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The Crystal Structure of Cobalt Sulfate Hexahydrate*

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Abstract

$CoSO_4 \cdot 6H_2O$ crystallizes in the monoclinic system, C2/c. The cell dimensions are $\underline{a}$ = 10.032 A, $\underline{b}$ = 7.233 A, $\underline{c}$ = 24.261 A, and β = 98.37°. There are 8 molecules in the unit cell; the X-ray density is 2.006 g/cc. The structure consists of sulfate tetrahedra and cobalt-centered water octahedra linked by a three dimensional network of hydrogen bonds. Eleven of the twelve hydrogen bonds are between water and sulfate oxygens; there is one water to water hydrogen bond. The average S-O sulfate distance is 1.46 A; the average Co-O distance in the water octahedra is 2.11A; and the average hydrogen bond (O-H···O) is 2.8 A. There are two crystallographically different Co^{++} ions in the structure. The hydrogen atoms are assigned an ordered configuration which would not contribute to residual entropy at low temperatures.

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Introduction

Calorimetric measurements by Rao and Giauque (1960) showed some unaccountable residual entropy in crystals of $CoSO_4.6H_2O$ at low temperatures. We have investigated the crystal structure in search of an explanation of the disorder. The resulting structure offers no possibility of disordered rings of hydrogen bonds such as were found in $Na_2SO_4 \cdot 10H_2O$ (Ruben, Templeton, Rosenstein and Olovsson, 1960), nor do we find any other explanation of the entropy discrepancy.

The crystal morphology was described by Marignac (1855), and Groth (1908).

Experimental

Crystals of $CoSO_4.6H_2O$ were grown from a saturated solution at 50 - 55°. The intensity data were obtained by multiple film Weissenberg techniques. The film photography was done using Fe Kα (λ=1.9373 A) X rays, on Ilford Industrial G film. Intensities were estimated visually by comparison with a calibrated set of spots. The scaling factor used between multiple films of the same layer was $\exp(2.0 \sec \mu)$, where μ is the equi-inclination angle and 2.0 is an empirically determined constant from the data; this scaling factor varied from 7.4 at the zero layer (μ=0°), to 12.9 at the sixteenth layer (μ=38.7°).

The first single crystal of $CoSO_4.6H_2O$ was enclosed in a .1 mm. glass capillary. At the time we felt the crystals would be unstable in the open atmosphere, however, later we found the crystals to be sufficiently stable to handle in air. This first crystal was aligned about the [101] direction. Seventeen layers were photographed and 737 reflections were observed of which

125 were below the detection limit and called zero. Later a second crystal was aligned about its b axis and photographed in air. An additional 99 zero layer reflections were measured of which 10 were below the detection limit. The sum total of intensities used was 836, of which 135 were recorded as zero.

For greater accuracy, the cell dimensions of $CoSO_4 \cdot 6H_2O$ were measured on a General Electric XRD-5 equipped with a goniostat using Mo Kα (λ=.7107 A) X rays.

In order to solve the structure we found it necessary to take some reflection data from $MgSeO_4 \cdot 6H_2O$ and $MgSO_4 \cdot 6H_2O$ both of which are isomorphic with $CoSO_4 \cdot 6H_2O$.

A crystal of $MgSO_4 \cdot 6H_2O$ was grown from its saturated solution at 50-55°. It was aligned about its b axis and photographed with Fe Kα X rays with the Weissenberg technique. Intensities were recorded of 102 $h0\ell$ reflections of which 6 were below the detection limit. Cell dimensions were measured on the goniostat as with the cobalt isomorph.

$MgSeO_4 \cdot 6H_2O$ crystals were prepared at room temperature by allowing a filtered solution of dilute selenic acid and excess MgO to evaporate in an open dish. A crystal was aligned along its b axis and photographed with the Weissenberg technique with Fe Kα X rays. Intensities were recorded of 102 $h0\ell$ reflections of which 15 were below the detection limit. The cell dimensions were obtained from the Weissenberg films.

