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The Molecular and Crystal Structure of Tris(1,2-ethanediol)-copper(II) Sulphate; $[Cu(C_2H_6O_2)_3]SO_4$

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The crystal structure of $[Cu(C_2H_6O_2)_3]SO_4$ has been determined and refined from three-dimensional X-ray data. The unit cell is monoclinic with the following cell dimensions and corresponding standard deviations: $a = 10.166 \pm 0.001$ Å, $b = 9.013 \pm 0.001$ Å, $c = 15.365 \pm 0.001$ Å and $\beta = 115.666 \pm 0.006°$ at 25°C. The space group is $P2_1/c$; there are four formula units per unit cell and all atoms occupy general fourfold positions. The intensity material was collected using conventional Weissenberg technique, and the intensities were estimated visually. The structure was solved by routine heavy-atom methods and refined by full matrix least squares methods. The copper atom is octahedrally surrounded by the six glycol* oxygen atoms, and these $Cu(C_2H_6O_2)_3^{2+}$ ions are linked through sulphate groups in long parallel sheets by means of hydrogen bonds.

A number of authors [1–3] have stated that cations such as Cu^{2+} will increase the enzymatic decarboxylation of oxaloacetate to pyruvate and CO_2, a reaction of importance in biochemistry. Bontchev, Yordanov and Michaylova [4] have shown that this catalytic ability of Cu^{2+} is further increased in a solvent such as dioxan, ethanol, or glycerol. They assume that this is due to complex formation between Cu^{2+} and the oxygen containing solvent because the effective charge of the metal ion is increased when water is substituted by the organic molecules. EPR and electronic spectra give evidence for the relationship between complex formation and the increase in rate of decarboxylation. The kinetic investigations were carried out earlier by the same authors. They concluded that the configuration of the complexes is square-planar, or more probably, pseudooctahedral with a strong distortion along the Z-axis. Their studies also indicated that the bond Cu – O in the complexes with ethanol and dioxan is more covalent and in the copper(II)-glycerol complexes more ionic than in Cu(II) aqua complexes.

* Throughout this paper 1,2-ethanediol will be referred to as glycol.

To make further investigations of this type of complex formation between Cu^{2+} and polyols we are studying such complexes in solutions and in the solid state. This work concerns complex formation between Cu^{2+} and glycol.

EXPERIMENTAL

Crystal preparation and analyses. The crystals were prepared according to the method of Gomer and Tyson [5] by dissolving as much as possible of $CuSO_4.5H_2O$ (*p.a.*) in 5 g glycol (*p.a.* Merck) on the water-bath. Unlike their procedure the saturated solution obtained was kept in a desiccator over sulphuric acid for a few days, after which time a pale blue crystal mass was obtained. Crystals from this first preparation were used as seeds to obtain suitable crystals from another saturated copper-glycol-sulphate solution. This gave pale blue crystals shaped as thin rectangular plates. The copper content of the crystals was determined electrolytically to be 17.44 %. Calc. for $[Cu(C_2H_6O_2)_3]SO_4$ 18.5 %. No other analyses were made.

Crystal data and space group. From rotation photographs around the *a*- and *b*-axes and the corresponding Weissenberg photographs (zero and first layers) taken with Cu$K\alpha$-radiation, it was concluded that the crystals are monoclinic. The cell dimensions were calculated and refined from a powder photograph giving 63 lines in a focusing camera of Guinier-Hägg type. The following parameters and their corresponding standard deviations were obtained (as internal standard Si was used): $a = 10.166 \pm 0.001$ Å; $b = 9.013 \pm 0.001$ Å; $c = 15.365 \pm 0.001$ Å; $\beta = 115.666° \pm 0.006°$.

By the flotation method, using bromoform and carbon tetrachloride, the density was determined to be 1.82 g/cm³. Four formula units in the unit cell gave a calculated density of 1.81 g/cm³. The following conditions limiting possible reflections were found.

$$\left.\begin{matrix} hkl \\ hk0 \\ 0kl \\ h00 \end{matrix}\right\} \text{ no conditions} \qquad \begin{matrix} 0k0;\ k = 2n \\ h0l;\ l = 2n \end{matrix}$$

which are characteristic for the space group $P2_1/c$ (No. 14).[6]

Intensity data. The crystals were very hygroscopic, and during the data collection, they were kept in a sealed capillary of Lindeman glass. Equi-inclination Weissenberg photographs were taken with Cu$K\alpha$-radiation. The crystal was rotated around the *b*-axis and 9 layers ($h0l - h8l$) were recorded. The intensities of 1945 independent reflections were estimated visually using the multiple film technique (four films). The number of possible reflections in the copper sphere is 2906.

No correction for absorption was made. The computer programs used were the same as in a paper by Antti and Lundberg.[7]

Structure determination and refinement. The copper and sulphur atoms were located from a three-dimensional Patterson synthesis and the other atoms were found by standard Fourier methods. The atomic parameters and the atomic temperature factors were refined using full matrix least-squares techniques, and the reflection material was weighted according to the method suggested by Cruickshank,[8] using the constants $A = 8.0$ and $C = 0.1$.

The atomic scattering factors for Cu^{2+}, S, O, and C used were taken from the International Tables.[9] The refinement using isotropic temperature factors was terminated at a final R-value $= (\sum ||F_o| - |F_c||)/\sum |F_o| = 0.124$.

All parameter shifts in the final cycle were less than 10 % of the estimated standard deviations. During the final refinements eight strong reflections which suffer severely from secondary extinction were excluded. Further refinements were performed with anisotropic temperature factors for all atoms. This reduced R to 0.098, In spite of the decrease in R-value when the reflection material was refined with anisotropic temperature factors, there were no significant changes in the atomic positional parameters. Since no absorption correction has been made even though the linear absorption coefficient is 44.2 cm^{-1} we prefer to present the results obtained using isotropic temperature factors.

