magnitude more important than those arising out of the additional cross-terms when a [(3-by-3)+(6-by-6)] method is replaced by a 9-by-9 one. This is quite evident in the middle stages of refinement.

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The Crystal Structure of Cobalt Sulfate Hexahydrate*

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$CoSO_4.6H_2O$ crystallizes in the monoclinic system, $C2/c$. The cell dimensions are

$$a=10{\cdot}032,\ b=7{\cdot}233,\ c=24{\cdot}261\ \text{Å};\ \beta=98{\cdot}37°.$$

There are 8 molecules in the unit cell; the X-ray density is 2·006 g.cm.$^{-3}$. 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 Å; the average Co–O distance in the water octahedra is 2·11 Å; and the average hydrogen bond ($O\text{–}H \cdots O$) is 2·8 Å. 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.

Introduction

Calorimetric measurements by Rao & 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 $Na_2SO_4.10H_2O$ (Ruben, Templeton, Rosenstein & 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 $K\alpha$ ($\lambda=1{\cdot}9373$ Å) 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 ($2{\cdot}0 \sec \mu$), 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 ($\mu=0°$), to 12·9 at the sixteenth layer ($\mu=38{\cdot}7°$).

The first single crystal of $CoSO_4.6H_2O$ was enclosed in a 0·1 mm. glass capillary. At the time we felt the

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* Work done under the auspices of the U.S. Atomic Energy Commission.

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 $CoSO_4.6H_2O$ were measured on a General Electric XRD-5 equipped with a goniostat using Mo $K\alpha$ ($\lambda = 0{\cdot}7107$ Å) X-rays.

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

A crystal of $MgSO_4.6H_2O$ was grown from its saturated solution at 50–55°. It was aligned about its *b* axis and photographed with Fe $K\alpha$ X-rays with the Weissenberg technique. Intensities were recorded of 102 *h0l* reflections of which 6 were below the detection limit. Cell dimensions were measured on the goniostat as with the cobalt isomorph.

$MgSeO_4.6H_2O$ 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 $K\alpha$ X-rays. Intensities were recorded of 102 *h0l* 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:

$a = 10{\cdot}032 + 0{\cdot}004$ Å $\quad \beta = 98{\cdot}37 \pm 0{\cdot}03°$
(98·7° by Marignac (1855))
$b = 7{\cdot}233 \pm 0{\cdot}003$ Å $\quad V = 1742 \pm 2$ Å^3
$c = 24{\cdot}261 \pm 0{\cdot}010$ Å $\quad Z = 8$
Space group $= C2/c(C_{2h}^6)$
$a:b:c = 1{\cdot}387:1:3{\cdot}354$
(1·396:1:3·381 by Marignac (1855))
X-ray density = 2·006 g.cm.$^{-3}$: measured density = 2·000 g.cm.$^{-3}$ (Goszner, 1907), 2·019 (Thorpe & Watt, 1880), 2·017 (*Handbook of Chemistry and Physics*, 1957).

The characteristic extinctions of the intensities 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 & 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:

$a = 10{\cdot}110 \pm 0{\cdot}005$ Å $\quad c = 24{\cdot}41 \pm 0{\cdot}01$ Å
$b = 7{\cdot}212 \pm 0{\cdot}004$ Å $\quad \beta = 98{\cdot}30 \pm 0{\cdot}04°$

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

$a = 10{\cdot}36 \pm 0{\cdot}03$ Å $\quad c = 25{\cdot}1 \pm 0{\cdot}1$ Å
$b = 7{\cdot}38 \pm 0{\cdot}04$ Å $\quad \beta = 98{\cdot}1 \pm 0{\cdot}2°$

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 *h0l* data we found the locations of the Co and S atoms.

Table 1. *The h0l observed structure factors for* $MgSO_4.6H_2O$

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* $MgSeO_4.6H_2O$

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					

A set of trial oxygen positions was obtained from an *h0l* 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.