Cell dimensions and space group

The cell dimensions of $CoSO_4.6H_2O$ are :

$\underline{a} = 10.032 \pm .004$ A $\beta = 98.37 \pm .03^\circ$ (98.7° by Marignac (1855))
$\underline{b} = 7.233 \pm .003$ A $V = 1742 \pm 2$ A^3
$\underline{c} = 24.261 \pm .010$ A $Z = 8$
space group = C2/c (C_{2h}^6)
$\underline{a}:\underline{b}:\underline{c} = 1.387:1:3.354$ (1.396:1:3.381 by Marignac (1855))

X-ray density = 2.006 g/cc: measured density = 2.000 (Gosner, 1907), 2.019 (Thorpe and Watt, 1880), 2.017 (Handbook of Chemistry and Physics, 1957).

The characteristic extinctions of the intensitdes indicated space group Cc or C2/c. As there are 8 molecules in the unit cell and C2/c has an 8 fold general position as opposed to 4 for Cc, C2/c appeared intuitively to be the most likely space group. A "zero moment test" on the 3 dimensional data was computed (Howells, Phillips and Rogers, 1950) and the results indicated a center of symmetry, space group C2/c. The best evidence we have for the space group C2/c is the successful solution of a chemically reasonable structure.

The cell dimensions of $MgSO_4.6H_2O$ are:

$\underline{a} = 10.110 \pm .005$ A $\underline{c} = 24.41 \pm .01$ A
$\underline{b} = 7.212 \pm .004$ A $\beta = 98.30 \pm .04$ A

The cell dimensions of $MgSeO_4.6H_2O$ are:

$\underline{a} = 10.36 \pm .03$ A $\underline{c} = 25.1 \pm .1$ A
$\underline{b} = 7.38 \pm .04$ A $\beta = 98.1 \pm .2^\circ$

Determination of Structure

The three-dimensional Patterson function of $CoSO_4.6H_2O$ was computed. Attempts were made to associate the larger peaks with Co-Co, S-S, and Co-S vectors; however, two trial structures with Co atoms in general positions failed to give a reasonable Fourier projection in the b direction. Later it was learned that Co atoms are in two sets of special positions.

Crystals of the isomorphic compounds $MgSO_4.6H_2O$ and $MgSeO_4.6H_2O$ were prepared and photographed. From the Patterson projections calculated from the three sets of h0*l* data we found the locations of the Co and S atoms.

A set of trial oxygen positions was obtained from an h0*l* Fourier projection of the $MgSO_4.6H_2O$. The signs of 54 of the 96 non-zero structure factors were estimated from the location of the Mg and S positions. All of the ten oxygen atoms were found. A new calculation of signs led to a sign change in only two of the original 54 data used. A second Fourier projection using 86 non-zero terms clearly showed the basic arrangement of $SO_4^{=}$ tetrahedra and $Mg(H_2O)_6^{++}$ octahedra.

The h0*l* data for the $MgSO_4.6H_2O$ and $MgSeO_4.6H_2O$ is shown in tables 1 and 2.

In $CoSO_4.6H_2O$ eight cobalt atoms occupy positions 4(a) and 4(e):

4(a) 0,0,0; 0,0,1/2 + C centering.

4(e) 0,y,1/4; 0,-y,3/4 + C centering.

The sulfur atoms and ten sets of oxygen atoms occupy the general 8(f) positions:

8(f) x,y,z; -x,-y,-z; -x,y,1/2-z; x,-y,1/2+z + C centering.

A fourier projection of the h0*l* data of $CoSO_4.6H_2O$ was calculated and the x and z parameters of the cobalt, sulfur and oxygen positions were evaluated. The y parameters were estimated from expected S-O bond distances in the sulfate ion and O-O distances about the hydrated cobalt ion.

Table 1: The h0ℓ observed structure factors for $MgSO_4 \cdot 6H_2O$

h=	-10	-8	-6	-4	-2	0	2	4	6	8	10
ℓ=0	28	49	25	40	38						
2	29	39	0	49	46	0	53	40	17	30	30
4	37	24	39	34	45	22	64	9	20	34	
6	29	15	13	38	49	0	86	17	54	18	
8	0	35	40	42	64	34	7	14	45	44	
10		13	18	31	18	39	31	65	40	22	
12		0	33	46	16	46	98	64	40	18	
14		6	43	27	33	32	25	26	19		
16		38	15	11	11	65	24	13	40		
18		20	21	10	37	33	71	33	34		
20			0	51	39	46	32	49			
22			14	13	17	9	39				
24				12	38	41					

