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On the Crystal Chemistry of Salt Hydrates. V. The Determination of the Crystal Structure of $CuSO_4 . 3H_2O$ (Bonattite)

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$CuSO_4.3H_2O$ crystallizes in space group *Cc* with $a=5·592$, $b=13·029$, $c=7·341$ Å, $\beta=97°3'$, $Z=4$. The structure has been determined from Patterson and Fourier syntheses using three-dimensional data collected on a precession camera with Mo $K\alpha$ radiation. The structure was refined by the method of least squares. The final *R* value for 936 observed structure factors is 0·069. The coordination polyhedra around the Cu^{2+} ions do not share any edges or corners with each other; they are connected by hydrogen bonds and *via* linking sulfate groups. The square planar coordination around the copper ion consists of three water oxygen atoms and one sulfate oxygen atom at an average distance of 1·96 Å. Two more sulfate oxygen atoms at 2·40 and 2·45 Å complete the distorted octahedral coordination. The average S–O bond length in the sulfate tetrahedron is 1·472 Å. The positions of the hydrogen atoms were not determined experimentally; they were calculated theoretically assuming that the hydrogen atoms are in positions of least electrostatic energy. Only four of the six crystallographically non-equivalent hydrogen atoms are involved in normal hydrogen bonds.

Introduction

Copper(II) sulfate trihydrate is the stable solid phase between 95·0 and 116·6 °C in contact with a saturated solution of $CuSO_4$ (Collins & Menzies, 1936). It has recently been found as a naturally occuring mineral and has been named bonattite (Garavelli, 1957). Copper(II) sulfate trihydrate belongs to a series of compounds $M^{2+}SO_4.nH_2O$, where M^{2+} is a cation with an approximate ionic radius of 0·7 Å. In this series (Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn) only copper is known beyond doubt to form a stable trihydrate. Sulfates of copper(II) also occur as the mono- and pentahydrates. The present investigation has been undertaken as part of a systematic study of the crystal structures of metal sulfate hydrates [previous paper in this series, Baur (1964)].

Experimental

Blue crystals of $CuSO_4.3H_2O$, up to 1 cm in their longest dimension, were grown at 105 °C from an aqueous solution of $CuSO_4$. Crystal plates ($0·2 \times 2·0 \times 2·0$ mm^3) were ground approximately perpendicular to [001] and [010]. The zero through third layer perpendicular to [001] and the zero through fifth layer perpendicular to [010] were recorded with Zr-filtered Mo $K\alpha$ radiation on a precession camera using the multiple exposure technique. On these layers, 610 unique reflections were estimated visually by comparing them with a calibrated strip. These data were used in the calculation of Patterson and Fourier syntheses, and in the early stages of refinement. It was observed that the anomalous absorption effects were pronounced. Therefore in the later stages of the refinement each F_{hkl} and its corresponding $F_{\bar{h}\bar{k}\bar{l}}$ were counted as separate unique reflections. Since the data did not include all F_{hkl}, $F_{\bar{h}\bar{k}\bar{l}}$ pairs, this procedure only increased the number of data to 936 unique reflections. The cell constants were derived from the precession photographs assuming Mo $K\alpha$ (mean) $=0·7107$ Å.

Crystal data

Copper(II) sulfate trihydrate is monoclinic, with $a=5·592(5)$*, $b=13·029(10)$, $c=7·341(6)$ Å, $\beta=97°3(7)'$; $V=531(1)$ Å^3, $Z=4$, $D_x=2·68$ g.cm^{-3}, $D_{\rm obs}=2·663$ g.cm^{-3} (Thorpe & Watts, 1880), F.W. 213·65. According to the systematic absences (*hkl* only present with $h+k=2n$, *h*0*l* only with $l=2n$) the space groups *Cc* or *C*2/*c* are possible. Since Scacchi (1870) found the crystals to be domatic, *Cc* is the obvious choice. This was proved to be correct by the observation of significantly different intensities in Friedel pairs and by the subsequent determination of the structure. The $a:b:c$ calculated from the above cell constants is 0·4292:1:0·5634. Scacchi found from optical measurements $a:b:c=$ 0·4321:1:0·5523 and $\beta=96°25'$.

Determination of the structure

From the three-dimensional Patterson synthesis the positions of Cu and S could be derived. A structure factor calculation including these two atoms yielded an *R* of 0·24. In two successive Fourier syntheses all the oxygen atoms could be found. The structure was then refined by least-squares methods to $R=0·069$ for all observed reflections. When the 40 strongest reflections, which seem to be affected by extinction, are

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* Throughout this paper the estimated standard deviations are given in parentheses following the value. They correspond to the last significant digits of these values.

omitted, R is 0·05. These strong F_{hkl} were given zero weight in the least-squares refinement, the other F_{hkl} were weighted according to Hughes's (1941) scheme. In Tables 1 and 3 the final parameters are presented. None of the parameters are involved in high correlations. The thermal parameters for O(1) and O(2) are not positive definite, but slight changes (smaller than one standard deviation) in B_{22} and B_{23} for O(1), and in B_{22} for O(2), would remove this condition. The form factors used for the F_c calculation were taken from *International Tables for X-ray Crystallography* (1962). The observed and calculated structure factors are listed in Table 4. The hydrogen atom positions could not be determined experimentally. The peaks found in the difference synthesis near the positions where hydrogen atoms are expected are approximately half as large as the largest background peaks.

