the water molecules, are obviously not as accurate as their formal standard deviations (about 0·05 Å) would suggest. Hydrogen atoms of water molecules are notoriously difficult to locate by X-ray diffraction methods, perhaps in part because of the high thermal motions that water molecules typically show and in part because of the decreased electron density around protons bonded to such electronegative atoms. Almost invariably O–H distances are observed to be much shorter than the standard internuclear separation of about 1·0 Å – a difficulty from which C–H distances have partially recovered

Table 2. *The heavy-atom parameters and their standard deviations*

Values for the zinc atom have been multiplied by 10^5; for the other atoms, by 10^4. The temperature factor is in the form $\exp\{-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)\}$.

	x	*y*	*z*	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Zn	79084 (4)	32121 (4)	62788 (6)	348 (4)	494 (4)	914 (11)	59 (6)	−102 (9)	−36 (10)
C(1)	6601 (3)	5303 (3)	7898 (5)	47 (3)	42 (2)	81 (6)	−14 (4)	−4 (7)	4 (7)
C(2)	5605 (3)	4623 (3)	6814 (5)	34 (2)	58 (3)	82 (6)	1 (5)	14 (7)	−1 (8)
C(3)	4641 (3)	4157 (3)	8128 (6)	32 (2)	68 (3)	106 (7)	−1 (4)	12 (7)	10 (8)
C(4)	5096 (3)	3275 (4)	9639 (6)	41 (3)	84 (3)	123 (8)	−2 (6)	13 (8)	49 (11)
C(5)	4110 (3)	2752 (3)	10879 (6)	39 (3)	59 (3)	123 (9)	−14 (5)	29 (7)	22 (8)
N	6102 (3)	3581 (3)	5674 (5)	35 (2)	67 (2)	99 (6)	−4 (4)	0 (6)	−28 (7)
O(1)	7654 (2)	4935 (2)	7736 (4)	38 (2)	55 (2)	133 (6)	−1 (3)	−19 (6)	−53 (6)
O(2)	6254 (2)	6212 (2)	8929 (4)	50 (2)	52 (2)	96 (5)	9 (3)	−15 (6)	−22 (6)
O(3)	4458 (2)	2153 (2)	12342 (4)	43 (2)	81 (2)	112 (6)	−3 (4)	12 (6)	47 (6)
O(4)	3028 (2)	2914 (3)	10554 (5)	40 (2)	94 (3)	139 (6)	−11 (4)	11 (6)	49 (7)
O(5)	7697 (3)	1318 (2)	5517 (4)	97 (3)	49 (2)	134 (6)	−7 (4)	−68 (8)	22 (6)
O(6)	6632 (2)	0976 (2)	2153 (4)	52 (2)	69 (2)	143 (6)	21 (4)	3 (6)	29 (7)

with the help of the better intensity data, form factors and refinement techniques of recent years.

Standard deviations in the coordinates of the C, N, and O atoms are in the range 0·003–0·004 Å; they are less than 0·001 Å for the Zn atom. Realistic values for the standard deviation in the interatomic distances are probably about 0·008 Å and in the bond angles about 0·4°.

Discussion

The principal difference between the structures of zinc and copper glutamate dihydrate is in the coordination about the metal atom. In both compounds the principal ligands of the metal atom are arranged in the form of an approximate square pyramid; but whereas the copper atom lies only 0·15 Å from the center of the square base and hence has coordination (4+1) (GM), the zinc atom lies 0·32 Å from the base and is approximately equidistant from all five atoms. The coordination about the zinc atom is shown in Fig. 2 and the distances and angles around the zinc atom are listed in Table 5. The angles about the zinc atom differ by an average of 4·0° from the values expected for a regular tetragonal pyramid; those about the copper atom differ by an average of 5·1° from the values for a square (4+1) coordination. The average distance from the metal atom to each of its five nearest neighbors is 2·069 in the zinc compound and 2·047 Å in the copper compound; in both compounds there is a sixth neighbor, O(4), 2·58 Å from the metal atom and opposite the basal plane but considerably displaced from the axial direction.

Table 4. *Observed and calculated structure factors*

The columns contain values of *k*, $10F_o$, $10F_c$, and α (°). Reflections indicated with an asterisk were given zero weight in the least-squares refinement.