As a final check the unobserved reflections were included in one cycle of refinement ($R = 0.112$). They were given F_o-values equal to half the threshold value for each separate layer. This increased the number of the independent reflections to 2518, but those where $0.49 > F_o/F_c > 2.01$ were given zero weight. The number of reflections thus included in the refinement was 2276. From the excluded reflections 140 calculated structure factors were less than one fourth of the threshold values and the rest between one to two times the threshold values.

A final difference Fourier synthesis was calculated in which no abnormalities could be detected. The final atomic parameters are given in Table 1. A comparison between observed and calculated structure factors is reported in Table 2.

Table 1. The atomic positional fractional parameters ($\times 10^4$) and the isotropic thermal parameters. (Standard deviations for the least significant figure are shown in parentheses.)

	X	*Y*	*Z*	*B*
Cu	2528 (1)	2044 (2)	3224 (1)	2.88 (5)
O(11)	3653 (8)	2255 (8)	4636 (5)	3.58 (13)
O(12)	861 (8)	1250 (8)	3798 (5)	3.75 (13)
O(21)	1336 (8)	1798 (8)	1836 (5)	3.90 (13)
O(22)	3030 (8)	9909 (8)	3093 (5)	3.66 (13)
O(31)	4415 (8)	3072 (8)	2959 (5)	3.80 (14)
O(32)	1970 (9)	4222 (9)	3080 (6)	4.02 (14)
C(11)	3056 (11)	3373 (13)	269 (7)	3.75 (18)
C(12)	1411 (12)	1835 (13)	4741 (8)	4.08 (20)
C(21)	1505 (12)	440 (13)	1444 (8)	3.94 (19)
C(22)	1887 (13)	9246 (14)	2209 (9)	4.38 (21)
C(31)	4302 (13)	4624 (14)	3027 (9)	4.51 (21)
C(32)	2690 (13)	5037 (14)	2608 (9)	4.30 (21)
S	2425 (2)	7387 (3)	4731 (2)	2.70 (5)
O(1)	3559 (8)	7897 (8)	4410 (5)	3.69 (13)
O(2)	1077 (8)	8202 (8)	4124 (5)	3.79 (13)
O(3)	2909 (9)	7198 (9)	754 (6)	4.01 (14)
O(4)	2191 (8)	5797 (9)	4588 (6)	4.08 (15)

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure is built up from discrete $[Cu(C_2H_6O_2)_3]^{2+}$-ions and SO_4^{2-}-ions. The SO_4^{2-}-ions link the $[Cu(C_2H_6O_2)_3]^{2+}$-ions through hydrogen bonds, forming sheets, which are parallel with the *b*-axis and approximately with the diagonal between *a* and *c*. (Fig. 1). The parallel sheets with displacement $c/2$ are held together through van der Waals bonds.

The coordination around Cu. In the $[Cu(C_2H_6O_2)_3]^{2+}$-ions the copper atom is octahedrally surrounded by six oxygen atoms from three glycol molecules. The arrangement is shown in Fig. 2 and distances and angles are given in Table 3. Four of the oxygen atoms form a nearly square plane around the copper atom and this plane is almost parallel to the *xy*-plane of the unit cell. The equation for the plane is $0.9543x + 0.2613y - 0.1452z + 0.2611 = 0$ and the atoms O(11) and O(21) are 0.063 Å and 0.076 Å below the plane, respectively, while O(22) and O(32) are 0.070 Å and 0.069 Å above the plane. The copper

Table 2. Observed and calculated structure factors (× 10). Values marked with an asterisk or a minus sign were not included in the refinements. (Minus signs mark those eight reflections which suffer severely from secondary extinction.)

