Acta Cryst. (1964). **17**, 1051

The Crystal Structure of Hydrozincite, $Zn_5(OH)_6(CO_3)_2$

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(*Received* 24 *July* 1963)

Hydrozincite, $Zn_5(OH)_6(CO_3)_2$ is monoclinic with $a_0 = 13{\cdot}62$, $b_0 = 6{\cdot}30$, $c_0 = 5{\cdot}42$ Å, $\beta = 95° 50'$, space group $C2/m$, two formula units per cell. The structure has been determined from Patterson projections and refined by the least-squares method with partial three-dimensional intensity data.

The structure is composed of zinc in both octahedral and tetrahedral coordination, in the ratio 3:2. The octahedral zinc atoms form part of a $C6$ type sheet with holes, which are distributed on a rectangular $6{\cdot}3 \times 5{\cdot}4$ Å net. Zinc atoms in tetrahedral coordination occur above and below these holes. The complex sheets parallel to (100) are held together by CO_3 groups, occurring normal to the sheets. Two oxygen atoms of the CO_3 group are bonded to an octahedral and a tetrahedral zinc atom each, while the third oxygen atom is hydrogen bonded to three OH groups. The average tetrahedral Zn–O distance, 1·95 Å, is significantly smaller than the average octahedral Zn–O distance, 2·10 Å.

The $OH:CO_3$ ratio is variable in natural and synthetic samples, the CO_3-deficient phases being highly stacking-disordered. On the basis of this structure these phenomena are understandable, since missing carbonate groups will facilitate mistakes in the layer sequence.

Introduction

The existence of zinc in both octahedral and tetrahedral coordination in the same structure has been shown recently in several zinc compounds, namely, $Zn_2Mo_3O_8$ (McCarroll, Katz & Ward, 1957), $Zn_5(OH)_8Cl_2.H_2O$ (Nowacki & Silvermann, 1961), β zinc hydroxide 2,4-dinitrophenolate (Locchi, Bürki & Nowacki, 1961), and $Zn_2(OH)_2SO_4$ (Iitaka, Locchi & Oswald, 1962), γ $Zn_3(PO_4)_2$ (Calvo, 1963), $Zn_3(PO_4)_2.4H_2O$, hopeite (Liebau, 1963). Hydrozincite, $Zn_5(OH)_6(CO_3)_2$, provides yet another example of such a structure, where the octahedral to tetrahedral zinc ratio is 3:2.

A stacking-disordered phase of hydrozincite is the usual corrosion product of zinc in moist air. A thin coating of basic zinc carbonate thus formed protects the metal from further corrosion. Feitknecht (1959) attributed the good protecting property of basic zinc carbonate to its tendency to crystallize with a disordered layer structure. The stacking-ordered and -disordered phases of hydrozincite have been synthesized as very fine grained precipitates. In nature it occurs in the oxidation zone of ore deposits as an alteration product of zinc blende, usually as earthy masses, rarely as thin needle-shaped crystals.

The crystal data

The crystals used for the structure determination came from Goodsprings, Nevada (U.S.N.M. Cat. no. 91355). They are colorless transparent needles, very thin bladelike in shape, often tapering to a sharp point. The needles are elongated parallel to [001], the only well developed form being the pinacoid {100}. The cell dimensions, determined by Ramsdell (1947) from rotation and Weissenberg photographs on crystals from the same locality, are as follows:

Monoclinic,

$$a_0 = 13{\cdot}48,\ b_0 = 6{\cdot}32,\ c_0 = 5{\cdot}37\ \text{Å};\ \beta = 95°\ 30'.$$

More accurate cell dimensions of two hydrozincite specimens from Lafatsch, Bavaria, and Pinte Co., Utah, have recently been determined by Oswald (1963) from Guinier powder photographs taken with Fe $K\alpha$ radiation. These cell dimensions, which have been used in this paper, are:

$$a_0 = 13{\cdot}62,\ b_0 = 6{\cdot}30,\ c_0 = 5{\cdot}42\ \text{Å};\ \beta = 95°\ 50'.$$

Space group $C2/m$, $C2$ or Cm. Two formula units per cell.

$$D_x = 4{\cdot}01\ \text{g.cm}^{-3};\ D_m \sim 4{\cdot}0\ \text{g.cm}^{-3}.$$

The space group $C2/m$ was adopted for the following structure determination and was subsequently found to be correct.