Table 3. *Observed and calculated structure factors for* $CoSO_4.6H_2O$

The observed values are listed above the calculated ones

K	H	-19	-18	-17	-16	-15	-14	-13	-12	-11	-10	-9	-8	-7	-6	-5	-4	-3	-2	-1	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
0	0																											182				0		64		
																												167				3		40		
	2				105		89		135		42		192		208		232		169		167		142		206		237		64		29		194		8		
					-79		-68		-114		38		124		-160		-221		172		-192		-163		-234		268		-76		35		-256		28		
	4				77		51		223		77		165		58		143		162		0		50		74		21		73		135		159				
					76		-49		217		65		150		46		148		168		21		-44		91		27		80		-112		163				
	6														0		103		0		91		16		36		93		106		43						
															7		-117		19		-98		18		-37		-101		-95		-54						
	8												95		27		70		46		119		42		0		31		82								
													85		-21		85		-60		122		-51		-2		27		81								
	10														40		69		26		58		24														
															-51		-77		30		-61		-37														
1	1			15	76	0	105	37	64	77	108	135	47	68	137	96	323	52	131	19	102	40	104	61	233	0	142	29	159	35	50	66	188	17	81	27	
				-17	-61	-9	84	-35	-56	68	-90	102	-57	56	116	-88	-329	42	-131	21	102	43	-123	-69	276	5	125	-21	154	34	-41	-51	202	-1	74	24	
	3	26	27	48	152	75	51	38	0	0	0	30	237	74	59	94	128	105	97	61	106	22	38	14	23	33	110	47	203	43	20	18	31	17			
		32	22	38	151	-67	32	-50	10	0	2	30	213	-66	-49	80	121	101	-109	63	-138	-28	44	-10	14	-37	113	50	-229	-46	22	-12	-38	-24			
	5			0	112	22	45	33	77	69	77	62	157	42	29	39	98	0	91	0	135	19	47	14	117	56	76	28	77	0	74	0					
				-4	-98	16	-48	44	-74	78	78	-58	-163	-40	-29	-45	116	1	94	-16	143	19	53	15	124	58	-79	-29	84	-8	82	-10					
	7													0	0	39	89	0	43	23	57	41		15	97	24	0	0	18	12							
														13	-0	45	-88	-18	37	-27	-70	-52		-4	-100	-27	15	7	-18	14							
	9											24	40	0	43	0	89	19	31	0	24	12	34	16	78	0	14	15									
												-28	42	-0	-40	-7	87	26	29	9	28	17	-29	-14	77	-4	19	-19									
2	0				139	106	28	74	178	94	15	0	178	52	156	30	29	37	43	74	200																
					-131	98	23	-58	-163	86	-5	9	-154	52	-124	19	-40	-24	-41	-78	-222																
	2		15	83	102	0	32	0	163	106	23	102	137	47	93	69	66	100	198	127	126	60	129	115	65	16	102	0	115	18	64	31	106	55	37		
			-14	83	88	-8	26	-1	156	-95	-16	100	130	-31	-71	55	76	-94	-203	-136	132	55	148	97	81	19	93	4	118	20	62	-28	80	51	-38		
	4			33	0	0	51	44	138	76	21	0	94	23	0	159	171	67	81	57	86	0	35	80	226	70	31	25	25	21	21	37	54				
				47	-5	1	-54	-33	-134	75	-28	8	-96	-21	-2	-150	-171	-79	83	53	-101	-20	-33	87	-246	-75	-38	27	-27	22	18	34	-45				
	6		31		0	53	69		37	0	56		39	23	0	0	72	0	49	0	113	117	66	41	104	0	68	20	112	42	60						
			38		18	-64	-72		47	16	71		36	-23	8	-12	69	-7	55	-7	126	128	-63	-46	122	6	69	-19	97	50	-57						
	8												90	0	50	0	0	0	0	32	92	22	14	29	23	0	16	43	81								
													-85	24	-52	-1	-13	-23	9	30	-81	-20	-19	-27	26	2	18	48	-78								
3	1			21	42	67	44	73	91	69	30	65	117	42	42	87	172	150	17	24	30	0	20	53	115	64	131	0	129	26	59	64	101	50	0	59	
				18	37	-50	-40	70	86	-65	38	57	124	-43	39	85	151	-137	-12	-16	19	-22	-19	-45	-108	-73	-128	12	-140	-29	-58	64	-98	-30	2	56	
	3		34	30	66	31	21	51	34	56	49	78	144	133	77	174	106	22	39	32	73	90	32	83	72	0	63	24	118	66	11	37	12	38			