H	L		
K=	0		
-1	2	763	1456 -
-1	4	168	134
-1	6	984	1240
-1	8	373	347
-1	10	168	156
-1	12	498	522
-1	16	181	171
-1	18	111	94
-2	2	111	67
-2	4	922	1517 -
-2	6	261	279
-2	8	760	838
-2	12	263	279
-2	14	307	307
-2	18	95	74
-3	2	620	818
-3	4	727	969
-3	6	244	294
-3	8	641	740
-3	10	514	507
-3	12	507	517
-3	14	151	98
-3	16	171	148
-3	18	209	165
-4	2	488	497
-4	4	437	488
-4	6	900	1182 -
-4	8	228	255
-4	10	104	82
-4	12	371	363
-4	14	341	334
-4	16	173	124
-5	2	647	778
-5	4	1040	1488 -
-5	6	238	251
-5	8	402	376
-5	12	445	665
-5	14	87	77
-5	18	137	103
-6	14	400	369
-6	12	147	118
-6	10	209	172
-6	8	232	190
-6	6	572	633
-6	4	361	375
-7	2	155	145
-7	6	371	375
-7	8	279	269
-7	10	203	202
-7	12	483	445
-7	14	328	304
-8	14	443	351
-8	12	174	168
-8	10	122	107
-8	8	119	102
-8	6	381	412
-8	4	325	315
-8	2	389	389
-9	2	123	105
-9	6	362	354
-9	8	400	408
-9	12	335	258
-9	14	259	223
-10	16	104	58
-10	14	178	135
-10	8	191	161
-10	6	357	352
-10	4	169	160
-11	2	120	89
-11	4	159	136
-11	6	134	93
-11	8	134	118
-11	12	212	155
-11	14	151	96
-12	14	76	60
-12	12	96	69
-12	10	130	88
-12	6	169	120
-12	2	127	94
0	2	135	84
0	4	486	539
0	6	786	908
0	8	878	1056
0	10	175	162
0	14	442	418
1	16	159	136
1	12	512	566
1	10	82	93
1	8	759	818
1	6	852	1043
1	4	686	886
1	2	880	1515-
2	0	1284	2523-
2	2	204	229
2	4	250	202
2	6	939	1111
2	8	471	461
2	10	148	129
2	14	472	391
3	14	150	98
3	12	318	268
3	10	123	105
3	8	561	604
3	6	598	618
3	4	777	861
3	2	207	150
3	0	245	234
4	0	479	519
4	2	313	298
4	4	140	137
4	6	224	211
4	8	244	266
4	14	202	187
5	12	174	143
5	10	166	131
5	8	229	231
5	6	363	369
5	4	459	472
5	2	525	617
5	0	341	253
6	0	638	728
6	2	223	246
6	4	267	272
6	6	151	159
6	8	320	290
7	10	78	70
7	8	303	259
7	6	117	98
7	2	583	666
8	0	398	424
8	2	87	72
8	4	143	135
8	6	214	169
8	8	152	129
9	6	217	181
9	4	100	81
9	2	214	216
9	0	148	100
10	0	320	260
11	2	169	163
K=	1		
0	2	524	637
0	3	294	220
0	4	885	1283 -
0	5	371	395
0	6	127	92
0	7	203	158
0	8	142	128
0	9	138	101
0	10	427	462
0	11	223	211
0	12	100	65
0	14	137	111
0	16	189	143
-1	18	125	118
-1	16	190	155
-1	14	318	305
-1	12	139	88
-1	10	328	298
-1	9	361	341
-1	8	331	339
-1	6	700	850
-1	5	419	397
-1	4	94	99
-1	3	116	76
-1	2	781	1614 -
-2	1	403	360
-2	2	464	547
-2	3	203	203
-2	4	492	581
-2	5	172	122
-2	6	275	208
-2	7	299	248
-2	8	118	86
-2	9	111	83
-2	10	710	834
-2	11	319	325
-2	14	101	80
-2	15	112	111
-2	16	400	332
-2	18	125	102
-3	18	195	155
-3	16	262	221
-3	14	165	173
-3	13	115	96
-3	12	442	431
-3	10	219	198
-3	9	430	470
-3	8	515	576
-3	7	55	46
-3	6	370	412
-3	5	133	145
-3	4	623	724
-3	3	785	981
-3	2	707	950
-3	1	433	468
-4	1	576	526
-4	2	764	917
-4	3	425	477
-4	4	776	893
-4	5	352	341
-4	6	133	129
-4	7	203	206
-4	9	161	146
-4	10	1089	1202
-4	12	111	110
-4	14	260	257
-4	15	222	180
-4	16	266	237
-4	18	232	177
-5	18	181	145
-5	16	358	278
-5	12	365	355
-5	10	191	182
-5	9	108	98
-5	8	565	619
-5	7	219	232
-5	6	274	269
-5	4	600	707
-5	3	222	252
-5	2	695	853
-5	1	207	211
-6	1	117	74
-6	2	350	339
-6	3	337	346
-6	4	461	538
-6	5	65	55
-6	6	228	241
-6	7	117	113
-6	8	110	89
-6	9	102	83
-6	10	559	564
-6	12	114	85
-6	14	312	247
-6	15	80	64
-6	16	228	184
-6	18	164	133
-7	18	157	135
-7	16	202	154
-7	15	96	82
-7	14	163	139
-7	12	259	258
-7	11	81	75
-7	10	79	83
-7	9	188	184
-7	8	294	301
-7	6	89	77
-7	4	413	428
-7	3	178	174
-7	2	494	524
-7	1	130	132
-8	2	150	149
-8	3	97	80
-8	4	223	220
-8	5	136	145
-8	7	279	257
-8	8	113	107
-8	10	319	308
-8	12	116	90
-8	14	79	73
-8	16	274	226
-9	16	111	98
-9	14	206	174
-9	12	161	151
-9	10	82	76
-9	9	82	89
-9	8	342	341
-9	7	164	151
-9	6	116	107
-9	4	285	270
-9	2	342	375
-9	1	82	86
-10	2	173	167
-10	4	226	246
-10	7	81	50
-10	10	209	222
-10	12	75	72
-10	14	118	89
-10	16	153	137
-10	17	90	66
-11	16	115	94
-11	8	252	226
-11	5	72	81
-11	4	86	86
-11	2	279	247
-12	3	103	89
-12	4	158	130
-12	10	171	146
-12	14	109	92
1	16	211	182
1	14	243	225
1	12	218	210
1	10	78	57
1	8	423	469
1	7	62	68
1	6	971	1229
1	5	585	639
1	4	523	510
1	2	824	991
1	1	360	360
2	11	184	160
2	10	601	672
2	9	173	185
2	8	178	160
2	7	166	140
2	5	289	289
2	4	829	1041
2	3	349	337
2	2	348	349
2	1	466	465
2	0	136	98
3	0	293	211
3	1	446	388
3	2	567	540
3	4	410	372
3	5	524	557
3	6	182	190
3	7	255	267
3	8	275	296
3	9	115	127
3	12	354	326
4	11	206	179
4	10	544	521
4	9	232	244
4	8	348	338
4	7	177	190
4	6	151	132
4	5	71	77
4	4	730	786
4	3	325	330
4	2	435	430
4	1	216	194
4	0	205	204
5	0	192	244
5	1	447	448
5	2	640	666
5	3	186	165
5	4	262	227
5	5	246	259
5	7	82	82
5	8	216	235
5	9	79	74
5	10	90	83
5	12	114	113
5	13	73	87
6	10	310	274
6	9	70	69
6	7	114	127
6	6	184	190
6	5	142	118
6	4	546	622
6	3	174	157
6	2	390	409
6	1	176	164
6	0	196	210
7	0	109	134
7	1	97	81
7	2	345	316
7	4	116	99
7	5	115	117
7	6	270	247
7	7	89	79
7	8	196	169
8	8	99	92
8	4	269	262
8	3	114	104
8	0	164	146
9	0	128	124
9	2	147	137
9	5	101	70
9	6	156	141
10	4	175	170
11	0	96	88
11	2	77	80
K=	2		
-1	2	600	756
-1	3	338	271
-1	4	131	126
-1	5	252	226
-1	6	301	257
-1	7	382	409
-1	8	565	598
-1	10	77	87
-1	11	82	88
-1	12	191	169
-1	13	184	162
-1	14	208	207
-1	15	239	231
-1	16	123	104
-1	17	88	82
-2	15	143	114
-2	14	172	174
-2	13	173	164
-2	12	188	183
-2	9	296	292
-2	8	476	519
-2	7	431	504
-2	6	281	347
-2	4	136	126
-2	2	621	693
-2	1	326	307
-3	1	265	269
-3	2	501	537
-3	3	64	45
-3	4	718	736
-3	5	581	623
-3	6	134	32*
-3	7	84	21*
-3	8	429	422
-3	9	69	60
-3	10	378	383
-3	11	224	214
-3	12	356	347
-3	14	193	190
-3	15	145	126
-3	16	135	131
-3	18	154	132
-4	14	150	109
-4	12	187	110
-4	11	113	95
-4	10	213	208
-4	9	100	111
-4	8	260	256
-4	7	351	361
-4	6	700	781
-4	5	311	283
-4	4	248	242
-4	3	243	260
-4	2	119	120
-4	1	265	247
-5	2	329	337
-5	3	150	145
-5	4	681	825
-5	5	332	324
-5	6	144	123
-5	7	134	122
-5	8	121	132
-5	9	128	141
-5	10	173	158
-5	11	128	115
-5	12	564	539
-5	14	173	152
-5	17	72	74
-5	19	124	98
-6	19	96	59
-6	15	145	144
-6	14	211	205
-6	13	87	95
-6	12	121	114
-6	10	161	154
-6	8	199	196
-6	7	369	390
-6	6	653	751
-6	5	110	105
-6	4	130	108
-6	3	121	111
-6	1	177	177
-7	1	81	81
-7	2	310	303
-7	3	206	211
-7	4	205	207
-7	5	245	255
-7	6	305	345
-7	8	283	269
-7	11	226	225
-7	12	397	453
-7	13	173	158
-7	14	134	119
-7	18	141	129
-7	19	62	60
-8	14	260	264
-8	11	194	196
-8	9	121	108
-8	8	332	370
-8	7	266	311
-8	6	473	536
-8	4	237	231
-8	3	134	122
-8	2	104	96
-8	1	243	255
-9	2	259	293
-9	3	123	109
-9	4	106	103