Table 1. *Positional parameters and their standard deviations*

	x	y	z
Cu	0·5000	0·3640 (1)	0·5000
S	0·2643 (2)	0·1115 (1)	0·4168 (2)
O(1)	0·1618 (10)	0·1639 (5)	0·2446 (7)
O(2)	0·8319 (9)	0·3057 (5)	0·0505 (6)
O(3)	0·4788 (9)	0·0536 (5)	0·3805 (8)
O(4)	0·0866 (8)	0·9562 (5)	0·9825 (7)
O(*W*1)	0·3360 (9)	0·3725 (4)	0·2462 (8)
O(*W*2)	0·6940 (8)	0·0911 (4)	0·0809 (7)
O(*W*3)	0·7840 (7)	0·3041 (5)	0·4103 (6)

Table 2. *Parameters of hydrogen atom positions calculated to have the least electrostatic energy*

	x	y	z
H(11)	0·428	0·397	0·151
H(12)	0·174	0·355	0·192
H(21)	0·635	0·093	0·200
H(22)	0·604	0·040	0·003
H(31)	0·930	0·276	0·476
H(32)	0·795	0·304	0·280

Discussion of the structure

Fig. 1 shows the main features of the structure. The coordination polyhedra around the copper atoms do not share any edges or corners with each other; they are connected by hydrogen bonds and by linking sulfate groups. The square planar coordination around the copper atom consists of 3 water oxygen atoms and the oxygen atom O(1) from the sulfate group. This grouping may be considered as the building block of the structure, since all the short strong bonds are contained in it. It is connected to neighboring units *via* hydrogen bonds and the long Cu–O bonds which, when combined with the square planar configuration, complete the distorted octahedron.

The coordination polyhedron around Cu^{2+} is typical of the arrangement found in light blue copper(II) compounds. The mean of the short Cu–O distances in the square planar coordination is 1·96 Å. The mean of the two long distances is 2·42 Å. The corresponding figures for $CuSO_4.5H_2O$ are 1·97 and 2·41 Å (Bacon & Curry, 1962). The square planar coordination is not as ideal as the name might imply: the four sides, of the square are O(1)–O(*W*2) 2·90 Å, O(*W*2)–O(*W*1) 2·72 Å, O(*W*1)–O(*W*3) 2·79 Å and O(*W*3)–O(1) 2·66 Å, and the four oxygen atoms and the central copper(II) atom are not exactly in one plane. The sides of the square resemble a rectangle with a mean length of the two longer sides of 2·85 Å, and of the two shorter sides of 2·69 Å.

The shape of the sulfate group is essentially the same as was found in a series of very accurate structure determinations of sulfate compounds. The mean value of 1·472 Å for the four S–O distances is not significantly different from the mean of 20 previously determined S–O distances which is 1·473 Å (Baur, 1964). The distance S–O(1) is significantly longer than the mean value, which is probably correlated to the fact that O(1) participates in the square planar coordination around the copper(II) atom.

A calculation of the positions of least electrostatic energy of the hydrogen atoms resulted in the parameter values given in Table 2. The calculation was performed in the same way as for $CuSO_4.5H_2O$ (Baur, 1965). The charges assumed on the different atoms were: copper +2·0e, sulfur 0·0e, sulfate oxygen −0·5e, water oxygen −1·0e, hydrogen +0·5e. The shape of the water molecule was held constant in these calculations (angle H–O(*W*)–H = 109·5°, O(*W*)–H = 0·97 Å). The results of this calculation show clearly that O(*W*1)–H(11)–O(4), O(*W*2)–H(21)–O(3), O(*W*2)–H(22)–O(3) and O(*W*3)–H(32)–O(2) are more or less normal straight hydrogen bonds. The assumed hydro-