0 K 0			
0	---*4938		0
2	576*	670	180
4	340	361	180
6	608*	655	0
8	187	194	180
10	165	160	0
12	44	37	0
1 K 0			
1	571*	664	90
2	86	90	90
3	269	288	270
4	113	113	90
5	751*	826	90
6	-22*	19	270
7	236	240	90
8	40	42	90
9	322	321	270
10	-27*	20	90
11	264	254	90
12	90	95	270
13	97	90	270
2 K 0			
0	776*	953	180
1	718*	822	0
2	188	177	0
3	385	389	180
4	211	225	0
5	48	47	180
6	580*	637	180
7	236	237	0
8	168	165	0
9	99	100	180
10	128	132	180
11	71	66	0
12	97	93	180
13	42	44	0
3 K 0			
1	34	30	90
2	760*	850	90
3	79	71	270
4	82	86	270
5	469*	520	270
6	74	77	90
7	69	70	90
8	187	190	90
9	195	184	90
10	246	233	270
11	334	330	270
12	219	211	90
13	33	35	270
4 K 0			
0	451	474	0
1	563*	655	180
2	199	203	180
3	101	101	0
4	177	174	0
5	380	400	0
6	399	414	0
7	599*	645	180
8	252	251	180
9	34	27	0
10	88	85	0
11	-27	5	0
12	134	131	0
5 K 0			
1	140	139	90
2	401	439	270
3	16	15	270
4	434	464	90
5	393	404	90
6	234	232	270
7	121	121	270
8	210	223	270
9	35	28	270
10	213	205	90
11	137	137	90
12	120	117	270
6 K 0			
0	173	175	180
1	823*	929	0
2	45	48	0
3	234	237	180
4	145	142	180
5	308	324	180
6	90	96	180
7	362	384	0
8	115	117	180
9	259	259	180
10	25	20	0
11	64	58	180
12	38	34	0
7 K 0			
1	158	152	270
2	222	222	90
3	84	83	270
4	598*	631	270
5	235	243	90
6	189	199	90
7	51	50	270
8	146	151	90
9	121	119	270
10	322	320	270
11	45	40	270
8 K 0			
0	266	264	180
1	492*	540	180
2	270	265	0
3	152	150	0
4	169	171	180
5	244	247	0
6	-29	17	180
7	235	234	180
8	231	229	0
9	168	163	0
10	37	36	180
11	-17	9	0
9 K 0			
1	54	60	270
2	83	78	270
3	220	224	90
4	158	148	90
5	36	20	270
6	120	118	270
7	-24	1	90
8	101	96	270
9	187	191	90
10	156	155	90
10 K 0			
0	259	265	0
1	209	212	0
2	375	400	180
3	142	144	0
4	127	131	180
5	117	111	180
6	261	260	0
7	73	67	0
8	182	179	180
9	78	77	180
11 K 0			
1	105	102	90
2	117	119	90
3	417	421	270
4	227	227	270
5	65	58	90
6	108	107	90
7	77	76	90
8	-20	14	270
12 K 0			
0	293	303	180
1	64	52	180
2	202	216	0
3	-29	11	0
4	120	120	0
5	91	88	0
6	159	154	180
7	26	20	180
13 K 0			
1	144	137	270
2	-26	9	270
3	228	227	90
4	92	91	270
5	128	126	270
14 K 0			
0	154	150	0
1	137	138	180
2	121	124	180
0 K 1			
1	457	507	270
2	884*	941	180
3	480	485	270
4	435	462	0
5	630*	664	90
6	298	296	180
7	265	271	270
8	48	40	180
9	51	50	270
10	294	292	0
11	-24	8	90
12	149	141	180
13	53	52	270
1 K 1			
0	25	12	90
1	683*	722	283
2	912*	971	42
3	623*	640	121
4	616*	668	191
5	316	335	59
6	327	330	355
7	466	489	261
8	93	92	61
9	143	142	93
10	204	195	206
11	94	86	38
12	120	120	344
13	63	65	262
2 K 1			
0	101	99	90
1	827*	868	115
2	184	187	22
3	216	221	164
4	485	505	217
5	528	556	309
6	158	158	80
7	280	282	101
8	151	153	328
9	166	163	217
10	222	215	168
11	153	152	337
12	131	129	18
13	85	90	71
3 K 1			
0	661*	716	90
1	320	321	111
2	218	209	317
3	365	358	39
4	464	461	334
5	481	506	222
6	360	359	155
7	212	222	65
8	232	234	259
9	144	144	297
10	293	282	22
11	86	80	193
12	175	180	133
13	115	122	57
4 K 1			
0	674*	729	270
1	62	63	248
2	314	308	155
3	281	279	36
4	290	288	43
5	387	389	176
6	322	327	232
7	178	182	220
8	177	172	117
9	259	255	21
10	58	49	2
11	116	115	171
12	97	105	213
5 K 1			
0	746*	787	270
1	541*	563	295
2	275	280	130
3	580	585	185
4	211	214	107
5	429	466	353
6	421	421	298
7	131	127	257
8	154	152	94
9	259	253	190
10	123	123	211
11	196	202	329
12	64	65	295
6 K 1			
0	367	389	90
1	448	459	25
2	296	307	261
3	486	509	167
4	208	201	264
5	308	323	334
6	382	399	64
7	32	32	119
8	221	220	306
9	77	76	181
10	68	67	340
11	163	164	358
12	86	94	75
7 K 1			
0	676	668	90
1	99	96	235
2	347	353	275
3	387	394	33
4	36	27	131
5	325	326	168
6	342	348	74
7	142	140	323
8	144	141	272
9	106	111	14
10	79	81	128
11	128	130	175
8 K 1			
0	201	197	270
1	271	263	185
2	273	269	22
3	152	148	339
4	161	166	129
5	239	229	185
6	191	180	286
7	225	220	111
8	154	150	88
9	135	132	326
10	42	41	229
11	131	147	199
9 K 1			
0	243	240	270
1	299	307	73
2	209	203	194
3	217	215	176
4	310	317	340
5	206	200	343