Table 2: The h0ℓ observed structure factors for $MgSeO_4 \cdot 6H_2O$

h=	-10	-8	-6	-4	-2	0	2	4	6	8	10
ℓ=0	0	47	17	51	25						
2	20	24	33	67	80	0	83	24	37	0	16
4	20	12	13	50	41	33	56	31	7	27	
6	21	0	20	20	73	0	114	11	49	8	
8	0	38	34	0	71	42	10	26	17	24	
10	11	10	13	20	39	17	15	38	0	13	
12		16	16	59	0	50	55	48	11	7	
14		0	41	7	45	9	39	17	20		
16		23	0	10	0	58	15	12	21		
18		10	17	10	33	20	59	16	26		
20			0	32	15	33	15	34			
22			15	0	18	0	23				
24					13	23					

Least squares refinement utilizing the full matrix (Busing and Levy, 1959) was performed for a total of 13 cycles on the IBM 704 computer. Atomic form factors of Co^{++} (Watson and Freeman, 1961), neutral S (Tomiie and Stam, 1958), and neutral O (Hartree and Hartree, 1939) were used in these calculations. 836 intensity data were used, 737 of which were obtained from a crystal rotated about the [101], and 99 of which were obtained from a zero layer about a [010] rotation. 18 scale factors, 34 positional parameters and 13 isotropic temperature factors for a total of 65 parameters were varied. The overall R factor, where $R = \frac{\Sigma||F_{obs}|-|F_{calc}|| \times 100}{\Sigma|F_{obs}|}$, was 54% before refinement commenced, dropped to 42% after the first refinement and then dropped steadily to the final value of 13%. The necessity to run so many cycles was in part due to certain blunders in the original estimate of the y parameters for the oxygen atoms. The final R factors are as follows:

R (including zeros) = 13.0%.

R (omitting zeros) = 10.9%.

The data are shown in table 3.

The atomic parameters are shown in table 4. By an oversight the dispersion correction $\Delta f'$ of about -1.8 electrons (for Fe $K\alpha$) was omitted from the cobalt form factor. As a result, the temperature factors for cobalt in Table 4 are larger than the true values by an unknown amount.

Table 3: Observed and calculated structure factors for $CoSO_4 \cdot 6H_2O$.
The observed values are listed above the calculated ones.

K= 0

L=	-19	-18	-17	-16	-15	-14	-13	-12	-11	-10	-9	-8	-7	-6	-5	-4	-3	-2
				105		89		135		42		192		208		232		169
H= 2				-79		-68		-114		38		124		-160		-221		172
				77		51		223		77		165		58		143		162
H= 4				76		-49		217		65		150		46		148		168
														0		103		0
H= 6														7		-117		19
												95		27		70		46
H= 8												85		-21		85		-60
														40		69		26
H=10														-51		-77		30

K= 1

L=	-19	-18	-17	-16	-15	-14	-13	-12	-11	-10	-9	-8	-7	-6	-5	-4	-3	-2
			15	76	0	105	37	64	77	108	135	47	68	137	96	323	52	131
H= 1			-17	-61	-9	84	-35	-56	68	-90	102	-57	56	116	-88	-329	42	-131
	26	27	48	152	75	51	38	0	0	0	30	237	74	59	94	128	105	97
H= 3	32	22	38	151	-67	32	-50	10	0	2	30	213	-66	-49	80	121	101	-109
			0	112	22	45	33	77	69	77	62	157	42	29	39	98	0	91
H= 5			-4	-98	16	-48	44	-74	78	78	-58	-163	-40	-29	-45	116	1	94
													0	0	39	89	0	43
H= 7													13	-0	45	-88	-18	37
											24	40	0	43	0	89	19	31
H= 9											-28	42	-0	-40	-7	87	26	29

K= 2

L=	-19	-18	-17	-16	-15	-14	-13	-12	-11	-10	-9	-8	-7	-6	-5	-4	-3	-2
				139	106	28	74	178	94	15	0	178	52	156	30	29	37	43
H= 0				-131	98	23	-58	-163	86	-5	9	-154	52	-124	19	-40	-24	-41
		15	83	102	0	32	0	163	106	23	102	137	47	93	69	66	100	198
H= 2		-14	83	88	-8	26	-1	156	-95	-16	100	130	-31	-71	55	76	-94	-203
			33	0	0	51	44	138	76	21	0	94	23	0	159	171	67	81
H= 4			47	-5	1	-54	-33	-134	75	-28	8	-96	-21	-2	-150	-171	-79	83
		31		0	53	69		37	0	56		39	23	0	0	72	0	49
H= 6		38		18	-64	-72		47	16	71		36	-23	8	-12	69	-7	55
												90	0	50	0	0	0	0
H= 8												-85	24	-52	-1	-13	-23	9