			-46	-12	-68	38	-12	-51	-35	-61	-48	-84	-145	141	62	-176	-109	24	39	26	64	94	-30	-84	73	11	65	-22	111	60	14	-29	12	-29			
	5			45	47	0	64	47	17	41	0	79	104	75	40	66	32	33	19	100	143	56	48	33	91	48	43	135	88	0	37	42					
				47	47	9	62	-48	25	-35	-11	88	98	-77	40	-64	-36	-42	-12	104	-144	-62	-54	31	-93	-48	33	146	-84	-5	-42	-37					
	7						22	39	83	56				25	27	19	62	56	0	16	29	16	46	67	117	95	0	0	0	0							
							-24	-43	-77	61				-21	24	-20	49	61	3	1	30	-21	39	-66	102	92	-12	2	1	-7							
	9											0	48	34	18	56	37	24	33	0	23	12	10	28													
												-0	-41	-41	20	51	-28	25	-32	2	-22	-13	-5	36													
4	0				51	77	0	26	24	29	30	41	51	46	22	0	56	79	69	149	176																
					57	-74	8	19	27	-28	33	39	51	-42	20	0	59	-82	63	142	162																
	2			56	36	0	45	21	38	0	0	70	66	0	77	31	51	104	0	112	88	61	80	25	69	65	0	68	30	86	0	37	75	77	24		
				-68	-31	2	-49	-29	-43	-1	-15	-68	-61	-9	-75	27	-57	108	-2	104	-86	-64	-76	-14	-71	-74	-8	68	-36	-88	-5	31	-53	-69	-25		
	4					0	0	102	102	70	68	0	61	0	44	47	77	84	19	0	0	63	16	97	88	57	35	0	41	0	23	73	45				
						2	-1	97	90	-71	69	11	54	-1	36	44	72	78	25	-3	1	-62	23	-96	77	58	36	-22	38	8	14	-72	42				
	6				28	54		72	23		36		84	106	25	27	0	0	0	0	32	90	16	68	41	40	57	25	67	65	19						
					-38	54		-82	-30		-41		-76	104	-19	24	-15	-11	-14	13	-36	-78	2	62	-35	38	-60	-29	-51	-58	-16						
	8												34	36	26	0	34	25		105	38	35	26	20	22	0											
													22	31	19	-4	30	26		-103	33	28	20	17	20	4											
5	1					0	23	47	31	0	17	67	0	44	64	81	72	98	50	19	44	89	43	146	19	47	35	0	38	88	28	77	19	27	24	20	
						9	-22	-55	-31	-12	-18	68	-18	56	-62	-73	-73	97	-62	15	50	76	42	-148	20	48	26	-15	31	75	26	-70	16	19	30	28	
	3			32	22	65	0	0	0	44	32	47	46	76	71	19	62	70	80	28	51	29	0	29	0	0	17	87	28	120	51	17	50	15			
				51	38	-63	10	9	0	43	31	44	39	-77	43	19	59	58	-81	29	-52	-27	-16	34	-5	-20	-18	81	-20	-127	-43	8	-50	-14			
	5					22	32		27	73	0	89		51	53	0	26	0	31	38	39	21	31	0	0	46	12	52	29	0	20	15					
						26	-45		-30	78	-5	-85		46	-46	11	37	9	28	-36	34	-20	27	6	-0	42	8	-47	26	0	35	9					
	7													24		53	28	74	33	24	25	17	26	27	21												
														-14		46	-24	-63	-32	24	-19	-13	-21	18	-24												
6	0						53		43	0	36	40	14	62	0	58	41	0	63	104	0																
							-49		-40	12	-38	-40	18	65	-8	40	-40	-3	-52	-93	8																
	2						30	0	17	55	52	33	23	23	0	0	0	87	94	76	53	17	50	0	15	87	59	40	21	11	19	18					
							39	6	16	-62	48	28	26	15	11	13	-8	-86	74	-70	52	-22	39	9	18	68	47	-30	20	2	13	-7					
	4									41	22	0	0	0	43	68	14	22	37	0	23	0	75	75	30	36	29	9	15	28							
										42	-15	4	-3	10	-34	-69	-11	-14	-26	9	-19	-6	-58	64	-22	-29	-23	-9	-15	-21							
	6																	0			0			7		0											
																		6			7			-20		4											
7	1											0		22	73	62	16	21	0	37	23	21	52	28	0	0	0	21									
												-4		-30	72	62	-14	-12	1	-30	-19	-19	-33	18	-1	-8	-5	-29									
	3																15	0	45	20	0	43		0		0											
																	-15	2	43	-23	-4	49		4		-10											

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 *h0l* data for the $MgSO_4.6H_2O$ and $MgSeO_4.6H_2O$ are 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, $\frac{1}{2}+C$ centering.

