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The Crystal Structure of Strontium Hydroxide Octahydrate, $Sr(OH)_2.8H_2O$*

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Strontium hydroxide octahydrate, $Sr(OH)_2.8H_2O$, is tetragonal and $a_0 = 9{\cdot}00\pm0{\cdot}01$, $c_0 = 11{\cdot}58 \pm0{\cdot}01$ Å. The space group is D_{4h}^8–$P4/ncc$ with four molecules per unit cell. The oxygen atoms of the water molecules occupy two sixteenfold sets of general positions related by a translation $\frac{1}{2}, \frac{1}{2}, 0$. Each oxygen atom is hydrogen bonded to at least three other oxygen atoms, using all 72 hydrogens in hydrogen-bond formation. It is impossible to determine whether the strontiums are in the set 0, 0, 0 or 0, 0, $\frac{1}{4}$ by X-ray diffraction data alone. An argument is presented for placing the strontiums in the set 0, 0, $\frac{1}{4}$, which results in a square Archimedean antiprism coordination of water molecules.

Introduction

In connection with the kinetics studies of the reaction of water vapor with strontium metal by H. J. Svec and D. S. Gibbs of this laboratory, powder photographs were taken to determine what hydrates of $Sr(OH)_2$ were formed. It became apparent that previous reports of the structure of the octahydrate of strontium hydroxide were questionable, and a complete structure determination seemed of interest since little work has been reported on the structures of hydrated hydroxides, particularly the higher hydrates.

The crystal structure of $Sr(OH)_2.8H_2O$ was first examined by Natta (1928). The space group was given as D_{4h}^1–$P4/mmm$ and the lattice dimensions were $a_0 = 6{\cdot}41$, $c_0 = 5{\cdot}807$ kX. with one molecule per unit cell. Each strontium atom was surrounded equidistantly by eight water molecules placed at the corners of a cube. Mellor (1938) reinvestigated the crystal structure and reported the space group as D_{4h}^2–$P4/mcc$ with the lattice dimensions $a_0 = 8{\cdot}97$, $c_0 = 11{\cdot}55$ kX., but did not determine the atomic positions.

Experimental data

The majority of the crystals appeared to be truncated tetragonal bipyramids, $\{hhl\}$, while a few were tetragonal prisms. Although they were not very stable in air, their stability was sufficiently prolonged to obtain X-ray diffraction data by coating them with Canada balsam. The crystals used were rotated about the [001] and [110] axes. Precession photographs using Mo $K\alpha$ radiation were obtained about the three principal axes from which the unit-cell dimensions were calculated. All of the intensity data were obtained from Weissenberg photographs using Cu $K\alpha$ radiation. Timed exposures were taken for zero-level data with a G. E. XRD–3 unit with stabilized current and voltage, and the multiple-film technique was used for the higher levels.

Unit cell and space group

The lattice constants of $Sr(OH)_2.8H_2O$ are

$$a_0 = 9{\cdot}00\pm0{\cdot}01,\ c_0 = 11{\cdot}58\pm0{\cdot}01\ \text{Å}\ .$$

The calculated density is 1·88 g.cm.$^{-3}$ with four molecules per unit cell, in agreement with previously reported densities. These axial directions are the same as those chosen by Mellor (1938).

In the space-group determination, the following systematic absences were noted:

$$\begin{array}{lll} (hk0) & \text{with} & h+k \neq 2n \\ (0kl) & \text{with} & l \neq 2n \\ (hhl) & \text{with} & l \neq 2n\ . \end{array}$$

In addition, all (hkl) reflections where $h+k \neq 2n$ were absent except for $l = 4n$, and these were very weak. These observations differ from those of Mellor (1938) in that he did not report those reflections $h+k \neq 2n$, $l = 0$ as being absent. Purposely over-exposed photographs did not indicate that any of the above reflections were present. It is concluded, then, that the correct space group is D_{4h}^8–$P4/ncc$ and not D_{4h}^2–$P4/mcc$. The origin of the unit cell was chosen to conform to that given in *Internationale Tabellen* (1935).