K= 3

L=	-19	-18	-17	-16	-15	-14	-13	-12	-11	-10	-9	-8	-7	-6	-5	-4	-3	-2
			21	42	67	44	73	91	69	30	65	117	42	42	87	172	150	17
H= 1			18	37	-50	-40	70	86	-65	38	57	124	-43	39	85	151	-137	-12
		34	30	66	31	21	51	34	56	49	78	144	133	77	174	106	22	39
H= 3		-46	-12	-68	38	-12	-51	-35	-61	-48	-84	-145	141	62	-176	-109	24	39
			45	47	0	64	47	17	41	0	79	104	75	40	66	32	33	19
H= 5			47	47	9	62	-48	25	-35	-11	88	98	-77	40	-64	-36	-42	-12
						22	39	83	56				25	27	19	62	56	0
H= 7						-24	-43	-77	61				-21	24	-20	49	61	3
											0	48	34	18	56	37	24	33
H= 9											-0	-41	-41	20	51	-28	25	-32

```
                                     K= 4
  L= -19 -18 -17 -16 -15 -14 -13 -12 -11 -10  -9  -8  -7  -6  -5  -4  -3  -2

                  51  77   0  26  24  29  30  41  51  46  22   0  56  79  69
H= 0              57 -74   8  19  27 -28  33  39  51 -42  20   0  59 -82  63
              56  36   0  45  21  38   0   0  70  66   0  77  31  51 104   0
H= 2         -68 -31   2 -49 -29 -43  -1 -15 -68 -61  -9 -75  27 -57 108  -2
                       0   0 102 102  70  68   0  61   0  44  47  77  84  19
H= 4                   2  -1  97  90 -71  69  11  54  -1  36  44  72  78  25
                  28  54      72  23      36      84 106  25  27   0   0   0
H= 6             -38  54     -82 -30     -41     -76 104 -19  24 -15 -11 -14
                                                  34  36  26   0  34  25
H= 8                                              22  31  19  -4  30  26

                                     K= 5
  L= -19 -18 -17 -16 -15 -14 -13 -12 -11 -10  -9  -8  -7  -6  -5  -4  -3  -2

                       0  23  47  31   0  17  67   0  44  64  81  72  98  50
H= 1                   9 -22 -55 -31 -12 -18  68 -18  56 -62 -73 -73  97 -62
              32  22  65   0   0   0  44  32  47  46  76  71  19  62  70  80
H= 3          51  38 -63  10   9   0  43  31  44  39 -77  43  19  59  58 -81
                      22  32      27  73   0  89      51  53   0  26   0  31
H= 5                  26 -45     -30  78  -5 -85      46 -46  11  37   9  28
                                                      24      53  28  74  33
H= 7                                                 -14      46 -24 -63 -32

                                     K= 6
  L= -19 -18 -17 -16 -15 -14 -13 -12 -11 -10  -9  -8  -7  -6  -5  -4  -3  -2

                          53      43   0  36  40  14  62   0  58  41   0  63
H= 0                     -49     -40  12 -38 -40  18  65  -8  40 -40  -3 -52
                          30   0  17  55  52  33  23  23   0   0   0  87  94
H= 2                      39   6  16 -62  48  28  26  15  11  13  -8 -86  74
                                      41  22   0   0   0  43  68  14  22  37
H= 4                                  42 -15   4  -3  10 -34 -69 -11 -14 -26
                                                                       0
H= 6                                                                   6

                                     K= 7
  L= -19 -18 -17 -16 -15 -14 -13 -12 -11 -10  -9  -8  -7  -6  -5  -4  -3  -2

                                               0      22  73  62  16  21   0
H= 1                                          -4     -30  72  62 -14 -12   1
                                                                  15   0  45
H= 3                                                             -15   2  43
```

```
                                      K= 0
   L=  -1   0   1   2   3   4   5   6   7   8   9  10  11  12  13  14  15  16

                                          182               0      64
H= 0                                      167               3      40
          167     142     206     237      64      29     194       8
H= 2     -192    -163    -234     268     -76      35    -256      28
            0      50      74      21      73     135     159
H= 4       21     -44      91      27      80    -112     163
           91      16      36      93     106      43
H= 6      -98      18     -37    -101     -95     -54