6	280	283	236
7	135	133	124
8	131	128	107
9	114	113	225
10	59	61	359
10 K 1			
0	235	237	90
1	224	227	328
2	189	182	235
3	47	41	248
4	213	207	350
5	198	204	48
6	93	90	86
7	101	104	253
8	150	161	198
9	67	65	117
11 K 1			
0	79	76	90
1	195	198	268
2	245	243	348
3	40	36	52
4	234	239	165
5	147	146	75
6	134	131	78
7	151	152	264
8	38	38	327
12 K 1			
0	82	77	270
1	227	227	90
2	163	157	20
3	61	53	338
4	161	171	169
5	161	165	236
6	133	133	5
7	111	107	96
13 K 1			
0	47	46	270
1	191	186	99
2	155	152	203
3	29	28	321
4	152	146	13
5	28	28	266
14 K 1			
0	-22	18	270
1	79	82	263
2	63	66	157
0 K 2			
0	296	286	180
1	23*	10	270
2	643*	637	180
3	725*	783	90
4	432	425	180
5	808*	850	270
6	82	79	0
7	135	139	90
8	41	32	0
9	335	343	90
10	112	115	180
11	189	177	270
12	48	47	180
13	44	44	90
1 K 2			
0	744*	806	0
1	351	345	294
2	538	535	140
3	184	172	299
4	539	532	220
5	438	446	284
6	493	503	10
7	163	159	200
8	379	384	186
9	173	170	335
10	66	54	74
11	101	94	25
12	146	145	355
13	71	73	179
2 K 2			
0	79	76	180
1	130	132	79
2	344	329	357
3	738*	791	275
4	470	480	78
5	473	496	87
6	338	337	305
7	174	174	229
8	57	52	45
9	261	272	258
10	208	209	81
11	278	274	87
12	107	107	325
3 K 2			
0	611*	614	180
1	430	423	68
2	649*	675	332
3	300	295	201
4	318	319	316
5	245	251	199
6	269	273	181
7	431	434	31
8	190	183	6
9	144	142	163
10	92	81	224
11	85	89	144
12	57	55	221
4 K 2			
0	22	15	180
1	476	466	198
2	678*	682	98
3	269	280	86
4	529	545	253
5	168	171	300
6	239	238	100
7	175	160	11
8	123	122	121
9	140	144	44
10	254	254	262
11	122	120	267
12	138	141	103
5 K 2			
0	401	391	0
1	857*	874	199
2	183	179	85
3	97	96	79
4	152	147	201
5	403	414	352
6	127	121	21
7	346	341	186
8	70	69	164
9	164	169	315
10	-29	15	129
11	52	51	13
12	56	60	118
6 K 2			
0	17	15	180
1	117	109	102
2	587	578	265
3	77	69	315
4	657*	676	72
5	68	61	172
6	176	165	322
7	67	61	292
8	159	157	252
9	96	89	353
10	189	192	83
11	-25	16	297
7 K 2			
0	199	187	0
1	451	455	11
2	48	45	334
3	88	86	63
4	161	154	103
5	356	368	195
6	42	24	221
7	255	252	7
8	98	95	118
9	129	132	169
10	66	66	315
11	79	86	111
8 K 2			
0	166	169	0
1	231	232	113
2	315	311	100
3	249	254	284
4	376	385	253
5	175	176	109
6	244	245	92
7	41	33	150
8	55	49	102
9	60	56	258
10	150	156	257
9 K 2			
0	256	256	180
1	276	269	177
2	101	100	32
3	124	119	301
4	119	111	337
5	88	87	354
6	250	250	188
7	279	274	200
8	148	134	40
9	99	101	358
10	27	23	253
10 K 2			
0	305	320	0
1	216	213	253
2	36	34	238
3	343	348	96
4	179	181	68
5	206	210	267
6	156	149	272
7	30	22	114
8	92	90	268
9	69	77	67
11 K 2			
0	277	271	0
1	163	159	36
2	182	170	168
3	79	70	147
4	52	52	157
5	49	49	113
6	204	205	359
7	57	60	62
8	125	145	184
12 K 2			
0	27	22	180
1	126	119	84
2	69	67	186
3	237	237	248
4	-29	4	336
5	212	219	76
6	57	58	256
13 K 2			
0	222	223	180
1	49	44	81
2	130	125	21
3	67	66	278
4	61	62	117
0 K 3			
1	494	487	90
2	125	116	0
3	279	283	270
4	387	373	0
5	211	207	270
6	131	135	180
7	512	521	90
8	361	368	180
9	88	87	270
10	325	315	0
11	28	12	270
12	105	106	180
1 K 3			
0	191	174	90
1	761*	823	266
2	662*	681	184
3	115	112	22
4	336	346	335
5	280	282	77
6	72	70	209
7	277	281	263
8	184	176	142
9	125	121	84
10	168	161	5
11	49	48	152
12	129	125	191
2 K 3			
0	398	417	270
1	412	427	266
2	243	237	55
3	286	283	57
4	336	336	152
5	148	143	66
6	290	296	331
7	247	245	270
8	94	84	57
9	285	288	131
10	150	149	193
11	159	153	14
12	68	71	337
3 K 3			
0	384	401	90
1	502	501	64
2	492	503	299
3	361	365	187
4	500	482	157
5	370	380	326
6	288	283	89
7	204	200	55
8	255	262	285
9	201	200	210
10	143	140	178
11	63	55	36
12	48	51	24
4 K 3			
0	747*	810	90
1	334	340	136
2	271	267	229
3	462	463	339
4	193	189	356
5	260	255	219
6	199	207	101
7	206	207	65
8	279	269	282
9	158	159	306
10	124	123	28
11	111	108	209
12	77	83	145
5 K 3			
0	545*	565	270
1	165	158	200
2	341	344	112
3	291	284	357
4	270	260	67
5	285	294	139
6	262	265	261
7	-27*	19	42
8	158	160	105
9	179	172	8
10	81	77	351
11	121	128	162
6 K 3			