Determination of the approximate structure

Since there are only four molecules per unit cell, the strontium atoms must occupy fourfold special positions and the hydroxyl groups are either in fourfold or eightfold special positions. The water molecules may be in fourfold and eightfold special positions, or in sixteenfold general positions. (In referring to the hydroxyl groups and water molecules the oxygen atoms

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associated with these units are meant, as the hydrogen atoms are neglected completely.)

The strontium atoms must be in the set 4(a) 0, 0, 0; 0, 0, $\frac{1}{2}$; $\frac{1}{2}$, $\frac{1}{2}$, 0; $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$; 4(b) $\pm 0, 0, \frac{1}{4}$; $\pm\frac{1}{2}, \frac{1}{2}, \frac{1}{4}$; or 4($c$) $0, \frac{1}{2}, z$; $\frac{1}{2}, 0, \bar{z}$; $0, \frac{1}{2}, \frac{1}{2}+z$; $\frac{1}{2}, 0, \frac{1}{2}-z$ with $z = 0$ or $\frac{1}{4}$, owing to the fact that reflections for $h+k \neq 2n$ are either absent or very weak.

Since all reflections where $h+k \neq 2n$, $l \neq 4n$ are absent, the 32 water molecules must occupy two sets of sixteenfold general positions with parameter values x_1, y_1, z_1 and $x_1, y_1, \bar{z}_1$. As the latter set produces the equivalent position $\frac{1}{2}+x_1, \frac{1}{2}+y_1, z_1$, the water molecules are in C-centered positions and the abovementioned weak reflections are due only to hydroxyl groups.

To explain the very weak reflections with $h+k \neq 2n$, $l = 4n$, four hydroxyl groups must be in 4(c), where $z \neq 0$ or $\frac{1}{4}$. To explain the absence of reflections for $h+k \neq 2n$, $l = 4n+2$, the remaining four hydroxyl groups must also be in 4(c) and the z parameters of the two sets differ by exactly $\frac{1}{4}$. Also, z cannot be 0, $\frac{1}{8}$, or some integral multiple thereof.

But if both strontium and the hydroxyl groups are in 4(c) there should be two prominent Sr–OH vector peaks on the c axis. No such peaks were observed. Besides, steric considerations rule out the possibility of placing this many atoms in the set 4(c). Therefore one must conclude that the strontium atoms are in 4(a) or 4(b).

On the (001) Patterson projection, only two crystallographically different vector peaks appear besides the peak at the origin. The two peaks at $x = 0$, $y = \frac{1}{2}$ and $x = 0.092$, $y = 0.225$ are interpreted as follows: the former peak is due to two fourfold sets of hydroxyl groups with the same x and y parameters while the latter is due to two sixteenfold sets of water molecules with the same x and y parameters.

Approximate z parameters may be obtained from the (110) Patterson projection. Corresponding to the set of water molecules at $x_1 = 0.092$, $y_1 = 0.225$, there is a Sr–H_2O vector peak at $z \cong 0.125$. At the position $(x+y) = 0.250$ there is a Sr–(OH) vector peak at $z \cong 0.125$ which corresponds to the overlap of the hydroxyl positions $0, \frac{1}{2}, z_2$ and $\frac{1}{2}, 0, \frac{1}{4}-z_2$.

Rotation photographs about the [110] axis yield alternately strong and very weak layer lines. (It is presumed that these weak reflections were not observed by Natta (1928) when he chose a smaller unit cell.) These odd layers contain only $h+k \neq 2n$ indices and are due solely to hydroxyl contributions. Since there is only one parameter to determine, it is possible to obtain its approximate value by visual inspection. The three reflections (674), (568) and (2,3,12) have about the same Lorentz-polarization and scattering factors and their intensities are proportional to $\sin^2(2\pi l z)$. Since the intensity of the (2,3,12) reflection is greater than (674) but less than (568), the z_2 parameter is 0.097 ± 0.003.

Structure factors were calculated for the ($hk0$) and (hhl) reflections and compared with the observed values, with very good agreement. For these calculations strontium was assumed to be in the set $0, 0, \frac{1}{4}$, although the magnitude of the calculated structure factors are the same as those for the set 0, 0, 0.