Table 3. *Thermal parameters and their standard deviations*

The definition of the Debye–Waller temperature factor is:

$$\exp\left[-\tfrac{1}{4}(h^2a^{*2}B_{11}+k^2b^{*2}B_{22}+l^2c^{*2}B_{33}+2hka^*b^*B_{12}+2hla^*c^*B_{13}+2klb^*c^*B_{23})\right].$$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0·65 (2)	0·71 (3)	0·44 (2)	−0·17 (2)	0·09 (2)	−0·04 (4)
S	0·52 (4)	0·38 (4)	0·46 (4)	−0·05 (3)	0·09 (3)	−0·06 (6)
O(1)	2·02 (17)	0·55 (15)	0·56 (17)	−0·05 (15)	−0·56 (15)	0·65 (19)
O(2)	1·88 (15)	0·91 (17)	0·61 (12)	0·77 (15)	−0·10 (13)	0·56 (22)
O(3)	1·40 (14)	2·07 (24)	1·49 (17)	0·99 (17)	0·82 (14)	0·66 (24)
O(4)	1·24 (13)	1·14 (17)	1·64 (16)	0·39 (15)	0·81 (13)	−0·15 (22)
O(*W*1)	1·05 (14)	1·06 (18)	0·92 (17)	−0·07 (15)	0·18 (15)	0·13 (20)
O(*W*2)	1·27 (14)	0·90 (15)	0·71 (12)	−0·32 (13)	0·55 (12)	−0·01 (22)
O(*W*3)	0·75 (11)	1·98 (22)	0·66 (12)	0·31 (15)	0·25 (11)	−0·04 (25)

Table 4. *Observed and calculated* $|F|$ *multiplied by* 10

The 40 $|F_o|$ which were omitted from the least-squares refinement are marked by a minus sign.