0	164	153	270
1	134	124	29
2	371	378	93
3	382	367	190
4	54	51	350
5	78	74	326
6	281	279	249
7	115	117	24
8	234	230	103
9	180	174	161
10	79	83	216
11	77	80	9
7 K 3			
0	499	492	90
1	101	100	334
2	329	332	244
3	426	427	193
4	253	237	257
5	155	152	359
6	174	163	104
7	47	46	283
8	158	158	252
9	154	155	156
10	52	51	26
8 K 3			
0	274	282	90
1	134	122	297
2	259	254	282
3	233	222	5
4	83	72	262
5	147	134	177
6	186	180	115
7	160	148	289
8	210	214	292
9	150	158	357
10	50	53	142
9 K 3			
0	147	135	270
1	293	289	117
2	254	252	77
3	262	262	334
4	160	159	171
5	117	108	223
6	67	63	349
7	87	88	85
8	154	155	58
9	70	75	320
10 K 3			
0	96	87	270
1	295	280	116
2	256	252	152
3	124	119	215
4	166	161	2
5	176	174	316
6	103	97	271
7	147	144	137
8	94	96	131
11 K 3			
0	49	37	270
1	229	230	283
2	137	137	177
3	179	170	143
4	233	233	331
5	114	112	93
6	40	42	121
7	141	160	265
12 K 3			
0	39	32	270
1	160	158	264
2	98	94	346
3	81	77	45
4	134	132	196
5	89	94	83
13 K 3			
0	35	29	90
1	71	67	27
2	100	106	3
3	45	44	229
0 K 4			
0	375	413	180
1	191	186	270
2	438	453	0
3	28	28	270
4	280	266	0
5	97	95	270
6	353	346	180
7	136	139	90
8	304	311	0
9	115	113	270
10	-23	2	180
11	-19*	18	270
12	64	69	180
1 K 4			
0	50	45	180
1	278	280	285
2	249	244	38
3	768*	788	92
4	129	119	257
5	165	171	245
6	177	172	324
7	133	135	176
8	160	158	41
9	228	216	96
10	117	115	232
11	172	168	259
12	49	47	111
2 K 4			
0	454	453	0
1	344	340	170
2	567	565	167
3	195	188	115
4	173	168	180
5	284	289	34
6	419	424	318
7	85	81	181
8	338	346	180
9	104	102	355
10	42	43	298
11	31	26	66
3 K 4			
0	172	167	180
1	160	157	153
2	373	388	237
3	559	562	294
4	415	420	92
5	344	341	76
6	114	114	299
7	165	163	239
8	94	97	212
9	145	148	274
10	107	111	87
11	86	87	88
4 K 4			
0	72	71	180
1	518	524	10
2	219	218	318
3	235	223	240
4	98	95	296
5	235	230	179
6	110	103	173
7	268	266	11
8	230	228	12
9	189	185	194
10	-24	24	101
11	63	62	238
5 K 4			
0	26	20	0
1	117	117	137
2	400	382	99
3	126	124	153
4	532	530	261
5	125	120	329
6	226	221	91
7	57	55	3
8	143	144	52
9	170	173	123
10	209	211	286
11	36	32	269
6 K 4			
0	70	69	0
1	322	304	199
2	160	155	254
3	118	111	337
4	52	51	203
5	261	255	20
6	69	59	239
7	359	360	177
8	55	47	143
9	159	160	3
10	-25	19	239
7 K 4			
0	211	211	180
1	97	97	212
2	283	277	261
3	80	85	1
4	315	301	71
5	76	68	262
6	113	109	266
7	36	31	201
8	114	113	263
9	72	71	18
10	161	186	92
8 K 4			
0	125	121	0
1	299	306	0
2	122	113	250
3	202	202	226
4	41	23	329
5	107	106	179
6	179	179	10
7	242	245	347
8	133	131	215
9	98	107	156
9 K 4			
0	78	73	0
1	154	143	50
2	300	304	99
3	178	171	282
4	239	247	295
5	195	193	80
6	97	97	64
7	42	40	32
8	41	37	64
10 K 4			
0	319	326	180
1	165	162	170
2	164	152	17
3	46	47	64
4	51	46	272
5	91	95	346
6	152	150	175
7	113	114	183
11 K 4			
0	66	62	180
1	140	140	281
2	92	83	295
3	223	215	102
4	72	67	129
5	186	193	281
6	23	24	146
12 K 4			
0	248	259	0
1	36	33	221
2	75	70	188
3	48	45	277
4	99	103	150
0 K 5			
1	484	493	90
2	295	304	0
3	116	117	90
4	286	281	180
5	345	333	270
6	184	177	0
7	75	75	90
8	102	95	0
9	173	157	270
10	124	118	180
11	40	34	270
1 K 5			
0	51	44	270
1	173	173	121
2	279	276	186
3	135	126	342
4	431	424	344
5	139	141	236
6	177	177	113
7	283	274	82
8	98	88	224
9	164	156	253
10	96	95	346
11	43	39	285
2 K 5			
0	130	132	270
1	272	276	237
2	411	426	169
3	270	266	9
4	466	487	10
5	140	133	133
6	162	160	219
7	178	171	267
8	99	94	136
9	72	69	29
10	96	100	347
11	50	55	175
3 K 5			
0	164	167	270
1	353	345	304
2	145	142	46
3	349	348	158
4	48	47	173
5	127	124	90
6	186	191	314
7	156	149	265
8	177	174	50
9	109	113	106
10	114	125	175
4 K 5			
0	110	102	90
1	229	232	29
2	367	374	316
3	368	373	196
4	152	141	193
5	248	248	7
6	222	216	104
7	198	194	112
8	103	97	295
9	90	85	211
10	36	37	178
5 K 5			
0	205	213	90
1	80	78	191
2	199	198	262
3	236	234	354
4	93	92	347
5	181	171	197
6	230	225	118
7	105	104	112
8	214	204	269
9	125	123	351
10	-19	16	61
6 K 5			
0	375	355	270
1	128	122	158
2	131	122	121