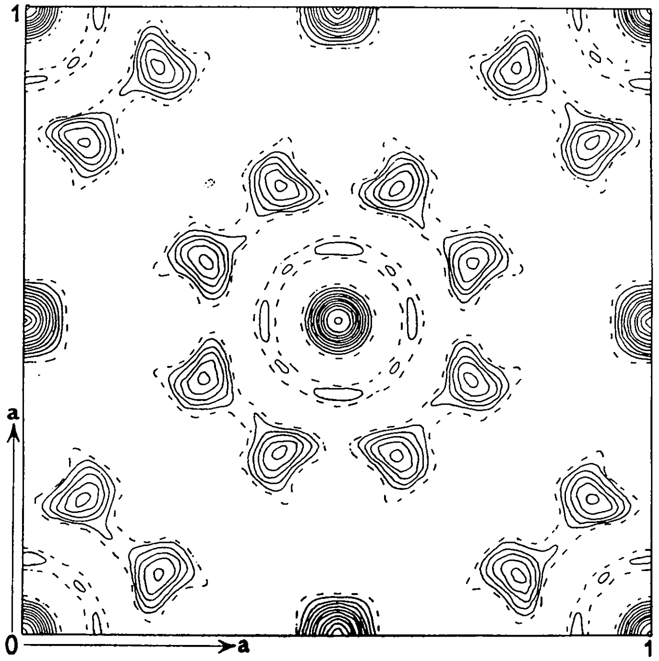

Fig. 1. Electron density projection onto (001). The contour lines are drawn at equal intervals on an arbitrary scale except for the strontium atoms at 0, 0 and $\frac{1}{2}$, $\frac{1}{2}$ where the intervals are five times as large. The broken lines represent the zero contour lines.

Fourier projections were then made onto the (001) and (110) planes. The resulting parameters differed only slightly from those given above.

Refinement of parameters

The first stage in refining the atomic positions was to compare synthetic two-dimensional Fourier projections, using the calculated structure factors, with the F_o Fourier projections. From the F_c projections one can obtain the series-termination errors (Booth, 1946) inherent in a Fourier analysis where the intensities of the unrecorded higher-order reflections are too large to be neglected. The magnitudes of these errors were as high as 0·05 Å for some of the peaks. These corrections were then applied to the corresponding maxima on the F_o projections. This was possible only for the water molecule positions as there was considerable overlap of the hydroxyl positions in the z direction. The water molecule positions were obtained by averaging the positions of two equivalent peaks, and the probable errors were taken as one-half the difference of the corresponding positions. The x, y, z coordinates of the water molecules determined by this method are $x_1 = 0{\cdot}097 \pm 0{\cdot}003$, $y_1 = 0{\cdot}219 \pm 0{\cdot}003$ and $z_1 = 0{\cdot}122_5 \pm 0{\cdot}000_8$. The x and y probable errors correspond to about 0·03 Å.

The x_1 and y_1 parameters were also determined graphically from (hkl) data as the strontium and hydroxyl contributions are zero for $l \neq 2n$. This was accomplished by fixing the x parameter and varying y until the best agreement was obtained between calculated and observed structure factors. This procedure was repeated for several values of x. The parameters determined by this method are $x_1 = 0{\cdot}093$, $y_1 = 0{\cdot}221$. It was difficult to estimate reliable limits of error since only 13 reflections were used in the determination.

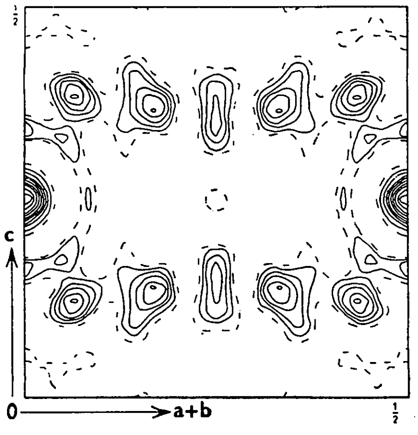

Fig. 2. Electron density projection onto (110). The contour lines are drawn on the same scale as Fig. 1.