H	K	L	FOBS	FCAL
0	0	2	-932	1597
0	0	-2	-949	1628
0	0	4	767	851
0	0	-4	749	868
0	0	6	271	251
0	0	-6	183	171
0	0	8	503	495
0	0	-8	464	470
0	0	10	395	393
0	0	-10	391	377
0	2	2	181	190
0	2	-2	190	176
0	2	3	-849	954
0	2	-3	-761	908
0	2	4	245	226
0	2	-4	239	223
0	2	5	760	821
0	2	-5	748	815
0	2	6	99	85
0	2	-6	85	70
0	2	7	611	630
0	2	-7	635	652
0	2	8	140	96
0	2	-8	99	82
0	2	9	442	433
0	2	-9	473	461
0	2	10	60	80
0	2	11	231	235
0	2	-11	231	248
0	4	0	-1124	1732
0	4	1	712	700
0	4	4	690	739
0	4	-4	723	752
0	4	5	173	158
0	4	-5	196	177
0	4	6	107	93
0	4	-6	83	75
0	4	7	176	170
0	4	-7	158	171
0	4	8	402	385
0	4	-8	373	370
0	4	9	303	285
0	4	-9	286	276
0	4	10	374	384
0	4	-10	360	358
0	4	11	182	168
0	4	-11	164	171
0	6	0	304	266
0	6	1	790	848
0	8	0	491	513
0	8	1	325	315
0	8	2	454	419
0	8	3	430	406
0	10	0	160	163
0	10	1	262	247
0	10	2	158	134
0	10	3	589	565
0	12	0	603	619
0	12	1	505	518
0	12	2	557	544
0	12	3	439	408
0	14	0	85	54
0	14	1	143	103
0	14	2	274	284
0	14	3	237	222
0	16	0	233	230
0	16	1	544	590
0	16	2	199	192
0	16	3	348	348
0	18	0	125	116
0	18	1	118	109
0	18	2	330	355
0	18	3	141	137
0	20	1	331	391
0	20	3	190	220
1	1	0	-676	653
-1	1	0	-635	817
1	1	1	702	693
1	1	-1	-802	1216
-1	1	1	-876	1242
-1	1	-1	-632	737
1	1	-2	224	220
-1	1	2	172	160
-1	1	-2	-919	1189
1	1	3	-926	1028
1	1	-3	238	255
-1	1	3	299	312
-1	1	-3	-883	1038
1	1	4	-1020	1227
1	1	-4	-521	540
-1	1	4	554	532
-1	1	-4	-984	1232
1	1	5	464	457
1	1	-5	578	603
-1	1	5	563	605
-1	1	-5	400	430
1	1	6	512	492
1	1	-6	482	502
-1	1	6	499	489
-1	1	-6	534	517
1	1	7	578	567
1	1	-7	235	245
-1	1	7	229	228
-1	1	-7	544	550
-1	1	8	592	559
-1	1	-8	190	198
1	1	9	308	294
1	1	-9	321	301
-1	1	9	306	289
-1	1	-9	274	265
1	1	10	95	105
1	1	-10	352	350
-1	1	10	361	346
-1	1	-10	55	64
1	3	0	-860	1059
-1	3	0	-719	1014
1	3	1	-842	941
-1	3	1	-753	937
1	3	3	151	144
1	3	-3	522	514
-1	3	3	524	493
-1	3	-3	187	187
1	3	4	725	768
1	3	-4	485	502
-1	3	4	514	515
-1	3	-4	701	781
1	3	5	360	357
1	3	-5	553	620
-1	3	5	576	590
-1	3	-5	312	310
1	3	6	370	357
1	3	-6	564	600
-1	3	6	608	638
-1	3	-6	390	401
1	3	7	509	517
1	3	-7	244	224
-1	3	7	218	207
-1	3	-7	502	489
1	3	8	290	279
1	3	-8	640	675
-1	3	8	657	683
-1	3	-8	308	304
1	3	9	329	329
1	3	-9	142	153
-1	3	9	179	165
-1	3	-9	320	331
1	3	10	115	115
1	3	-10	390	373
-1	3	10	382	373
-1	3	-10	115	108
1	3	-11	235	234
-1	3	11	248	267
1	5	0	566	521
-1	5	0	550	563
1	5	1	586	578
-1	5	1	-1002	1220
1	5	4	663	696
-1	5	-4	695	702
1	5	5	476	498
1	5	-5	831	916
-1	5	5	831	901
-1	5	-5	480	492
1	5	6	328	350
1	5	-6	168	155
-1	5	6	168	153
-1	5	-6	323	332
1	5	7	556	557
1	5	-7	321	319
-1	5	7	280	280
-1	5	-7	565	564
1	5	8	53	40
1	5	-8	341	331
-1	5	8	361	341
-1	5	-8	53	63
1	5	9	322	324
1	5	-9	313	300
-1	5	9	293	286
-1	5	-9	317	312
1	5	10	154	155
1	5	-10	290	277
-1	5	10	280	268
-1	5	-10	136	130
1	5	-11	187	180
-1	5	11	187	193
1	7	0	-873	1012
-1	7	0	-883	1023
1	7	1	451	415
-1	7	1	453	432
1	7	2	555	553
-1	7	2	705	706
1	9	0	74	88
-1	9	0	81	89
1	9	1	361	349
-1	9	1	762	839
1	9	2	407	394
-1	9	2	420	407
1	9	3	324	323
-1	9	3	695	689
1	11	0	639	675
-1	11	0	638	683
1	11	1	324	300
-1	11	1	242	223
1	11	2	581	575
-1	11	2	690	723
1	11	3	170	165
-1	11	3	306	292
1	13	0	393	359
-1	13	0	385	366
1	13	1	507	495
-1	13	1	487	491
1	13	2	404	373
-1	13	2	380	389
1	13	3	405	414
-1	13	3	383	368
1	15	0	315	325
-1	15	0	324	343
1	15	1	300	285
-1	15	1	141	136
1	15	2	266	263
-1	15	2	418	441
1	15	3	341	319
-1	15	3	72	71
1	17	0	199	198
-1	17	0	212	215
1	17	1	438	446
-1	17	1	250	262
1	17	2	139	131
-1	17	2	226	235
1	17	3	492	502
-1	17	3	213	214
1	19	1	202	236
1	19	3	238	256
-1	19	3	100	100
2	0	0	117	98
-2	0	0	146	156
2	0	-2	-765	921
-2	0	2	-791	912
-2	0	-2	534	560
2	0	-4	-762	863
-2	0	4	-751	858
-2	0	-4	-687	809
2	0	6	-1023	1152
2	0	-6	-943	1020
-2	0	6	-918	1006
-2	0	-6	-958	1149
2	0	8	700	723
2	0	-8	570	573
-2	0	8	540	534
-2	0	-8	696	732
2	0	-10	398	338
-2	0	10	279	283
2	2	0	444	399
-2	2	0	470	411
2	2	1	480	537
2	2	-1	-1029	1428
-2	2	1	-1116	1417
-2	2	-1	476	512
2	2	-2	604	615
-2	2	2	652	631
-2	2	-2	204	172
2	2	-3	700	799
-2	2	3	733	787
-2	2	-3	906	978
2	2	-4	175	138
-2	2	4	175	149
-2	2	-4	155	156
2	2	5	288	285
2	2	-5	780	856
-2	2	5	799	857
-2	2	-5	346	340
2	2	6	136	137
2	2	-6	118	113
-2	2	6	118	105
-2	2	-6	136	144
2	2	7	341	353
2	2	-7	317	321
-2	2	7	384	371
-2	2	-7	354	362
2	2	-8	83	97
-2	2	8	58	86
2	2	9	300	296
2	2	-9	478	469
-2	2	9	508	507
-2	2	-9	237	249
2	2	-10	59	85
-2	2	10	59	89
2	2	-11	315	312
-2	2	11	320	345
2	4	0	234	213
-2	4	0	242	240
2	4	1	223	199
-2	4	1	549	586
2	4	2	639	632
-2	4	-2	583	604