          119      42       0      31      82
H= 8      122     -51      -2      27      81
           58      24
H=10      -61     -37
                                      K= 1
   L=  -1   0   1   2   3   4   5   6   7   8   9  10  11  12  13  14  15  16

       19 102  40 104  61 233   0 142  29 159  35  50  66 188  17  81  27
H= 1   21 102  43-123 -69 276   5 125 -21 154  34 -41 -51 202  -1  74  24
       61 106  22  38  14  23  33 110  47 203  43  20  18  31  17
H= 3   63-138 -28  44 -10  14 -37 113  50-229 -46  22 -12 -38 -24
        0 135  19  47  14 117  56  76  28  77   0  74   0
H= 5  -16 143  19  53  15 124  58 -79 -29  84  -8  82 -10
       23  57  41      15  97  24   0   0  18  12
H= 7  -27 -70 -52      -4-100 -27  15   7 -18  14
        0  24  12  34  16  78   0  14  15
H= 9    9  28  17 -29 -14  77  -4  19 -19
                                      K= 2
   L=  -1   0   1   2   3   4   5   6   7   8   9  10  11  12  13  14  15  16

       74 200
H= 0  -78-222
      127 126  60 129 115  65  16 102   0 115  18  64  31 106  55  37
H= 2 -136 132  55 148  97  81  19  93   4 118  20  62 -28  80  51 -38
       57  86   0  35  80 226  70  31  25  25  21  21  37  54
H= 4   53-101 -20 -33  87-246 -75 -38  27 -27  22  18  34 -45
        0 113 117  66  41 104   0  68  20 112  42  60
H= 6   -7 126 128 -63 -46 122   6  69 -19  97  50 -57
       32  92  22  14  29  23   0  16  43  81
H= 8   30 -81 -20 -19 -27  26   2  18  48 -78
                                      K= 3
   L=  -1   0   1   2   3   4   5   6   7   8   9  10  11  12  13  14  15  16

       24  30   0  20  53 115  64 131   0 129  26  59  64 101  50   0  59
H= 1  -16  19 -22 -19 -45-108 -73-128  12-140 -29 -58  64 -98 -30   2  56
       32  73  90  32  83  72   0  63  24 118  66  11  37  12  38
H= 3   26  64  94 -30 -84  73  11  65 -22 111  60  14 -29  12 -29
      100 143  56  48  33  91  48  43 155  88   0  37  42
H= 5  104-144 -62 -54  31 -93 -48  33 146 -84  -5 -42 -37
       16  29  16  46  67 117  95   0   0   0   0
H= 7    1  30 -21  39 -66 102  92 -12   2   1  -7
        0  23  12  10  28
H= 9    2 -22 -13  -5  36
```

```
                                   K= 4
   L=  -1   0   1   2   3   4   5   6   7   8   9  10  11  12  13  14  15  16

      149 176
H= 0  142 162
      112  88  61  80  25  69  65   0  68  30  86   0  37  75  77  24
H= 2  104 -86 -64 -76 -14 -71 -74  -8  68 -36 -88  -5  31 -53 -69 -25
        0   0  63  16  97  88  57  35   0  41   0  23  73  45
H= 4   -3   1 -62  23 -96  77  58  36 -22  38   8  14 -72  42
        0  32  90  16  68  41  40  57  25  67  65  19
H= 6   13 -36 -78   2  62 -35  38 -60 -29 -51 -58 -16
      105  38  35  26  20  22   0
H= 8 -103  33  28  20  17  20   4

                                   K= 5
   L=  -1   0   1   2   3   4   5   6   7   8   9  10  11  12  13  14  15  16

       19  44  89  43 146  19  47  35   0  38  88  28  77  19  27  24  20
H= 1   15  50  76  42-148  20  48  26 -15  31  75  26 -70  16  19  30  28
       28  51  29   0  29   0   0  17  87  28 120  51  17  50  15
H= 3   29 -52 -27 -16  34  -5 -20 -18  81 -20-127 -43   8 -50 -14
       38  39  21  31   0   0  46  12  52  29   0  20  15
H= 5  -36  34 -20  27   6  -0  42   8 -47  26   0  35   9
       24  25  17  26  27  21
H= 7   24 -19 -13 -21  18 -24

                                   K= 6
   L=  -1   0   1   2   3   4   5   6   7   8   9  10  11  12  13  14  15  16

      104   0
H= 0  -93   8
       76  53  17  50   0  15  87  59  40  21  11  19  18
H= 2  -70  52 -22  39   9  18  68  47 -30  20   2  13  -7
        0  23   0  75  75  30  36  29   9  15  28
H= 4    9 -19  -6 -58  64 -22 -29 -23  -9 -15 -21
            0           7       0
H= 6        7         -20       4

                                   K= 7
   L=  -1   0   1   2   3   4   5   6   7   8   9  10  11  12  13  14  15  16

       37  23  21  52  28   0   0   0  21
H= 1  -30 -19 -19 -33  18  -1  -8  -5 -29
       20   0  43       0       0
H= 3  -23  -4  49       4     -10
```