4(*e*) 0, *y*, $\frac{1}{4}$; 0, $-y$, $\frac{3}{4}+C$ centering.

Table 4. *Atomic parameters for* $CoSO_4.6H_2O$

		x	y	z	B
Co_1		0	0	0	3·3 Å^2
Co_2		0	0·949 ± 0·001	$\frac{1}{4}$	3·0
S		0·868 ± 0·001	0·452 ± 0·001	0·1244 ± 0·0003	2·2
O_1	Sulfate oxygens	0·778 ± 0·001	0·601 ± 0·002	0·1352 ± 0·0006	2·6
O_2		0·980 ± 0·002	0·446 ± 0·003	0·1695 ± 0·0007	3·9
O_3		0·918 ± 0·002	0·492 ± 0·003	0·0698 ± 0·0007	3·9
O_4		0·799 ± 0·001	0·276 ± 0·002	0·1193 ± 0·0006	2·9
O_5	Water octahedra about Co_1	0·592 ± 0·001	0·723 ± 0·002	0·0469 ± 0·0006	2·8
O_6		0·535 ± 0·002	0·325 ± 0·002	0·0673 ± 0·0006	3·2
O_7		0·305 ± 0·002	0·557 ± 0·003	0·0216 ± 0·0006	3·3
O_8	Water octahedra about Co_2	0·885 ± 0·002	0·159 ± 0·002	0·2823 ± 0·0007	2·3
O_9		0·886 ± 0·002	0·740 ± 0·002	0·2832 ± 0·0007	2·7
O_{10}		0·858 ± 0·001	0·949 ± 0·003	0·1771 ± 0·0006	3·3

Table 5. *Interatomic distances in* $CoSO_4.6H_2O$

Standard deviations are about ± 0·03 Å

	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*	1·44*	1·51*	1·45*						
O_1		2·36	2·40	2·40	2·77†			2·79†		2·79†
O_2	2·36		2·43	2·37				2·65†	2·69†	
O_3	2·40	2·43		2·40	2·72†	2·68†	2·93†			
O_4	2·40	2·37	2·40			2·78†	2·86†			2·76†
O_5	2·77†		2·72†			2·89 2·99	2·90 3·10			
O_6			2·68†	2·78†	2·89 2·99		2·94 2·99			
O_7			2·93†	2·86†	2·90 3·10	2·94 2·99				
O_8	2·79†	2·65†						2·97	3·00† 3·03	2·94 3·04
O_9		2·69†						3·00† 3·03	2·99	2·96 3·03
O_{10}	2·79†			2·76†				2·94 3·04	2·96 3·03	

* S–O bond in SO_4^{--}. † Hydrogen bond distances.

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

$$8(f)\quad x,y,z;\ -x,-y,-z;\ -x,y,\tfrac{1}{2}-z;\ x,-y,\tfrac{1}{2}+z+C \text{ centering.}$$

A Fourier projection of the $h0l$ 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.

Least squares refinement utilizing the full matrix (Busing & Levy, 1959) was performed for a total of 13 cycles on the IBM 704 computer. Atomic form factors of Co^{++} (Watson & Freeman, 1961), neutral S (Tomiie & Stam, 1958), and neutral O (Hartree & 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 the zero layer of 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 $R=\Sigma||F_o|-|F_c||\times 100/\Sigma|F_o|$, 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:

$$R \text{ (including zeros)} = 13{\cdot}0\%\,.$$
$$R \text{ (omitting zeros)} = 10{\cdot}9\%\,.$$

The data from the [101] setting are shown in Table 3.

The atomic parameters are shown in Table 4. By an oversight the dispersion correction $\Delta f'$ of about $-1{\cdot}8$ 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.

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.