Experimental

Multiple-film integrating Weissenberg photographs were taken of *hk*0, *hk*1, *hk*2, *hk*3 and *h*0*l* layers on a Nonius integrating type Weissenberg camera with Cu $K\alpha$ radiation. The intensities were measured by means of a Joyce Loebl double-beam microdensitometer. They were corrected for Lorentz and polarization factors, but no absorption corrections were made. The observed structure factors were put on an absolute basis in the course of the structure determination.

All the calculations were carried out on the Bull Gamma AET computer with the data reduction and structure factor programs written by Iitaka (1961) and the Fourier program by Bürki (1961), except the least-squares refinement which was done on the IBM 650 computer with the LS II program of Senko & Templeton (1957). The infrared spectra were recorded on a Perkin Elmer model 13 infrared spectrometer with a calcium fluoride prism, the Nujol mull technique being used.

The structure determination and refinement

Since the structure contains ten zinc atoms per unit cell, two of them must lie in a special position. They were arbitrarily placed at 2(*a*): 000, $\frac{1}{2}\frac{1}{2}0$. From analogy with the structure of pseudomalachite, $Cu_5(PO_4)_2(OH)_4$ (Ghose, 1963), where copper occurs in one twofold and two fourfold positions, it was expected that the rest of the zinc atoms in hydrozincite would occur also in two fourfold positions, namely 4(*g*): 0*y*0 *etc.*, 4(*h*): $0y\frac{1}{2}$ *etc.*, or 4(*i*): *x*0*z* *etc.* The presence of an octahedral chain, formed of one Zn(1) and two Zn(2) octahedra sharing four and three edges respectively, was suspected in the light of a similar chain found in pseudomalachite. From the [001] Patterson projection Zn(2) was immediately located at 4(*h*) with $y=0{\cdot}264$. The third zinc atom was found next in 4(*i*) with $x=0{\cdot}373$. The *R* index for the *hk*0 reflexions with the contributions of the zinc atoms only was 0·33. The [001] Fourier synthesis indicated the presence of a layer of zinc atoms parallel to (100), with some zinc atoms above and below the layer. The only unknown parameter of Zn(3), namely *z*, was readily found from the [010] Patterson projection. The *R* index for the *h*0*l* reflexions calculated with the zinc atoms alone was 0·30. Fourier and (F_o-F_{Zn}) Fourier syntheses of [001] and [010] projections clearly indicated the positions of the carbonate group and the OH ions. It is interesting to note here that since two Zn(2) atoms are exactly superposed on each other in the [010] projection owing to symmetry, the [010] Patterson projection looks almost exactly like the electron-density projection with the origin shifted to $00\frac{1}{2}$.

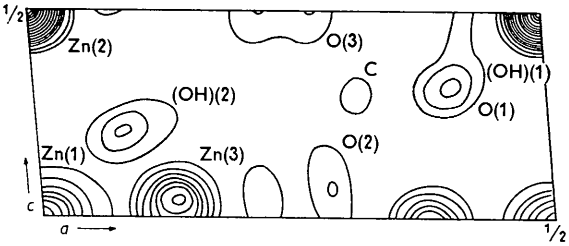

Fig. 1. Electron-density projection of hydrozincite, $Zn_5(OH)_6(CO_3)_2$ along [010]. Contour intervals at 4 e.Å^{-2}. Zero contour omitted.

Refinement of the two projections was carried out by difference Fourier syntheses till the *R* indices were 0·15 and 0·19 for *hk*0 and *h*0*l* reflexions respectively. The electron-density projection along *b* calculated at this stage is shown in Fig. 1. Four cycles of least-squares refinement were run for 284 observed *hkl* reflexions till *R* was reduced to 0·16, varying 16 positional, 9 thermal and 5 scale factor parameters. The refinement was terminated at this point, since the shifts in the atomic parameters were below the standard deviation. The rather high disagreement index may at least partially be attributed to the differential absorption effects not having been taken into account because of the very thin needle shape of the crystal used for the intensity measurements. The final positional and thermal atomic parameters are listed in Table 1. The scattering curves for Zn (corrected for dispersion), C and O, used for the structure factor calculations, have been taken from *International Tables for X-ray Crystallography* (1962). The estimated standard deviations of the bond distances are: Zn–Zn ±0·006 Å, Zn–O ±0·04 Å, C–O ±0·06 Å and O–O ±0·05 Å.