2	4	-3	253	259
-2	4	3	273	267
-2	4	-3	517	508
2	4	-4	805	927
-2	4	4	883	953
-2	4	-4	552	608
2	4	5	330	328
2	4	-5	350	347
-2	4	5	350	342
-2	4	-5	269	301
2	4	6	742	741
2	4	-6	811	909
-2	4	6	856	910
-2	4	-6	702	743
2	4	7	281	277
2	4	-7	214	189
-2	4	7	183	181
-2	4	-7	269	273
2	4	8	449	461
2	4	-8	455	447
-2	4	8	448	443
-2	4	-8	457	477
2	4	9	200	190
2	4	-9	216	211
-2	4	9	208	195
-2	4	-9	208	212
2	4	10	274	265
2	4	-10	274	260
-2	4	10	246	235
-2	4	-10	298	285
2	6	0	383	356
-2	6	0	354	363
2	6	1	985	1021
-2	6	1	-938	1273
2	6	2	579	556
-2	6	2	453	424
2	6	3	850	919
2	8	0	349	322
-2	8	0	346	340
2	8	1	164	132
-2	8	1	399	407
2	8	2	636	622
-2	8	2	546	560
2	8	3	444	455
-2	8	3	489	458
2	10	0	855	862
-2	10	0	774	848
2	10	1	677	672
-2	10	1	558	619
2	10	2	647	673
-2	10	2	603	656
2	10	3	503	515
-2	10	3	347	330
2	12	0	275	283
-2	12	0	310	314
2	12	1	158	153
-2	12	1	297	288
2	12	2	421	394
-2	12	2	256	250
2	12	3	429	422
-2	12	3	390	388
2	14	0	516	532
-2	14	0	516	536
2	14	1	329	318
-2	14	1	302	305
2	14	2	462	452
-2	14	2	400	414
2	14	3	227	216
-2	14	3	280	247
2	16	0	182	191
-2	16	0	204	218
2	16	1	193	208
-2	16	1	208	204
2	16	2	169	188
-2	16	2	104	109
2	16	3	316	317
-2	16	3	409	409
2	18	1	123	129
-2	18	1	152	150
2	18	3	121	117
-2	18	3	68	70
-2	20	1	139	151
3	1	0	491	471
-3	1	0	468	463
3	1	1	549	563
3	1	-1	612	635
-3	1	1	604	625
-3	1	-1	538	572
3	1	2	565	569
3	1	-2	-877	1055
-3	1	2	-909	1062
-3	1	-2	543	547
3	1	3	349	488
3	1	-3	386	418
-3	1	3	402	403
-3	1	-3	490	501
3	1	-4	561	556
-3	1	4	552	552
-3	1	-4	187	192
3	1	-5	366	353
-3	1	5	362	361
-3	1	-5	428	428
3	1	-6	431	428
-3	1	6	387	393
-3	1	-6	341	333
3	1	-7	441	414
-3	1	7	445	426
-3	1	-7	357	353
3	1	8	317	306
3	1	-8	172	182
-3	1	8	151	151
-3	1	-8	288	284
3	1	9	214	216
3	1	-9	458	430
-3	1	9	420	428
-3	1	-9	254	233
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3	3	8	307	305
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3	3	-9	388	401
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4	14	2	178	173
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5	13	3	332	360
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6	0	-4	697	720
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-6	0	-4	396	418
6	0	-6	331	330
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6	4	-2	395	390
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-6	4	-4	359	396
6	4	-5	135	136
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-6	4	-5	181	165
-6	4	6	431	437
6	4	-7	120	138
6	6	0	298	268
-6	6	0	271	272
6	6	1	584	561
-6	6	1	483	519
6	6	2	226	212
-6	6	2	144	98
6	6	3	393	385
-6	6	3	227	211
6	8	0	177	169
-6	8	0	169	168
6	8	1	152	145
-6	8	1	200	196
6	8	2	207	209
-6	8	2	254	260
6	8	3	215	196
-6	8	3	243	230
6	10	0	320	305
-6	10	0	294	298
6	10	1	437	409
-6	10	1	386	381
6	10	2	309	269
-6	10	2	185	184
6	10	3	315	316
6	10	3	191	316
-6	10	3	193	173
-6	12	1	238	203
-6	12	2	222	220
-6	12	3	311	335
7	1	0	381	353
-7	1	0	369	371
7	1	1	323	295
7	1	-1	292	279
-7	1	1	293	276
-7	1	-1	275	291
7	1	2	183	175
7	1	-2	285	279
-7	1	2	292	289
-7	1	-2	205	199
7	1	3	408	406
7	1	-3	79	88
-7	1	3	96	111
-7	1	-3	384	406
7	1	-4	272	270
-7	1	4	256	269
7	1	-5	194	194
-7	1	5	208	209
7	3	0	478	454
-7	3	0	455	459
7	3	1	261	239
7	3	-1	142	137
-7	3	1	112	122
-7	3	-1	209	220
7	3	2	215	200
7	3	-2	420	436
-7	3	2	414	416
-7	3	-2	221	227
7	3	3	368	372
7	3	-3	54	78
-7	3	3	116	110
-7	3	-3	333	356
7	3	4	173	157
7	3	-4	403	406
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-7	3	-4	179	164
7	3	-5	201	192
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7	5	0	337	310
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7	5	1	264	237
7	5	-1	226	222
-7	5	1	207	217
-7	5	-1	211	215
7	5	2	108	120
7	5	-2	280	264
-7	5	2	278	277
-7	5	-2	121	128
7	5	3	360	360
7	5	-3	181	182
-7	5	3	232	221
-7	5	-3	346	360
7	5	-4	203	203
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7	5	-5	365	355
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7	7	0	428	332
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7	7	1	204	190
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7	7	3	271	266
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7	9	1	177	189
-7	9	1	263	275
-7	9	2	261	294
7	9	3	253	261
-7	9	3	330	308
-8	0	2	258	260
8	2	0	58	67
8	2	1	73	87
8	2	-1	241	240
-8	2	1	271	259
8	2	2	79	81
-8	2	-2	56	77
8	2	3	297	278
8	2	-3	323	311
-8	2	3	325	327
8	4	0	349	367
-8	4	0	334	355
8	4	1	115	126
8	4	-1	165	162
-8	4	1	167	157
-8	4	-1	100	120
8	4	2	382	402
8	4	-2	329	338
-8	4	2	291	301
-8	4	-2	401	406
-8	6	1	321	345
-8	6	3	319	340