Structure factors were calculated for $(hk2)$ data, assuming the intensities are due only to the strontium contributions, and were compared with the observed structure factors. For this set of data the index of reliability, R, is 0·108 where $R = \Sigma||F_o| - |F_c|| \div \Sigma|F_o|$. This close agreement indicates that the z_1 parameter of the water molecules is 0·125 or very nearly so.

It is desirable to know the atomic positions with greater precision than is given by the above methods and also to have more reliable values of the errors involved. Since the only x, y parameters that have to be determined are those of the water molecules, it was thought that a least-squares treatment of the $(hk0)$ data would give the best possible results. The observational equation given by Hughes (1941) was used to obtain the least-squares normal equations. The assumed parameters were $x_1 = 0{\cdot}093$, $y_1 = 0{\cdot}221$, $z_1 = 0{\cdot}125$, $z_2 = 0{\cdot}097$. The weighting factor w was chosen as follows: $w_{hk0} = 1/F_o^2$ for $F_o \geqq 4F_{\text{min.}}$ and $w_{hk0} = F_o^2/256F_{\text{min.}}^4$ for $F_o \leqq 4F_{\text{min.}}$. The resulting corrections to be applied and their standard errors of deviation are $\Delta x_1 = 0{\cdot}003 \pm 0{\cdot}002$, $\Delta y_1 = 0{\cdot}002 \pm 0{\cdot}002$. Using the results obtained above, the z parameters of the oxygen atoms were also calculated by least squares from (hhl) data with the following results: $\Delta z_1 = 0{\cdot}000_6 \pm 0{\cdot}001$ and $\Delta z_2 = 0{\cdot}004 \pm 0{\cdot}003$. Since the reflections where $h+k \neq 2n$ are due only to the z_2 parameter, it was felt that a more accurate value could be obtained by a least-squares treatment of these data. The calculated correction is $\Delta z_2 = -0{\cdot}001 \pm 0{\cdot}001$. The final atomic positions of $Sr(OH)_2.8H_2O$ are given in Table 1 and the interatomic distances between nearest neighbors are given in Table 2.

Structure factors were calculated using the final positions and compared with the observed values. These are listed in Table 3. It has been mentioned previously that all reflections of the type $h+k \neq 2n$, $l \neq 4n$ are absent. The calculated structure factors for these indices are identically zero and, therefore, are not listed. The over-all index of reliability, R, is 0·117. The combined absorption and temperature factors were considered negligible and were not applied to the reported structure factors. This assumption was based

Table 1. *Final positions in* $Sr(OH)_2.8H_2O$

	x	y	z
4 Sr:	0·000	0·000	0·250
4(OH):	0·000	0·500	0·096 ±0·001
4(OH):	0·000	0·500	0·346 ±0·001
16(H_2O):	0·096±0·002	0·219±0·002	$0{\cdot}124_4 \pm 0{\cdot}001$
16(H_2O):	0·096±0·002	0·219±0·002	$0{\cdot}875_6 \pm 0{\cdot}001$

Table 2. *Interatomic distances between nearest neighbors*

$Sr–H_2O$	2·60±0·03 Å
$H_2O–H_2O^1$	2·88±0·02
$H_2O–H_2O^2$	2·82±0·06
$H_2O–H_2O^3$	3·04±0·03
$H_2O–H_2O^4$	3·28±0·03
H_2O–OH	2·70±0·03
OH–OH	2·90±0·02

1—distance between x_1, y_1, z_1 and $x_1, y_1, \bar{z}_1$.
2—distance between x_1, y_1, z_1 and $\frac{1}{2}-x_1, \frac{1}{2}-y_1, z_1$.
3—distance between x_1, y_1, z_1 and $y_1, \bar{x}_1, z_1$.
4—distance between x_1, y_1, z_1 and $y_1, x_1, \frac{1}{2}-z_1$.

on the results obtained by applying an absorption correction ($\mu r = 1{\cdot}1$) using Bradley's data (1935) and also an empirically determined temperature correction ($\exp[-0{\cdot}63 \sin^2\theta/\lambda^2]$) to the ($hk0$) data. The two factors cancelled each other within 2%, which is much less than the experimental errors encountered in the visual estimation of intensities. It was assumed that this holds true for the higher-level data and the low over-all R factor appears to substantiate this assumption.