-9	5	173	169
-9	6	339	372
-9	8	229	246
-9	11	171	169
-9	12	290	277
-9	15	72	64
-9	18	91	105
-10	17	55	42
-10	16	84	55
-10	14	148	178
-10	13	129	127
-10	10	116	100
-10	8	205	225
-10	7	146	145
-10	6	252	250
-10	4	203	168
-10	3	116	110
-10	2	80	48
-10	1	134	123
-11	1	75	67
-11	2	140	140
-11	3	120	100
-11	4	124	132
-11	5	90	76
-11	6	158	156
-11	7	75	44
-11	8	92	68
-11	9	91	91
-11	10	73	52
-11	11	122	112
-11	12	143	144
-12	13	68	65
-12	10	99	98
-12	7	89	77
-12	6	100	114
-12	5	68	61
-12	4	52	42
-12	3	47	31
-12	2	59	60
0	2	948	1099
0	3	430	414
0	4	188	120
0	5	416	393
0	6	479	430
0	7	363	361
0	8	519	531
0	9	182	165
0	11	84	60
0	12	150	134
0	13	172	166
0	14	322	291
0	15	159	147
1	15	131	109
1	14	95	89
1	12	274	298
1	11	122	126
1	10	144	145
1	9	157	152
1	8	553	573
1	7	116	105
1	6	394	351
1	5	478	424
1	4	70	88
1	3	195	168
1	2	340	372
1	1	111	43*
2	0	704	779
2	1	412	414
2	2	422	410
2	3	199	172
2	4	79	0*
2	5	123	138
2	6	610	683
2	7	334	339
2	8	175	176
2	11	194	188
2	12	133	147
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-2	9	117	93
-2	7	596	604
-2	6	118	113
-2	5	321	291
-2	4	139	106
-2	3	52	72
-2	2	321	357
-2	1	497	568
-3	1	361	329
-3	2	190	149
-3	3	435	452
-3	4	186	198
-3	5	308	304
-3	6	131	114
-3	7	75	55
-3	8	193	186
-3	9	117	91
-3	10	190	204
-3	11	161	148
-3	12	207	200
-3	13	157	156
-3	14	102	91
-3	15	98	91
-3	16	63	75
-4	16	75	91
-4	15	100	98
-4	14	92	89
-4	13	141	155
-4	10	85	65
-4	9	186	181
-4	7	299	281
-4	6	166	143
-4	5	87	73
-4	4	110	99
-4	3	68	66
-4	2	416	374
-4	1	295	253
-5	1	192	171
-5	3	187	177
-5	4	121	113
-5	5	212	183
-5	8	249	239
-5	9	190	204
-5	10	149	164
-5	11	218	227
-5	12	145	125
-5	14	158	157
-5	15	100	111
-5	16	67	73
-6	16	45	49
-6	15	96	100
-6	14	89	77
-6	13	179	186
-6	11	85	74
-6	9	121	117
-6	8	85	81
-6	7	357	369
-6	6	270	256
-6	5	102	76
-6	4	226	202
-6	2	353	344
-6	1	84	80
-7	1	105	106
-7	3	257	260
-7	4	86	89
-7	5	317	315
-7	8	160	172
-7	9	191	197
-7	10	119	122
-7	11	202	214
-7	12	119	128
-7	13	75	90
-7	14	102	110
-7	15	63	66
-8	15	63	81
-8	14	43	42
-8	13	103	108
-8	12	52	49
-8	11	78	87
-8	10	57	47
-8	9	58	37
-8	8	132	119
-8	7	282	277
-8	6	158	167
-8	5	134	122
-8	4	119	128
-8	3	84	85
-8	2	203	187
-8	1	244	253
-9	1	61	59
-9	3	113	118
-9	5	151	161
-9	10	89	107
-9	11	104	116
-9	12	56	73
-9	13	88	100
-9	14	61	76
-10	13	87	117
-10	11	60	59
-10	8	65	75
-10	7	99	126
-10	6	57	49
-10	5	46	42
-10	4	55	61
-10	3	43	43
-10	2	97	117
-10	1	97	111
-11	4	36	50
-11	6	30	39
0	1	228	284
0	2	390	388
0	3	61	45
0	4	214	182
0	5	195	159
0	7	517	491
0	8	82	76
0	10	121	105
0	11	84	95
0	12	119	125
0	13	242	239
0	15	46	51
1	2	99	99
1	3	40	30
1	4	358	310
1	5	455	394
1	6	268	231
1	8	296	287
1	9	149	139
1	10	164	176
1	11	122	126
1	12	74	84
1	13	79	71
1	14	35	31
2	13	129	154
2	12	115	126
2	10	82	59
2	9	104	105
2	7	231	212
2	6	81	60
2	5	94	64
2	4	399	361
2	3	147	132
2	2	254	225
2	1	441	498
2	0	279	267
3	0	116	112
3	1	398	348
3	3	471	459
3	4	368	325
3	5	348	317
3	6	190	171
3	8	147	128
3	9	172	170
3	10	146	145
3	11	140	150
3	12	37	37
4	11	44	44
4	10	79	73
4	9	90	88
4	7	206	189
4	5	210	210
4	4	133	100
4	3	199	164
4	2	156	137
4	1	418	403
4	0	278	247
5	0	339	327
5	1	232	224
5	3	300	262
5	4	257	253
5	5	170	168
5	6	101	94
5	7	78	91
5	8	50	49
5	9	182	212
5	10	88	133
6	8	27	31
6	7	150	171
6	2	121	100
6	1	235	222
7	0	209	227
7	1	188	199
7	3	96	63
7	4	110	124
7	5	142	155
7	6	112	122
8	5	38	52
8	4	50	53
8	2	107	96
8	1	214	196
9	1	148	182
9	2	64	68
10	0	28	42
K=	7		
-1	1	300	336
-1	2	96	103
-1	3	156	129
-1	4	309	269
-1	5	255	237
-1	5	282	237
-1	7	122	98
-1	9	84	87
-1	11	200	180
-1	13	105	93
-1	14	61	72
-2	14	95	103
-2	13	56	53
-2	12	149	145
-2	11	203	177
-2	10	147	123
-2	9	252	213
-2	8	200	201
-2	7	85	93
-2	6	46	53
-2	5	43	51
-2	3	444	486
-2	2	95	89
-3	1	424	421
-3	2	221	203
-3	3	245	242
-3	4	134	117
-3	5	269	278
-3	6	217	206
-3	7	111	80
-3	8	90	74
-3	9	184	194
-3	10	76	49
-3	11	158	147
-3	12	87	81
-3	13	114	102
-3	14	112	123
-3	15	79	82
-4	14	51	56
-4	12	239	205
-4	11	223	189
-4	9	131	120
-4	8	210	199
-4	7	89	77
-4	6	121	114
-4	4	47	40
-4	3	366	404
-4	2	308	303
-4	1	67	68
-5	1	200	179
-5	2	197	184
-5	3	232	215
-5	4	176	162
-5	5	234	235
-5	6	180	177
-5	8	131	125
-5	9	185	202
-5	10	75	54
-5	11	156	136
-5	13	160	165
-5	14	87	103
-5	15	92	112
-6	13	54	48
-6	12	102	104
-6	11	175	170
-6	9	184	187
-6	8	131	133
-6	7	54	44
-6	6	245	289
-6	5	206	202
-6	4	92	90
-6	3	264	295
-6	2	84	74
-7	3	119	116
-7	1	209	201
-7	4	113	105
-7	5	172	152
-7	6	184	168
-7	7	158	140
-7	9	199	176
-7	11	83	74
-7	13	87	83
-7	14	61	64
-7	15	104	141
-8	14	67	73
-8	13	87	90
-8	12	98	106
-8	11	75	58
-8	10	56	58
-8	9	131	141
-8	8	134	135
-8	7	96	98
-8	6	50	63
-8	5	142	183
-8	3	156	193
-9	1	157	185
-9	6	132	163
-9	7	76	91
-9	9	124	138
-9	10	68	67
-9	11	54	66
-10	9	89	102
-10	8	39	45
-10	7	57	77
-10	6	40	39
-10	5	39	41
-10	4	36	43
0	1	49	11*
0	3	233	189
0	4	89	68
0	6	264	232
0	8	184	175
0	9	254	222
0	10	53	47
0	11	173	164
0	12	124	129
0	13	67	66
0	14	27	44
1	0	401	413
1	1	135	119
1	2	285	229
1	3	216	174
1	5	165	125
1	6	277	252
1	7	105	92
1	8	151	156
1	10	72	64
1	11	81	80
1	13	67	76
2	12	70	91
2	11	135	155
2	10	47	43
2	9	72	61
2	8	184	174
2	6	204	188
2	5	114	98
2	4	152	132
2	3	269	235
2	2	160	141
3	0	310	283
3	1	141	105
3	2	283	245
3	3	210	190
3	4	73	61
3	5	331	288
3	7	145	108
3	9	81	85
3	10	88	89
4	9	35	48
4	8	125	114
4	7	105	94
4	6	143	129
4	5	146	119
4	4	53	14*
4	3	350	361
4	2	236	213
4	1	71	47
4	0	205	196
5	0	240	234
5	1	106	85
5	2	76	66
5	3	131	137
5	4	74	68
5	5	258	233
5	6	48	46
5	7	75	93
5	8	46	49
5	9	65	104
6	6	69	86
6	5	95	97
6	4	84	80
6	3	264	263
6	2	157	154
6	0	54	43
7	0	125	119
7	1	136	136
7	3	54	55
7	4	60	56
7	5	83	101
8	3	137	186
8	1	115	121
8	0	45	45
9	0	107	140
9	1	64	91
K=	8		
-1	1	119	135
-1	2	69	69
-1	3	116	119
-1	4	145	136
-1	5	254	275
-1	9	120	122
-1	10	252	218
-1	13	75	104
-2	13	85	76
-2	12	113	88
-2	11	56	58
-2	8	134	129
-2	7	318	303
-2	6	158	132
-2	5	85	74
-2	4	97	77
-2	3	73	57
-2	2	186	189
-2	1	137	118
-3	1	41	40
-3	2	221	187
-3	3	82	42
-3	4	289	229
-3	5	181	219
-3	6	147	139
-3	8	120	98
-3	9	121	101
-3	10	288	243
-3	13	90	82
-3	14	65	68
-4	14	68	80
-4	13	91	72
-4	12	110	97
-4	11	56	51
-4	8	156	137
-4	7	238	257
-4	6	159	151
-4	4	225	208
-4	3	46	35
-4	2	144	125
-4	1	160	130
-5	14	46	75
-5	13	88	82
-5	12	71	60
-5	11	116	115
-5	10	237	212
-5	5	169	171