3	359	345	3
4	32	33	287
5	149	147	175
6	167	156	282
7	66	65	288
8	170	172	94
9	122	128	340
7 K 5			
0	83	72	270
1	169	163	15
2	161	152	53
3	185	172	151
4	188	191	38
5	288	284	344
6	124	123	259
7	23	21	117
8	145	147	100
9	104	118	148
8 K 5			
0	187	183	90
1	87	82	335
2	142	142	186
3	303	303	165
4	114	110	353
5	147	155	13
6	165	163	108
7	43	44	254
8	102	109	228
9 K 5			
0	237	237	90
1	136	129	241
2	201	195	307
3	70	73	338
4	122	122	208
5	133	138	130
6	118	121	51
7	88	97	259
10 K 5			
0	173	181	270
1	108	102	122
2	95	101	10
3	149	160	358
4	171	178	172
5	88	93	237
6	84	97	352
11 K 5			
0	30	34	90
1	79	84	59
2	180	188	161
3	70	71	256
4	80	89	0
12 K 5			
0	56	63	90
1	138	161	250
0 K 6			
0	216	213	180
1	338	347	90
2	112	114	0
3	345	354	270
4	24	6	180
5	296	291	90
6	26	1	180
7	-24	3	270
8	120	124	180
9	145	141	270
10	33	30	180
1 K 6			
0	389	388	180
1	118	110	348
2	237	243	13
3	89	84	241
4	183	186	154
5	50	44	54
6	329	333	176
7	125	119	328
8	256	255	357
9	40	34	269
10	55	61	172
2 K 6			
0	59	55	0
1	265	261	255
2	204	204	41
3	214	212	76
4	154	152	264
5	201	194	245
6	145	140	83
7	111	113	276
8	125	132	78
9	99	105	98
3 K 6			
0	388	399	0
1	339	337	185
2	131	126	146
3	180	182	85
4	74	59	244
5	103	100	31
6	210	198	21
7	226	220	181
8	119	120	178
9	105	110	5
4 K 6			
0	120	113	0
1	198	204	111
2	185	173	252
3	269	274	282
4	277	271	110
5	124	122	117
6	67	68	252
7	93	91	104
8	175	172	265
9	50	49	248
5 K 6			
0	136	134	180
1	303	306	3
2	109	101	359
3	99	100	200
4	53	42	18
5	110	110	190
6	78	78	198
7	208	202	13
8	33	29	354
9	128	122	201
6 K 6			
0	77	76	0
1	73	66	111
2	328	320	98
3	47	41	20
4	227	217	273
5	51	52	245
6	67	63	88
7	39	36	179
8	75	81	52
7 K 6			
0	125	123	180
1	309	315	173
2	133	130	24
3	114	110	5
4	67	66	303
5	154	152	358
6	93	95	196
7	213	231	161
8	46	30	317
8 K 6			
0	54	53	180
1	52	43	264
2	237	235	248
3	149	149	85
4	228	226	78
5	53	47	354
6	32	34	193
7	43	50	179
9 K 6			
0	194	186	0
1	96	102	328
2	157	154	211
3	80	82	173
4	85	87	159
5	86	93	198
10 K 6			
0	32	30	180
1	53	48	13
2	86	93	98
3	153	161	264
4	72	77	273
0 K 7			
1	292	302	270
2	73	71	0
3	133	131	90
4	245	245	180
5	70	60	90
6	71	73	0
7	142	130	270
8	25	25	0
1 K 7			
0	187	179	90
1	135	126	67
2	140	135	344
3	147	144	220
4	244	233	167
5	54	54	292
6	63	58	29
7	156	151	78
8	112	110	315
2 K 7			
0	184	174	90
1	188	188	106
2	297	300	218
3	67	66	317
4	142	132	353
5	172	174	219
6	130	119	121
7	157	152	87
8	81	84	223
3 K 7			
0	32	21	90
1	103	108	213
2	211	213	169
3	190	189	345
4	134	126	352
5	95	90	99
6	108	106	260
7	129	121	259
8	92	100	141
4 K 7			
0	89	90	270
1	138	141	303
2	170	169	52
3	174	170	176
4	89	90	167
5	93	90	34
6	164	163	262
7	135	137	268
5 K 7			
0	170	176	90
1	121	120	51
2	146	145	335
3	151	155	192
4	91	96	239
5	119	114	348
6	145	141	72
7	53	49	258
6 K 7			
0	235	249	90
1	138	137	185
2	123	117	261
3	206	197	344
4	40	37	35
5	169	161	156
6	126	126	73
7 K 7			
0	164	177	270
1	123	125	149
2	44	48	82
3	113	126	22
4	83	85	191
5	144	159	193
8 K 7			
0	234	248	270
1	157	161	59
2	115	121	146
3	89	95	191
4	117	122	357
9 K 7			
0	-19	11	90
1	120	126	316
2	82	83	225
0 K 8			
0	119	119	0
1	114	118	270
2	180	180	180
3	48	41	270
4	26	14	180
5	27	27	270
6	170	166	0
1 K 8			
0	125	120	0
1	180	173	131
2	155	156	279
3	264	268	270
4	74	69	55
5	162	157	84
6	79	73	331
2 K 8			
0	219	211	180
1	158	156	25
2	71	65	327
3	23	16	329
4	38	39	28
5	114	115	148
6	130	137	186
3 K 8			
0	-28	7	0
1	134	132	282
2	144	141	107
3	162	172	61
4	197	197	275
5	127	132	274
6	63	66	177
4 K 8			
0	103	101	0
1	120	118	166
2	65	67	189
3	27	30	310
4	25	26	8
5	123	139	327
5 K 8			
0	65	65	0
1	50	47	96
2	140	141	261
3	99	84	249
4	187	192	84
6 K 8			
0	-23	1	0
1	118	127	356
2	-21	9	29
3	87	90	186
7 K 8			
0	41	46	180
1	26	29	58
0 K 9			
1	76	81	270
2	94	100	180
3	36	36	90
1 K 9			
0	87	90	270
1	129	140	288
2	139	119	349
2 K 9			
0	138	153	90
1	105	125	48
2	88	99	3
3 K 9			
0	98	110	90
1	102	122	120