Discussion of the structure

The crystal structure of $Sr(OH)_2.8H_2O$ has been shown to be based on a primitive tetragonal lattice. The space group is D_{4h}^8–$P4/ncc$ and there are four molecules per unit cell. The strontium atoms are in C-centered positions and since the two sixteenfold sets of water molecules occupy the general positions x_1, y_1, z_1 and $x_1, y_1, \bar{z}_1$, they also are in C-centered positions. The twofold sets of hydroxyl groups are in the special positions $0, \frac{1}{2}, z_2$ and $0, \frac{1}{2}, z_2+\frac{1}{4}$, where $z_2 = 0{\cdot}096$. If the z_2 parameter was either $0{\cdot}000$ or $0{\cdot}125$ the hydroxyl groups would be in C-centered positions and the space group would be D_{4h}^2–$C4/mcc$. A primitive tetragonal unit cell could then be chosen by a rotation of 45° about the c_0 axis and the resulting space group would be D_{4h}^2–$P4/mcc$ with two molecules per unit cell.

Table 3. *Comparison of observed and calculated structure factors**

hkl	F_c	F_o
200	135	125
400	149	166
600	46	52
800	103	87
10,0,0	125	114
110	111	101
310	26	28
510	101	113
710	19	36
910	89	99
11,1,0	39	34
220	113	109
420	211	206
620	153	162
820	99	88
10,2,0	60	68
330	91	122
530	87	89
730	81	74
930	37	48
11,3,0	41	47
440	60	62
640	89	89
840	83	95
10,4,0	92	87
550	−17	11
750	72	88
950	40	51
660	121	119
860	83	80
770	83	82
970	19	29
880	77	72
311	−92	93
511	9	< 9
711	25	18
911	18	20
11,1,1	− 1	0
421	−46	47
621	40	40
821	−16	18
10,2,1	21	23
531	27	32
731	−29	35
931	−18	18
11,3,1	16	10
641	10	<11
841	−34	32
10,4,1	9	<10
751	12	11
951	9	<11
861	30	27
971	0	0
202	−129	98
402	−109	93
602	−91	97
802	−78	79
10,0,2	−69	72
112	−134	89
312	−117	96
512	−99	92
712	−83	88
912	−73	79
11,1,2	−64	65
222	−121	94
422	−104	91
622	−89	90
822	−76	79
10,2,2	−68	72
332	−106	87
532	−92	88
732	−80	85
932	−71	79
11,3,2	−62	54
442	−94	94
642	−82	88
842	−73	80
10,4,2	−65	65
552	−83	88
752	−75	70
952	−67	70
662	−75	70
862	−69	72
772	−69	74
972	−62	54
882	−63	59
104	31	34
204	130	113
304	24	31
404	79	74
504	18	27
604	134	130
704	13	16
804	58	72
904	10	12
10,0,4	28	39
11,0,4	9	5
114	125	106
214	−27	35
314	172	140
414	−21	25
514	85	87
614	−15	23
714	134	120
814	−11	14
914	53	63
10,1,4	− 9	10
11,1,4	85	83
224	131	122
324	22	29
424	16	31
524	17	25
624	35	45
724	13	17
824	54	76
924	10	12
10,2,4	77	89
334	107	113
434	−17	27
534	88	96
634	−13	20
734	73	83
834	−11	14
934	99	93
10,3,4	− 9	7
444	128	136
544	14	23
644	78	80
744	11	16
844	57	80