K= 0

L=	-24	-23	-22	-21	-20	-19	-18	-17	-16	-15	-14	-13	-12	-11	-10	-9
	62		12		84		89		74		79		100		31	
H= 2	-70		-21		-90		81		-79		-68		-113		38	
			18		99		27		76		49		204		70	
H= 4			-29		106		-17		76		-49		217		65	
					27		41		65		95		111		33	
H= 6					-14		-49		-70		93		-121		32	
							27		88		0		0		0	
H= 8							37		98		8		3		1	

K= 0

L=	-8	-7	-6	-5	-4	-3	-2	-1	0	1	2	3	4	5	6	7	8
											0		55		0		138
H= 0											5		53		8		167
	144		153		197		175		186		178		231		302		79
H= 2	124		-160		-220		172		-192		-163		-233		268		-76
	147		59		147		181		10		50		85		27		79
H= 4	150		46		148		168		21		-44		91		27		80
	128		0		120		0		107		24		43		108		101
H= 6	-130		7		-117		19		-98		18		-37		-101		-95
	93		27		79		54		133		48		0		29		95
H= 8	85		-21		85		-60		122		-51		-2		27		81
	16		46		71		25		57		26						
H=10	-13		-51		-77		30		-61		-37						

K= 0

L=	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
		40		0		41		151		36		37		0		60
H= 0		-38		3		40		160		47		-45		-7		84
		41		275		40		79		130		53		30		
H= 2		35		-256		28		-80		-139		-57		37		
		122		170		41		56		32		60				
H= 4		-112		163		18		57		-49		78				
		54		91		20		70								
H= 6		-54		-80		-8		-68								
		10		28												
H= 8		12		20												

Table 4: Atomic parameters for $CoSO_4 \cdot 6H_2O$.

		x	y	z	B(Å^2)
Co_1		0	0	0	3.3
Co_2		0	.949 ± .001	1/4	3.0
S		.868 ± .001	.452 ± .001	.1244 ± .0003	2.2
O_1	sulfate oxygens	.778 ± .001	.601 ± .002	.1352 ± .0006	2.6
O_2		.980 ± .002	.446 ± .003	.1695 ± .0007	3.9
O_3		.918 ± .002	.492 ± .003	.0698 ± .0007	3.9
O_4		.799 ± .001	.276 ± .002	.1193 ± .0006	2.9
O_5	water octahedra about Co_1	.592 ± .001	.723 ± .002	.0469 ± .0006	2.8
O_6		.535 ± .002	.325 ± .002	.0673 ± .0006	3.2
O_7		.305 ± .002	.557 ± .003	.0216 ± .0006	3.3
O_8	water octahedra about Co_2	.885 ± .002	.159 ± .002	.2823 ± .0007	2.3
O_9		.886 ± .002	.740 ± .002	.2832 ± .0007	2.7
O_{10}		.858 ± .001	.949 ± .003	.1771 ± .0006	3.3

Discussion of the Structure and Hydrogen Bonding

The structure consists of discrete $SO_4^{=}$ tetrahedra and $Co(H_2O)_6^{++}$ octahedra, Fig. 1. There are just enough water molecules to satisfy this octahedral hydration of each cobalt ion.