Table 2. Continued.

H	L			H	L			H	L			H	L			H	L			H	L		
K=	8			-6	3	98	105	-8	6	51	59	0	8	255	244	2	8	114	108	3	6	48	55	5	4	238	225
				-6	2	155	144	-8	4	140	136	0	10	56	48	2	7	188	206	3	7	88	75	5	5	105	120
				-6	1	154	141	-8	3	71	74	0	12	52	59	2	6	85	68	3	9	79	90	6	5	42	32
-5	4	265	287	-7	1	96	103	-8	2	68	65	1	0	71	42	2	5	69	57	3	10	67	111	6	3	105	103
-5	3	84	71	-7	2	80	97	-8	1	65	63	1	1	223	254	2	4	319	233	4	8	61	69	6	2	136	130
-5	2	206	211	-7	3	47	49	-9	4	65	78	1	2	96	106	2	3	89	93	4	7	167	167	6	1	188	189
-5	1	85	91	-7	4	115	122	-9	5	96	110	1	3	188	184	2	2	144	118	4	5	82	91	7	0	53	64
-6	13	81	81	-7	5	158	146	0	1	173	193	1	4	115	122	2	1	265	258	4	4	69	54	7	1	143	167
-6	12	67	76	-7	6	47	37	0	2	212	223	1	5	186	193	2	0	87	60	4	3	85	85	7	3	41	56
-6	11	90	69	-7	10	125	133	0	3	97	110	1	7	99	92	3	0	201	196	4	2	231	218	7	4	59	85
-6	9	47	54	-7	11	106	100	0	4	99	101	1	8	49	48	3	1	210	206	4	1	327	298	8	1	61	99
-6	8	170	155	-7	13	64	67	0	5	44	47	1	9	114	102	3	3	107	109	5	0	60	55				
-6	7	214	183	-8	8	98	133	0	6	124	117	1	10	215	204	3	4	170	178	5	1	160	175				
-6	4	170	144	-8	7	101	118	0	7	291	285	1	11	64	47	3	5	135	125	5	3	68	53				