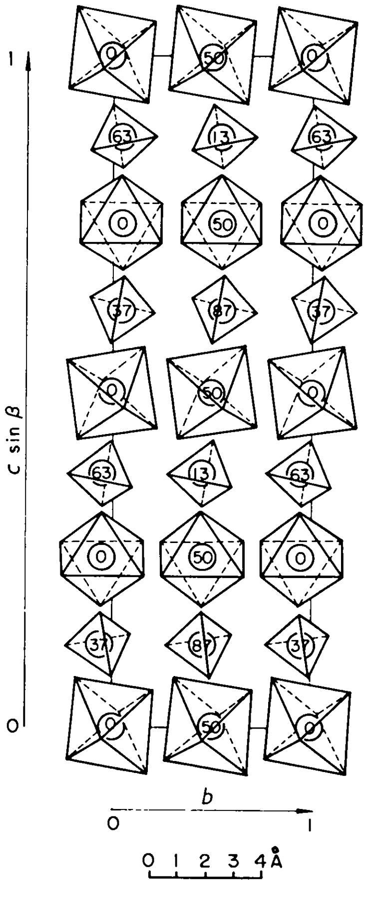

Fig. 1. Packing of SO_4^{--} tetrahedra and $Co(H_2O)_6^{++}$ octahedra. The encircled numbers are the parameters of the Co and S atoms in the a direction.

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 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 Å for the bonds to sulfate and 3·00 Å for the water–water

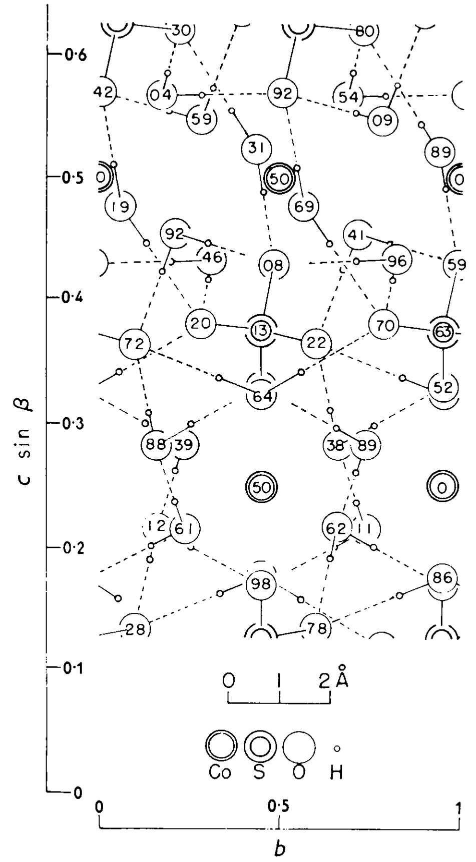

Fig. 2. Hydrogen bond network in $CoSO_4 . 6H_2O$. The numbers are the parameters along the a axis of the Co, S, and O atoms. The complete environment about each of the two different $Co(H_2O)_6^{++}$ and SO_4^{--} is shown.

bond. The shortest non-bonded oxygen–oxygen distances other than edges of the octahedra, are 3·13 Å between O_7 pairs (through a center of symmetry) and 3·22 Å 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 Å
O–O(SO_4^{--})	2·39 Å
Co–O($Co(H_2O)_6^{++}$)	2·11 Å
O–H–O (hydrogen bond)	2·79 Å

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 & 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.

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The Crystal Structure of $Ce_{24}Co_{11}$*

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The structure of $Ce_{24}Co_{11}$, the most cerium-rich compound in the Ce–Co system, has been determined by single crystal X-ray methods. The compound is hexagonal, space group $P6_3mc$ with $a = 9{\cdot}587$ and $c = 21{\cdot}825$ Å, $Z = 2$. The structure was solved by applying Buerger's minimum function. Nearly all of the Ce atoms have rather close Co neighbors, some Ce–Co distances being as short as 2·61 Å.

Introduction

Vogel (1947), in a study of the cerium–cobalt phase diagram, reported Ce_3Co as the most cerium rich compound in the system. Coffinberry (1960) prepared alloys of this composition but was unable to obtain a single phase, excess cerium always being present. In fact, alloys containing as much as 30 at.% cobalt contained a small amount of excess cerium. It was not possible to establish the exact formula of this cerium rich compound by using metallographic techniques although it was known that the composition was approximately 30 at.% cobalt.

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