Table 3 (*cont.*)

hkl	F_c	F_o
944	10	8
10,4,4	42	45
554	166	144
654	−12	13
754	66	82
854	−10	11
954	89	93
664	36	48
764	10	12
864	58	75
964	9	7
774	51	71
874	−9	9
002	−139	110
004	−100	98
006	−108	90
008	207	180
0,0,10	−77	88
0,0,12	13	30
0,0,14	−68	74
116	−104	93
118	103	92
1,1,10	−78	89
1,1,12	53	66
1,1,14	−65	70
226	−96	83
228	57	59
2,2,10	−78	90
2,2,12	100	80
2,2,14	−63	70
336	−91	92
338	89	88
3,3,10	−74	88
3,3,12	52	63
446	−82	87
448	39	52
4,4,10	−72	81
4,4,12	103	91
556	−75	89
558	14	29
5,5,10	−68	83
666	−71	80
668	89	96
6,6,10	−63	66
776	−65	71
018	25	25
128	−24	24
238	21	22
348	−19	19
458	17	16
568	−15	14
678	14	11
0,1,12	−13	14
1,2,12	13	14
2,3,12	−12	12
3,4,12	12	12
4,5,12	−11	9

* F_c and F_o are zero for the general (*hkl*) reflections where $h+k \neq 2n$, $l \neq 4n$. (These are not space group absences.)

Four of the water molecules at $z = 0{\cdot}125$ and four at $z = -0{\cdot}125$ are at the corners of a cube (approximately) with the origin as the center. Similarly, the water molecules at $z = 0{\cdot}375$ and $z = -0{\cdot}375$ are at the corners of a cube with the point 0, 0, $\frac{1}{2}$ as the center; however, this cubic arrangement is rotated 45° about the c_0 axis with respect to the arrangement at the origin to form square Archemidean antiprism configurations of water molecules whose centers are at 0, 0, $\frac{1}{4}$ and 0, 0, $\frac{3}{4}$. A similar arrangement occurs again in the unit cell owing to a translation of the water molecules by $\frac{1}{2}$, $\frac{1}{2}$, 0.

The hydroxyl groups form continuous chains throughout the crystal separated by the distance $\frac{1}{4}c_0$. Each hydroxyl group is surrounded octahedrally by four water molecules and two hydroxyl groups.

It has been stated previously that the strontium atoms are either in the set of positions 0, 0, 0 or 0, 0, $\frac{1}{4}$. In the set 0, 0, 0 the atoms are at the center of a cube, whereas, in the set 0, 0, $\frac{1}{4}$, they are at the center of a square antiprism. The two structures represent another example of the so-called 'Patterson ambiguities', in that it is impossible to determine which is the correct set by X-ray diffraction data alone since the calculated intensities are the same in both cases. It is important to note that the ambiguity depends on the z parameters of the hydroxyl groups being different by exactly $\frac{1}{4}$ and on the z parameters of the water molecules being exactly $\pm\frac{1}{8}$, as they very nearly are.

The choice of the set 0, 0, $\frac{1}{4}$ was influenced partly by the probable arrangement of the hydrogen atoms. The infra-red spectrum of a mull of the crystals in hexachlorobutadiene exhibits several O–H peaks in the region 3300 cm.$^{-1}$. According to the curve published by Rundle & Parasol (1952), which relates the O · · · H—O distances to the O–H stretching frequencies, there are O · · · H—O distances which lie between 2·7 and 2·9 Å. It is therefore assumed that all the oxygen atoms within 2·9 Å of each other are hydrogen bonded while O–O distances greater than 2·9 Å are not hydrogen bonded. This assumption is substantiated by the fact that all 72 hydrogen atoms would then be used in hydrogen-bond formation. On this basis, then, if strontium is at the origin, the hydrogen atoms bonding the oxygen atoms x_1, y_1, z_1 and $x_1, y_1, \bar{z}_1$ would be directed toward the positive metal ions, which does not seem as likely as the assumed arrangement where they are directed away from the positive ions. Pauling (Mellor, 1938) suggested that the square antiprism configuration would be more stable than the cubic arrangement.