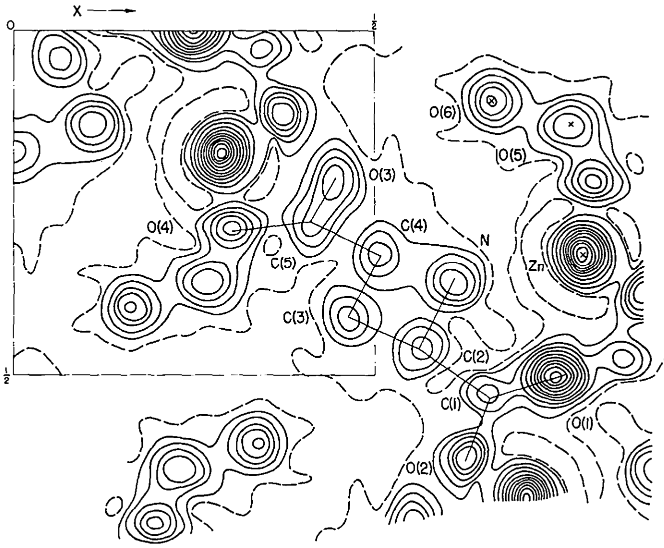

Fig. 1. An electron density projection onto (001), calculated at the conclusion of the refinement. Contours are at 4, 6, 8... e.Å^{-2} for the light atoms and 4, 10, 15, 20... for the zinc atom; the 2 e.Å^{2} contour is dashed.