gen bond between O(*W*1) and O(2) is rather long (3·13 Å) and, in the absence of further evidence, its existence cannot be taken as completely proved. The distance H(12)–O(2) is calculated to be 2·16 Å. A comparable distance is reported for the H---O separation in a hydrogen bond in natrolite (Torrie, Brown & Petch, 1964) where it was established by neutron diffraction to be 2·13 Å. The O(*W*)–O distance in the case of natrolite is 3·01 Å, and the bond is bent (∠O(*W*)–H---O = 154°). Atom O(1) is nearer to O(*W*1) (2·89 Å) than is atom O(2). However, it is not likely to correspond to a hydrogen bond since H(12)–O(1) is calculated to be 2·52 Å and therefore is too long to be considered a hydrogen bond. Also, the Cu–O(*W*1)–O(1) angle is 94°, which means in this case that the plane containing the hydrogen bonds would almost make a right angle with the bond direction Cu–O(*W*1). Such an arrangement is extremely unlikely. The only oxygen atom, except O(2), which is within hydrogen bonding distance from O(*W*3) is atom O(*W*2) at a distance of 2·83 Å. The distance H(31)–O(*W*2) however is 2·35 Å, while the angle O(*W*3)–H(31)–O(*W*2) is 110°. The angle O(*W*3)–H(31)–O(2) is 163° hence, closer to the ideal value of 180°, but in this case H(31)–O(2) is even longer (2·48 Å). It appears that atom H(31) does not participate in any hydrogen bonding. Fig. 2 shows the proposed hydrogen bonding scheme for $CuSO_4.3H_2O$.