Hydrogen bonds are assigned to the twelve shortest oxygen-oxygen distances (Table 5) after disregarding these between oxygen atoms of the same sulfate ion or of the same coordination octahedron. This assignment is checked by consideration of the hydrogen atom configuration and bond angles. Except for one water molecule (O_9) each water has two hydrogen bonds to sulfate oxygen atoms. Water molecule O_9 has one such bond and also a bond to atom

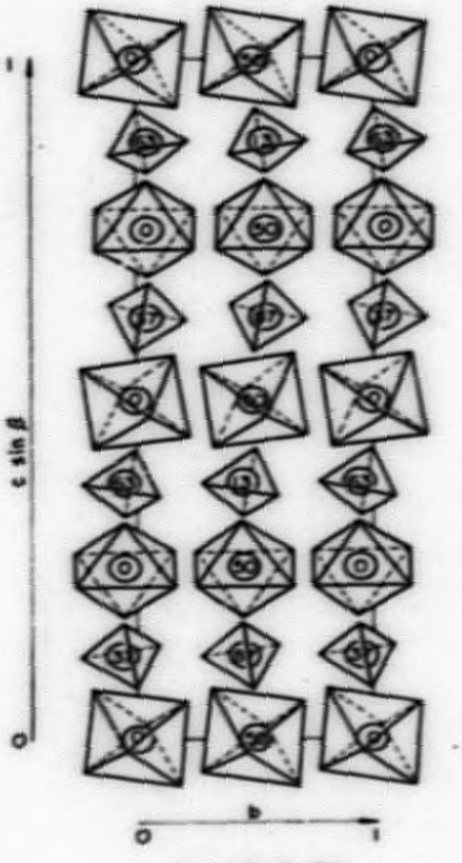

Fig. 1. Packing of $SO_4^=$ tetrahedra and $Co(H_2O)_6^{++}$ octahedra. The encircled numbers are the parameters of the Co and S atoms in the *a* direction.

Table 5: Interatomic Distances in $CoSO_4 \cdot 6H_2O$. Standard deviations are about ± .03 A.

	sulfate oxygens				water oxygens					
					about Co_1			about Co_2		
	O_1	O_2	O_3	O_4	O_5	O_6	O_7	O_8	O_9	O_{10}
Co_1					2.11 2.11	2.05 2.05	2.14 2.14			
Co_2								2.13 2.13	2.12 2.12	2.11 2.11
S	1.46^s	1.44^s	1.51^s	1.45^s						
O_1		2.36	2.40	2.40	2.77^h			2.79^h		2.79^h
O_2	2.36		2.43	2.37				2.65^h	2.69^h	
O_3	2.40	2.43		2.40	2.72^h	2.68^h	2.93^h			
O_4	2.40	2.37	2.40			2.78^h	2.86^h			2.76^h
O_5	2.77^h		2.72^h			2.89 2.99	2.90 3.10			
O_6			2.68^h	2.78^h	2.89 2.99		2.94 2.99			
O_7			2.93^h	2.86^h	2.90 3.10	2.94 2.99				
O_8	2.79^h	2.65^h						2.97	3.00^h 3.03	2.94 3.04
O_9		2.69^h						3.00^h 3.03	2.99	2.96 3.03
O_{10}	2.79^h			2.76^h				2.94 3.04	2.96 3.03	

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[h] hydrogen bond distances.

[s] S-O bond in $SO_4^=$.

O_8. In this bond geometry, there is only one configuration of hydrogen atoms with two hydrogen atoms on each water molecule. The angles between hydrogen bonds at these water molecules (Table 6) range from 97° to 126° and are within the range found for other hydrated sulfate crystals. The hydrogen bonds make angles of 111° to 124° with the water-cobalt vectors. The third hydrogen bond to O_8 makes angles of 80° and 117° with the two hydrogen bonds for which O_8 provides the hydrogen atoms.

Table 6: Hydrogen bond angles. O_1 through O_4 are sulfate oxygens. O_5 through O_{10} are water molecules.

atoms	angles
$O_1 - O_5 - O_3$	117°
$O_3 - O_6 - O_4$	105°
$O_3 - O_7 - O_4$	126°
$O_1 - O_8 - O_2$	97°
$O_2 - O_9 - O_8$	116°
$O_1 - O_{10} - O_4$	124°

The hydrogen bond lengths are 2.65 to 2.93 A for the bonds to sulfate and 3.00 A for the water-water bond. The shortest non-bonded oxygen-oxygen distances other than edges of the octahedra, are 3.13 A between O_7 pairs (through a center of symmetry) and 3.22 A between O_9 and O_4.