Table 5. *Bond distances and angles about the metal atoms in zinc and copper glutamate dihydrate*

	Zn.glu	Cu.glu		Zn.glu	Cu.glu		Zn.glu	Cu.glu
M–N	2·103 Å	1·998 Å	N–M–O(1)	79·4 Å	83·2 Å	O(1)–M–O(5)	159·5 Å	169·4 Å
M–O(1)	2·106	1·967	N–M–O(3)	162·6	171·7	O(1)–M–O(2)	103·0	100·9
M–O(3)	2·036	1·981	N–M–O(5)	90·6	92·9	O(3)–M–O(5)	92·7	90·3
M–O(5)	2·070	1·991	N–M–O(2)	102·4	93·7	O(3)–M–O(2)	94·1	94·1
M–O(2)	2·030	2·299	O(1)–M–O(3)	91·8	92·4	O(5)–M–O(2)	96·6	89·2

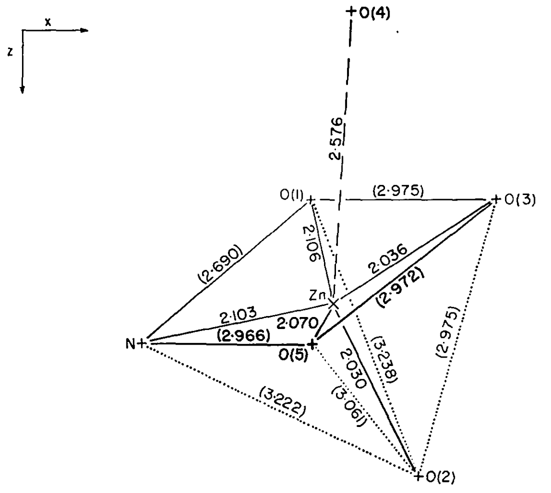

Fig. 2. The coordination about the zinc atom.

A somewhat analogous relationship between the coordination of zinc and copper atoms has recently been reported for the diethyldithiocarbamate compounds (Bonamico, Dessy, Mugnoli, Vaciago & Zambonelli, 1965; Bonamico, Mazzone, Vaciago & Zambonelli, 1965); however, the five nearest sulfur ligands of the zinc atom form a severely distorted tetragonal pyramid, one sulfur atom being approximately 0·4 Å further from the zinc atom than are the other four. A distorted coordination intermediate between a tetragonal pyramid and a trigonal bipyramid is also reported by Montgomery & Lingafelter (1963) in monoaquobisacetonylacetonatozinc.

The bond distances and angles within the glutamate group are shown in Fig. 3. Although in general these dimensions agree, within experimental error, with those found in Cu.glu, a comparison of the dimensions of the carboxyl group C(1), O(1), O(2) points up some interesting consequences of the difference in coordination about the metal atom. The shortening of the apical Zn–O(2) distance (Table 5) decreases the double-bond character of the C(1)–O(2) bond, which is nearly 0·03 Å longer than in the copper compound. The double-bond character of the C(1)–O(1) bond is accordingly increased, and this bond is shortened by about 0·04 Å. Finally, the remaining bonding power of O(1) is then decreased, as reflected by an increase of 0·14 Å in the Zn–O(1) distance. The change in double-bond character of the C–O bonds is also reflected in the C–C–O bond angles.

Differences between the other dimensions of the glutamate group in the two compounds are probably not significant, although it is tempting to correlate the shortening of the C(2)–N and C(5)–O(3) distances in the zinc compound with the lengthening of the Zn–N and Zn–O(3) distances. The nitrogen atom lies almost exactly in the plane of the neighboring carboxyl group, while it is displaced from the plane by 0·06 Å in the copper compound. Data for this and other planes of interest are given in Table 6.

Covalent bond distances and angles involving the hydrogen atoms are given in Table 7. They are more uniform than the values found in copper glutamate but, as discussed earlier, many of the distances are obviously unrealistic representations of the true internuclear separations.

Table 6. *Some planes of interest*

The coefficients q_i are direction cosines relative to **a**, **b**, and **c**; D is the origin-to-plane distance. Atoms indicated with an asterisk were omitted from the calculations of the least-squares planes; the remaining atoms were given equal weights.