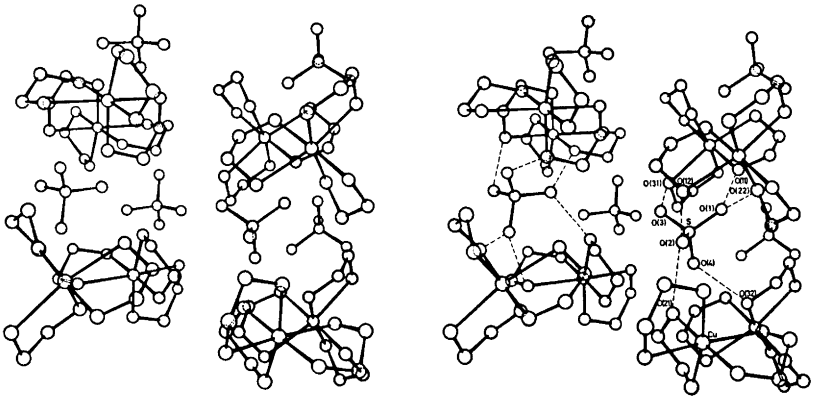

Fig. 1. A stereoscopic illustration of the molecular packing of $[Cu(C_2H_6O_2)_3]SO_4$ viewed along the *b*-axis.