We find no reasonable alternative to this hydrogen configuration, and the entropy discrepancy is not explained by our work.

The hydrogen bonds tie the sulfate ions and water octahedra together in a three-dimensional network as indicated in Fig. 2. In this figure, the hydrogen configuration is indicated by small circles on the hydrogen bonds. Because of the bond angles the hydrogen atoms are expected to fall slightly off these lines joining oxygen atoms. We do not have a direct determination of the hydrogen positions from the diffraction data.

The two cobalt ions, Co_1 and Co_2, have point symmetries $\bar{1}$ and 2 respectively. The water octahedron about Co_1 is hydrogen bonded exclusively to sulfate ions. The Co_2 water octahedron has ten hydrogen bonds to sulfate ions and four involving water molecules of neighboring Co_2-type octahedra.

The average interatomic distances are as follows:

S - O ($SO_4^=$) 1.46 A
O - O ($SO_4^=$) 2.39 A
Co- O ($Co(H_2O)_6^{++}$) 2.11 A
O-H-O (hydrogen bond) 2.79 A..

Several other substances have the same structure as $CoSO_4.6H_2O$. In addition to the two magnesium compounds, $CoSeO_4.6H_2O$, $ZnSO_4.6H_2O$, and one form of $NiSO_4.6H_2O$ are isomorphous (Groth, 1908). This structure has been recognized in nature as the minerals hexahydrite, $MgSO_4.6H_2O$, and bianchite, $ZnSO_4.6H_2O$ (Palache, Berman and Frondel, 1952).

A more thorough study of the structure of $MgSO_4.6H_2O$ is in progress, and the location and refinement of the hydrogen parameters in that crystal will be the topic of another article shortly.

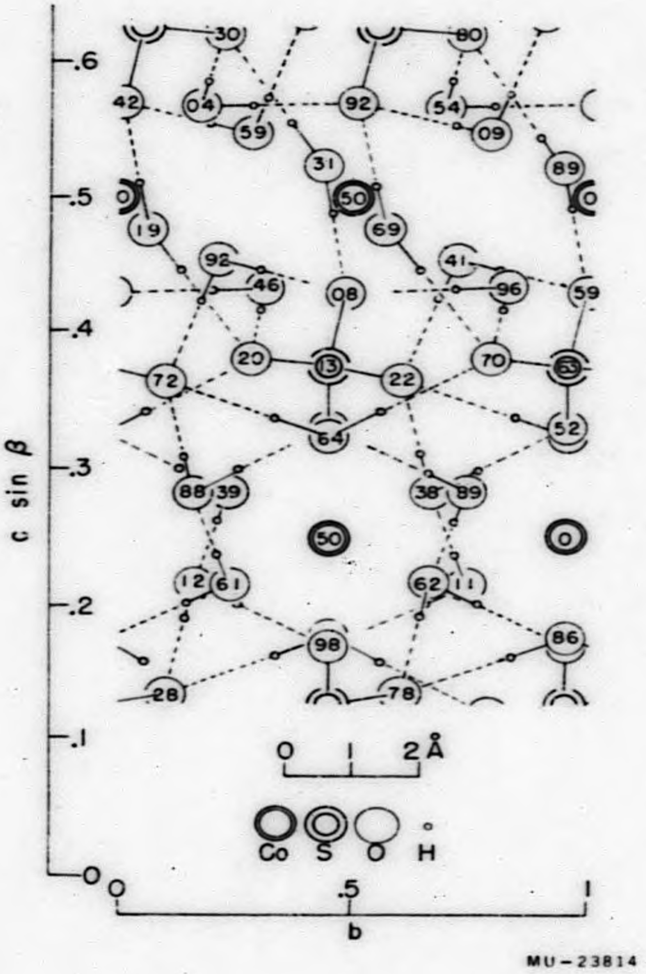

Fig. 2. Hydrogen bond network in $CoSO_4 \cdot 6H_2O$. The numbers are the parameters along the a axis of the Co, S, and O atoms. The complete environment about each of the two different $Co(H_2O)_6^{++}$ and $SO_4^=$ is shown.

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