	Atom	Deviation
(1) Carboxyl group		
$q_1 = -0·1286$	C(1)	−0·005 Å
$q_2 = -0·6397$	C(2)	0·001
$q_3 = 0·7577$	O(1)	0·002
$D = -0·1741$ Å	O(2)	0·002
	*N	0·003
	*Zn	0·321
(2) Carboxyl group		
$q_1 = 0·0079$	C(4)	0·003
$q_2 = 0·8554$	C(5)	−0·010
$q_3 = 0·5177$	O(3)	0·003
$D = 6·5769$ Å	O(4)	0·004
	*C(3)	0·223
	*Zn′	0·178
(3) Zinc ligands		
$q_1 = -0·3952$	N	−0·029
$q_2 = -0·3619$	O(1)	0·029
$q_3 = 0·8442$	O(5)	0·026
$D = -0·5665$ Å	O(3)′	−0·026
	*Zn′	−0·320
	*O(2)′	−2·340
	*O(4)′	1·985

The hydrogen-bond arrangement in zinc glutamate dihydrate is the same as in the copper compound (see GM, Fig. 2). The hydrogen-bond distances and angles for the two compounds are compared in Table 8. Although there appear to be significant differences in the distances and angles involving the water molecule O(6) in the two compounds, the reasons for these differences are not obvious. As in the copper compound, one of the protons [H(7)] on the nitrogen atom does not form a hydrogen bond.

Table 9. *Magnitudes and direction cosines, relative to the crystallographic axes, of the principal axes of the thermal ellipsoids*

	B_i	q_i	q_i	q_i
	2·24	−0·351	−0·880	0·319
Zn	1·95	−0·359	0·441	0·822
	1·62	0·865	−0·174	0·471
	2·53	−0·892	0·442	0·096
C(1)	1·72	0·371	0·593	0·714
	1·66	−0·259	−0·673	0·693

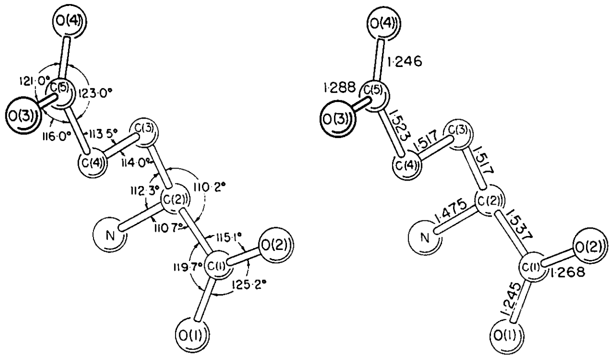

Fig. 3 Bond distances and angles within the glutamate group.

Table 7. *Bond distances and angles involving the hydrogen atoms*

C(2)–H(1)	1·09 Å	C(1)—C(2)–H(1)	102°	C(3)–C(2)–H(1)	108°
		N——C(2)–H(1)	113		
C(3)–H(2)	1·04	C(2)—C(3)–H(2)	106	C(4)–C(3)–H(2)	110
C(3)–H(3)	0·95	C(2)—C(3)–H(3)	114	C(4)–C(3)–H(3)	106
		H(2)—C(3)–H(3)	106		
C(4)–H(4)	1·03	C(3)—C(4)–H(4)	114	C(5)–C(4)–H(4)	107
C(4)–H(5)	1·14	C(3)—C(4)–H(5)	102	C(5)–C(4)–H(5)	106
		H(4)—C(4)–H(5)	114		
N—H(6)	0·86	C(2)—N—H(6)	121	Zn —H—H(6)	95
N—H(7)	0·85	C(2)—N—H(7)	105	Zn —N—H(7)	104
		H(6)—N—H(7)	117		
O(5)–H(8)	0·62	Zn —O(5)–H(8)	128		
O(5)–H(9)	0·71	Zn —O(5)–H(9)	108	H(8)–O(5)–H(9)	118
O(6)–H(10)	0·64				
O(6)–H(11)	1·02	H(10)–O(6)–H(11)	92		

Table 8. *Hydrogen bond distances and angles in zinc and copper glutamate dihydrate*

	Zn.glu	Cu.glu		Zn.glu	Cu.glu
N···O(1)	2·975 Å	2·966 Å	M–N···O(1)	78·1°	86·2°
			C(2)–N···O(1)	100·9	98·7
O(5)···O(6)	2·729	2·720			
O(5)···O(6)′	2·779	2·811	O(6)···O(5)···O(6)′	112·5	113·5
O(6)···O(3)	2·730	2·781	O(3)···O(6)···O(4)···	110·5	107·8
O(6)···O(4)	2·758	2·722			

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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References

Bonamico, M., Dessy, G., Mugnoli, A., Vaciago, A. & Zambonelli, L. (1965). *Acta Cryst.* **19**, 886.

Bonamico, M., Mazzone, G., Vaciago, A. & Zambonelli, L. (1963). *Acta Cryst.* **16**, 748.

Gramaccioli, C. M. & Marsh, R. E. (1966). *Acta Cryst.* **21**, 594.

Montgomery, H. & Lingafelter, E. C. (1963). *Acta Cryst.* **16**, 748.

Acta Cryst. (1966). **21**, 605

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