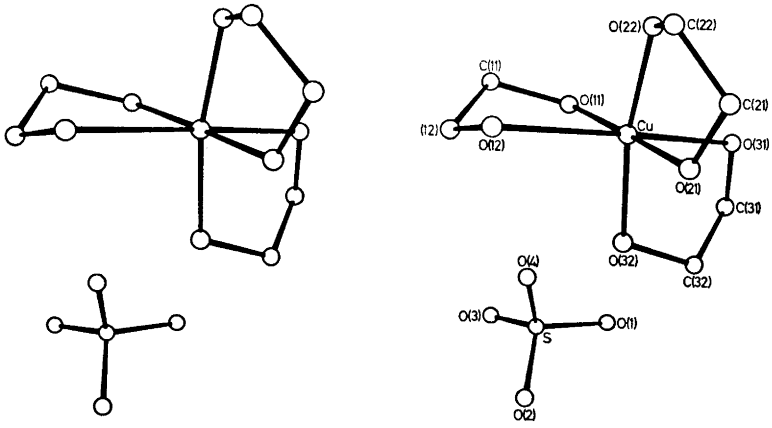

Fig. 2. A stereoscopic illustration of the atoms in the asymmetric unit, showing the coordination around copper.

Table 3. Bond lengths and bond angles and their estimated standard deviations for the arrangement around copper.

Bond	l, Å	Angle	θ°
Cu – O(21)	1.957 (8)	O(11) – Cu – O(21)	177.3 (4)
Cu – O(11)	1.975 (7)	O(22) – Cu – O(32)	168.6 (3)
Cu – O(22)	2.023 (7)	O(31) – Cu – O(12)	168.2 (3)
Cu – O(32)	2.030 (8)	O(11) – Cu – O(32)	91.6 (4)
Cu – O(31)	2.320 (8)	O(32) – Cu – O(21)	88.7 (4)
Cu – O(12)	2.335 (7)	O(21) – Cu – O(22)	81.2 (3)
		O(22) – Cu – O(11)	98.6 (3)

atom is 0.023 Å below the plane. The Cu – O distances to these four oxygen atoms range between 1.957 and 2.030 Å. One may note that two of the oxygen atoms in the plane, O(21) and O(22), belong to the same glycol molecule, whereas O(11) and O(32) belong to different glycol molecules. The distances from copper to the oxygen atoms above and below the plane are 2.328 Å and 2.335 Å. Within the octahedron the angles O(11) – Cu – O(21) and O(22) – Cu – O(32) are 177.3° and 168.6°, respectively, while the angle O(31) – Cu – O(12) is 168.2°. Thus the octahedron around the copper atom is distorted. This is what could be expected for an octahedral complex containing Cu^{2+}, due to its d^9 electron configuration. Furthermore this octahedral arrangement with four short and two long bonds is in agreement with what has been found in most other octahedral copper complexes.[10]

Prout *et al.*[11] have reported distances between copper and carboxy-oxygens and hydroxy-oxygens, respectively. They have found the bonds between copper and carboxy-oxygens (1.924 Å) to be significantly shorter than the bonds between copper and hydroxy-oxygens (1.970 Å). In the copper-glycol complex the mean value of the four short Cu – O distances of 1.997 Å also shows a significant difference from the reported copper – carboxy-oxygen distances but is of the same order of magnitude as the copper – hydroxy-oxygen distances.

The glycol ligands. These form a chelate with the copper atom, with the oxygen atoms at the corners of a distorted octahedron as described above. As already mentioned one of the ligands Glycol II, has its two oxygen atoms in the square plane surrounding the copper atom, while the other two glycol ligands (I and III) have one of their oxygen atoms in this plane and the other above, respectively below, the plane. This arrangement makes Glycol II more distorted in its configuration compared to Glycol I and III. The angles between connected planes in the glycol ligands (for each ligand one plane is defined by one oxygen atom and the two carbon atoms and the other plane defined by the two carbon atoms and the other oxygen atom), are 52.9°, 45.9°, and 55.3° for Glycol I, II, and III, respectively. The equations for these planes are given in Table 4. In order to obtain the most stable configuration at the same time as it is chelated to copper in the way described above, the glycol molecule should be in its *gauche* conformation,[12] *i.e.* the angle between

Table 4. The equations for the planes 1 – 6 in the glycol molecules. The numbering of the planes is the same as in Table 5.

1: $0.3147x + 0.8858y - 0.3410z - 1.3156 = 0$
2: $0.1164x - 0.8912y - 0.4385z - 4.5532 = 0$
3: $-0.9325x - 0.1946y - 0.3042z - 1.2162 = 0$
4: $0.9023x - 0.3498y - 0.2519z - 0.1286 = 0$
5: $0.4154x + 0.1086y - 0.9031z - 2.3541 = 0$
6: $0.0893x - 0.7300y - 0.6776z - 5.6724 = 0$

these planes should be $\approx 55°$. The deviations increase in the series III→I→II. These deviations are reflected in the differences in the tetrahedral angles O – C – C in the glycol ligands. Glycol III shows a mean value of 109.6°, Glycol I 108.4° and Glycol II 107.8°. The deviations from the tetrahedral arrangement are the consequence of the octahedral configuration which gives different O – O distances in the glycol ligands. For Glycol III, I, and II these distances are 2.773 Å, 2.714 Å, and 2.591 Å, respectively. Thus, in order to fit into the arrangement around the copper atom the glycol molecule that has its two oxygen atoms in the square plane has to change from its most stable conformation. For a complete list of distances and angles in the glycol ligands, see Table 5.

Table 5. Bond lengths and bond angles and their estimated standard deviations in the three glycol molecules. The roman figures I, II, and III refer to the glycol ligands I, II, and III, respectively.