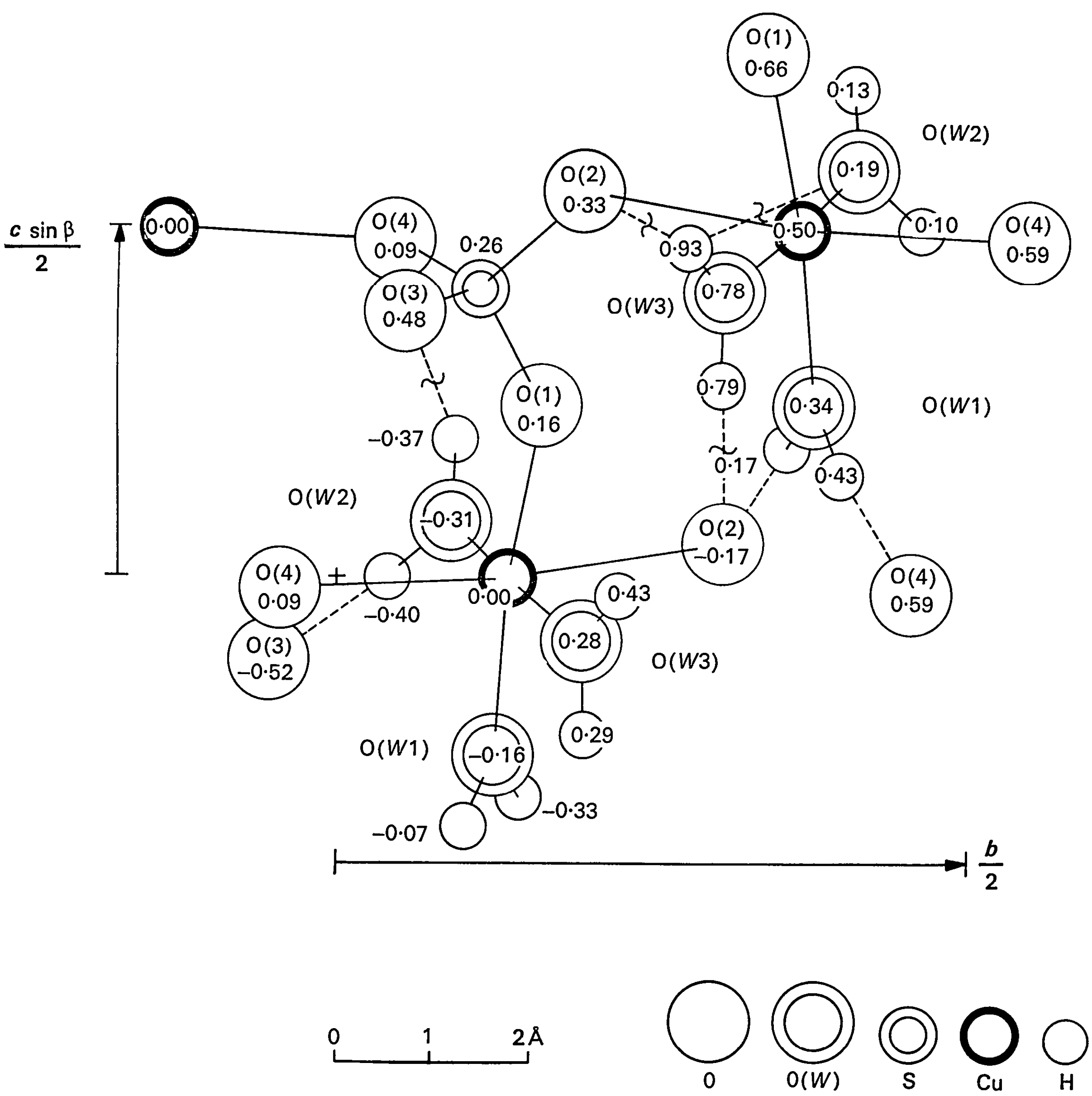

Fig. 1. $CuSO_4.3H_2O$, schematic projection parallel to [100]. The numbers in the circles representing the atoms are the *x* parameters of these atoms. Dashed lines lead to neighboring atoms of the hydrogen atoms, but do not necessarily represent hydrogen bonds.

Based on their structure determination of $CuSO_4.5H_2O$, Beevers & Lipson (1934) proposed a theory to explain the successive stages of dehydration observed in the copper sulfate hydrates. They assumed that the pentahydrate, when dehydrated, loses the water molecules around one of the two crystallographically different copper atoms, while the fifth water molecule which is not bonded to a copper atom remains in its tetrahedral coordination. This theory is not valid, as the structure of $CuSO_4.3H_2O$ proves. Beevers & Lipson further assumed that upon dehydration of the trihydrate the monohydrate is formed in such a way that the remaining water molecule is again not coordinated to a cation. According to Coing-Boyat & LeFur (1966) $CuSO_4.H_2O$ is isostructural with $MgSO_4.H_2O$ (Leonhardt & Weiss, 1957), and thus the water molecule should be coordinated to two copper atoms, again in contradiction to Beevers & Lipson's hypothesis.

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Table 5. *Interatomic distances and bond angles*

(*a*) Coordination around Cu^{2+}

Distances	
Cu–O(1)	1·943 (5) Å
Cu–O(2)	2·448 (6)
Cu–O(4)	2·399 (6)
Cu–O(*W*1)	1·976 (7)
Cu–O(*W*2)	1·968 (5)
Cu–O(*W*3)	1·955 (5)
Mean of short bonds Cu–O	1·961
Mean of long bonds Cu–O	2·424

Distances		Angles	
O(1)——O(*W*1)	3·910 (8)	O(1)——Cu–O(*W*1)	172·4 (0·3)°
O(1)——O(*W*2)	2·900 (8)	O(1)——Cu–O(*W*2)	95·7 (0·2)
O(1)——O(*W*3)	2·660 (7)	O(1)——Cu–O(*W*3)	86·1 (0·2)
O(*W*1)–O(*W*2)	2·715 (8)	O(*W*1)–Cu–O(*W*2)	87·0 (0·2)
O(*W*1)–O(*W*3)	2·789 (8)	O(*W*1)–Cu–O(*W*3)	90·4 (0·2)
O(*W*2)–O(*W*3)	3·916 (7)	O(*W*2)–Cu–O(*W*3)	173·1 (0·2)

(*b*) SO_4-tetrahedron

Distances	
S–O(1)	1·488 (5) Å
S–O(2)	1·476 (5)
S–O(3)	1·469 (5)
S–O(4)	1·455 (5)
Mean value	1·472