Shineman & King (1951) have reported preliminary

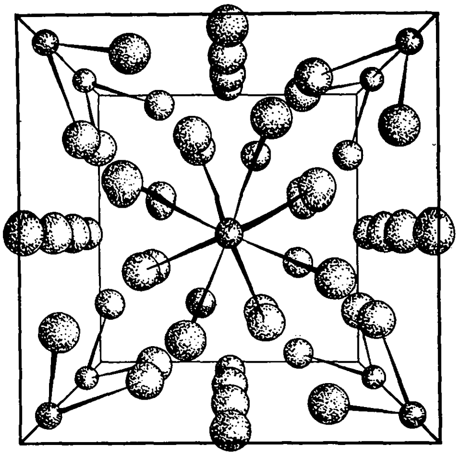

Fig. 3. Perspective view of the structure of $Sr(OH)_2 \cdot 8\,H_2O$ looking down the fourfold axis.

results of their investigation of the structure of calcium peroxide octahydrate, which is isomorphous with strontium and barium peroxide octahydrate. Their proposed structure of $CaO_2.8H_2O$ is quite similar to that of $Sr(OH)_2.8H_2O$, the main difference being the arrangement of the oxygen ions in the c_0 direction. They have reported that the calculated structure factors based on the square antiprism configuration of water molecules about the positive metal ion gave slightly better agreement with the observed structure factors than those based on the cubic arrangement.

From the above discussion it is concluded that the correct set of strontium positions is the set $0, 0, \frac{1}{4}$.

The author wishes to express his sincere appreciation to Dr R. E. Rundle for his many helpful discussions during the course of this investigation. He wishes to thank Mr D. S. Gibbs for growing the single crystals of $Sr(OH)_2.8H_2O$ and making a hydrate analysis of the compound, and Mr Marvin Margoshes for supplying the infra-red spectrum of the compound.

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The Crystal Structures of Nickel Acetate, $Ni(CH_3COO)_2.4H_2O$, and Cobalt Acetate, $Co(CH_3COO)_2.4H_2O$

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Crystals of nickel acetate, $Ni(CH_3COO)_2.4H_2O$, are monoclinic with space group $P2_1/c$. The unit cell, of dimensions $a = 4\cdot75$, $b = 11\cdot77$, $c = 8\cdot44$ Å, $\beta = 93° 36'$, contains two formula units. Projections of the structure on two crystallographic planes are given.

The unit cell dimensions of cobalt acetate, $Co(CH_3COO)_2.4H_2O$, are $a = 4\cdot77$, $b = 11\cdot85$, $c = 8\cdot42$ Å, $\beta = 94° 30'$. The space group is $P2_1/c$, and the unit cell contains two formula units. By analogy it is shown that the two compounds are isostructural.

In both cases the metal atoms are surrounded octahedrally by four water molecules and by two oxygen atoms which belong to two different acetate groups. It is shown that these octahedral bonds are probably ionic in character. In the structure the individual formula units are firmly linked by a three-dimensional network of hydrogen bonds.

Introduction

In three earlier communications the authors (van Niekerk & Schoening, 1953*a*, *b*; van Niekerk, Schoening & de Wet, 1953) have reported the existence of direct metal-to-metal bonds in the structures of cupric and chromous acetate. The unusual structural features of these two compounds have led to a systematic X-ray examination of the acetates of other transition elements of which the present investigation forms the first part. Although only the structure of nickel acetate is described in detail in this paper, it is shown that nickel and cobalt acetate are in fact isostructural so that the interatomic distances given for the former also apply to corresponding distances for the latter.

Crystal data

Crystals of nickel acetate, $Ni(CH_3COO)_2.4H_2O$, are monoclinic and emerald green in colour. The unit-cell dimensions, as determined from rotation and Weissenberg photographs, are:

a (Å)	b (Å)	c (Å)	β
4·75	11·77	8·44	93° 36′

These are in good agreement with the values $a = 4\cdot75$, $b = 11\cdot75$, $c = 8\cdot46$ Å and $\beta = 93° 34'$ previously obtained by Hull (1938).

Systematic extinctions occur for $h0l$ with l odd and for $0k0$ with k odd. The space group is therefore $P2_1/c$. The number of formula units (Z) in the unit cell is two.