Bond	l, Å	Angle	θ°
I		I	
O(12) – C(12)	1.410 (13)	(plane 1) O(12) – C(12) – C(11)	110.9 (9)
C(12) – C(11)	1.521 (15)	(plane 2) O(11) – C(11) – C(12)	105.9 (9)
C(11) – O(11)	1.465 (13)	plane 1 – plane 2	52.9
II		II	
O(21) – C(21)	1.408 (14)	(plane 3) O(21) – C(21) – C(22)	108.9 (9)
C(21) – C(22)	1.515 (17)	(plane 4) O(22) – C(22) – C(21)	105.2 (9)
C(22) – O(22)	1.478 (14)	plane 3 – plane 4	45.9
III		III	
O(31) – C(31)	1.410 (15)	(plane 5) O(31) – C(31) – C(32)	108.6 (10)
C(31) – C(32)	1.525 (17)	(plane 6) O(32) – C(32) – C(31)	110.6 (10)
C(32) – O(32)	1.436 (14)	plane 5 – plane 6	55.3

Since there is no crystal structure determination of ethylene glycol, it is not possible to compare the bond distances within the glycol ligands with those in the free glycol molecule and to see to what extent the chelation affects the bond distances. However, comparisons can be made with some

polyols and some carboxylate complexes containing a chelating OH-group. For β-D-mannitol [13] are reported C–C and C–O distances with mean values of 1.516 Å and 1.437 Å, respectively; galactitol [14] has the corresponding mean values of 1.520 Å and 1.449 Å and arabitol [15] 1.523 Å and 1.434 Å. For the carboxylate complexes mentioned above [11] the mean value for the C–C bonds is 1.545 Å and the mean value for the C–O bonds is 1.426 Å. We have found values for C–C and C–O bonds which range between 1.515–1.525 Å and 1.408–1.478 Å, respectively. The chelation does not seem to significantly affect these bond lengths.

The sulphate group and the hydrogen bonds. The sulphur-oxygen distances found in this structure range from 1.454 to 1.509 Å with three distances around 1.47 Å and one longer at 1.509 Å. As a result of the unequal lengths of the S–O distances the tetrahedral angles range from 105.8° to 111.6° with a mean value of 109.4°.

In earlier reports on S–O distances in sulphate groups, the four S–O distances are of the same order of magnitude and around 1.47 Å.[16] In order to explain the significantly longer distance of 1.509 Å obtained in this work one can study the list of sulphur-oxygen distances and compare it to the list of hydrogen bonds (Tables 6 and 7). The oxygen atom which lies farthest away from the sulphur atom, *i.e.* O(1), is in fact the same atom which gives two short hydrogen bonds 2.570 Å, 2.593 Å to oxygen atoms lying in the plane around copper. These comparatively strong interactions could be an explanation of the longer S–O distance.

Table 6. Bond lengths and bond angles and their estimated standard deviations in the sulphate group.

Bond	l, Å	Angle	θ°
S–O(1)	1.509 (8)	O(1)–S–O(2)	105.8 (5)
S–O(2)	1.476 (8)	O(1)–S–O(3)	108.8 (5)
S–O(3)	1.477 (8)	O(1)–S–O(4)	110.4 (5)
S–O(4)	1.454 (9)	O(2)–S–O(3)	109.7 (5)
		O(2)–S–O(4)	110.4 (5)
		O(3)–S–O(4)	111.6 (5)

Table 7. Hydrogen bond lengths and their estimated standard deviations.

Bond	l, Å
O(11)–H···O(1)	2.570 (10)
O(12)–H···O(2)	2.784 (11)
O(21)–H···O(2)	2.581 (11)
O(22)–H···O(1)	2.593 (10)
O(31)–H···O(3)	2.696 (11)
O(32)–H···O(4)	2.642 (11)

As mentioned before sulphate groups link $[Cu(C_2H_6O_2)_3]^{2+}$-ions through hydrogen bonds. This results in parallel sheets which are held together by hydrogen bonds (Fig. 1). Between the sheets no hydrogen bonds appear, merely van der Waals contacts. A list of the hydrogen bonds is given in Table 7. Each sulphate group seems to give six different hydrogen bonds, O(1) and O(2) give two hydrogen bonds each and O(3) and O(4) one each.

As discussed earlier by Raymond *et al.*[12] it is possible to establish different conformations for the ethylenediamine rings in tris(ethylenediamine)metal complexes being in their *gauche* conformation. In tris(ethylenediamine)-chromium(III) pentacyanonickelate(II) sesquihydrate [17] there are two different chromium(III) ions, both with a distorted octahedral configuration, and the conformations of the ions are $\delta\lambda\lambda$ for Cr_1 and $\delta\delta\lambda$ for Cr_2. The fact that the less stable $\delta\lambda\lambda$ and $\delta\delta\lambda$ conformations arise is due to the possibility of a greater number of hydrogen bonds between the amine nitrogens and the surrounding complex cyanide anions and water of crystallization than in tris(ethylenediamine)copper(II)sulphate [18] which evidently can crystallize in the more stable $\delta\delta\delta$ conformation.[19] In tris(1,2-ethanediol)copper(II) sulphate, the subject of this report, it is also possible to define the conformation for the copper(II) ion in the way described by Raymond *et al.*,[12] and it is approximately the same as that for Cr_2 in the structure described above, *i.e.* $\delta\delta\lambda$. Compared to tris(ethylenediamine) copper(II) sulphate the change in this case from δ to λ conformation could be a consequence of the formation of stronger hydrogen bonds between hydroxyl oxygens and sulphate oxygens as compared with hydrogen bonds between amine nitrogens and sulphate oxygens. As described Glycol II is more distorted in its configuration than Glycol I and III and has in fact a λ conformation. This is achieved by short hydrogen bond distances (see Table 7). For Glycol I there is one short (2.570 Å) and one long (2.784 Å) hydrogen bond, and this glycol ligand is expected to have a conformation somewhat less stable than the δ conformation, which is also indicated earlier. In this case it would perhaps be more adequate to describe the conformation for the copper(II) ion as something between $\delta\delta\lambda$ and $\delta\lambda\lambda$.

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