Distances		Angles	
O(1)–O(2)	2·363 (7) Å	O(1)–S–O(2)	105·7 (0·3)°
O(1)–O(3)	2·402 (8)	O(1)–S–O(3)	108·6 (0·4)
O(1)–O(4)	2·420 (8)	O(1)–S–O(4)	110·6 (0·3)
O(2)–O(3)	2·417 (9)	O(2)–S–O(3)	110·3 (0·4)
O(2)–O(4)	2·410 (8)	O(2)–S–O(4)	110·6 (0·3)
O(3)–O(4)	2·407 (7)	O(3)–S–O(4)	110·8 (0·4)
Mean value	2·403	Mean value	109·4

(*c*) Hydrogen bond geometry

Distances		Angles	
O(*W*1)–O(2)	3·126 (8) Å	O(2)–O(*W*1)–O(4)	107·2 (0·2)°
O(*W*1)–O(4)	2·751 (8)	Cu—O(*W*1)–O(4)	117·9 (0·3)
		Cu—O(*W*1)–O(2)	134·9 (0·3)
		Sum	360·0
H(12)–O(2)	2·16	O(*W*1)–H(12)–O(2)	174°
H(11)–O(4)	1·79	O(*W*1)–H(11)–O(4)	173
O(*W*2)–O(3)	2·678 (7)	O(3)–O(*W*2)–O(3)	96·3 (0·2)
O(*W*2)–O(3)	2·595 (8)	Cu—O(*W*2)–O(3)	113·9 (0·2)
		Cu—O(*W*2)–O(3)	142·9 (0·3)
		Sum	353·1
H(21)–O(3)	1·75	O(*W*2)–H(21)–O(3)	159
H(22)–O(3)	1·63	O(*W*2)–H(22)–O(3)	173
O(*W*3)–O(2)	2·687 (7)	Cu——O(*W*3)–O(2)	120·7 (0·2)
H(32)—O(2)	1·72	O(*W*3)–H(32)—O(2)	177

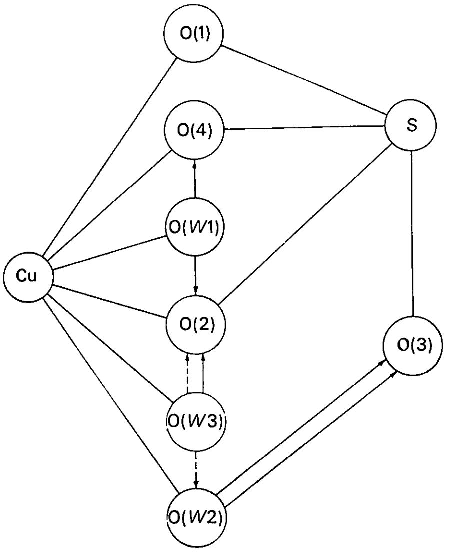

Fig. 2. $CuSO_4.3H_2O$, hydrogen bonding scheme. The dashed lines from O(*W*3) lead to neighboring atoms, but do not represent hydrogen bonds.

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Structure Cristalline de Composés Antituberculeux. I. Structure Cristalline du Chlorhydrate d'Éthionamide

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Ethionamide (2-ethyl-4-thiocarbamoylpyridine) hydrochloride crystallizes in the monoclinic system, space group $P2_1/c$, with cell dimensions $a = 8\cdot82 \pm 0\cdot02$, $b = 13\cdot51 \pm 0\cdot02$, $c = 10\cdot28 \pm 0\cdot02$ Å, $\beta = 127° \pm 20'$ and 4 molecules per cell. The refinement was carried out by least-squares calculations including anisotropic temperature factors. The final R is 0·118. The structure is built with layers of molecules parallel to (100); within these layers, the molecules are linked together by hydrogen bonds.

Introduction

Le chlorhydrate de thiocarbamoyl-4-éthyl-2-pyridine (ou d'éthionamide) a été préparé par Libermann et ses collaborateurs. Ces auteurs recherchaient une molécule active sur le B.K. isoniazidorésistant. Ils obtinrent une série de dérivés parmi lesquelles l'éthyl-2-thiocarbamoyl-4-pyridine est l'un des plus actifs.

Ce produit est utilisé en thérapeutique sous forme de chlorhydrate. Les structures de l'isoniazide (base et chlorhydrate) étant connues, il nous a paru intéressant de déterminer celles des dérivés de la série de l'éthionamide, dans le but de rechercher une éventuelle corrélation entre l'activité et la structure de ces molécules.

Dans un précédent travail (Colleter & Gadret, 1966) nous avons obtenu celle de la thiocarbamoyl-4-pyridine, la présente publication concerne celle du chlorhydrate d'éthyl-2-thiocarbamoyl-4-pyridine ($C_8H_{10}N_2S$, HCl).

Partie expérimentale

Par cristallisation dans l'éthanol on obtient de petits prismes monocliniques rouge orangé de dimension convenable (0,6 mm de diamètre sur 2 à 3 mm de long).

Le groupe spatial et les dimensions de la maille ont été déterminés sur des diagrammes de Bragg et de