Table 1. *Atomic parameters of hydrozincite,* $Zn_5(OH)_6(CO_3)_2$

	x	*y*	*z*	*B*
Zn(1)	0	0	0	0·59 Å^2
Zn(2)	0	0·263	0·5	0·56
Zn(3)	0·129	0·5	0·038	0·67
C	0·322	0·5	0·309	0·90
O(1)	0·421	0·5	0·318	0·69
O(2)	0·266	0·5	0·069	1·00
O(3)	0·275	0·5	0·500	0·90
(OH)(1)	0·410	0	0·324	0·81
(OH)(2)	0·078	0·245	0·198	0·81

Description of the structure

The complex sheet structure

The structure of hydrozincite can be regarded as a variation of the hypothetical *C*6 type $Zn(OH)_2$ structure. If one quarter of the zinc atoms are removed from the octahedral sheet and one quarter of the OH ions are replaced by O, so that each filled Zn octahedron has common edges with four other filled and two unoccupied octahedra, the resulting $Zn_3(OH)_6O_2^{4-}$ sheet becomes negatively charged. To satisfy this charge, tetrahedral Zn atoms and CO_3 groups occur above and below the missing zinc positions, one oxygen atom of the carbonate group being a part of the $Zn_3(OH)_6O^{4-}$ sheet. The octahedral to tetrahedral zinc ratio in the sheet structure thus formed is 3:2.

The complex sheet structure can be described also in terms of coordination octahedra and tetrahedra around zinc. Chains composed of one $Zn(1)(OH)_4O_2$ octahedron and two $Zn(2)(OH)_4O_2$ octahedra sharing four and three edges alternately run parallel to [001]. These chains are joined together by sharing an

Table 2. *Observed and calculated structure factors of hydrozincite* $Zn_5(OH)_6(CO_3)_2$

h	*k*	*l*	F_o	F_c
2	0	0	120.7	146.9
4	0	0	31.5	43.1
6	0	0	47.2	44.4
8	0	0	153.1	151.6
10	0	0	105.7	88.5
12	0	0	59.3	67.2
14	0	0	92.5	93.4
16	0	0	65.9	74.1
1	1	0	15.1	- 9.1
3	1	0	106.5	84.4
5	1	0	127.9	128.9
7	1	0	61.2	- 62.0
11	1	0	51.8	55.9
13	1	0	48.4	54.9
15	1	0	16.2	- 24.3
0	2	0	145.9	115.2
2	2	0	132.1	- 108.2
4	2	0	110.5	- 100.2
6	2	0	37.9	- 39.8
8	2	0	34.1	45.1
10	2	0	28.7	- 39.3
12	2	0	83.9	- 63.4
14	2	0	13.0	- 14.0
3	3	0	110.3	97.4
5	3	0	139.8	126.7
7	3	0	22.6	- 24.6
9	3	0	16.2	19.7
11	3	0	66.0	63.3
13	3	0	58.1	59.6
0	4	0	284.1	265.8
2	4	0	104.8	93.0
4	4	0	26.2	27.0
6	4	0	44.9	42.5
8	4	0	93.7	109.0
10	4	0	58.9	63.1
12	4	0	43.0	49.0
14	4	0	60.4	71.5
1	5	0	24.5	- 24.4
3	5	0	40.2	35.8
5	5	0	44.0	51.5
7	5	0	37.8	- 51.1
11	5	0	25.4	27.8
13	5	0	23.5	29.1
0	6	0	44.2	51.0
2	6	0	32.9	- 40.2
4	6	0	47.8	- 51.3
8	6	0	15.1	26.5
10	6	0	14.9	- 19.6
3	7	0	56.0	58.9
5	7	0	54.5	71.6
0	8	0	68.4	106.9
1	1	1	38.4	29.4
3	1	1	143.2	131.4
5	1	1	80.8	76.0
11	1	1	63.6	73.1
13	1	1	29.7	33.6
0	2	1	203.6	181.4
2	2	1	205.2	173.7
4	2	1	129.9	107.9
6	2	1	173.3	166.3
8	2	1	180.3	131.9
14	2	1	71.6	88.2
16	2	1	51.3	88.2
3	3	1	101.5	85.9
5	3	1	54.0	44.0
7	3	1	29.8	- 29.2
11	3	1	38.1	46.4
15	3	1	18.4	- 27.2
0	4	1	36.2	27.2
2	4	1	57.3	- 39.5
4	4	1	112.9	- 93.9
10	4	1	35.6	- 46.4
12	4	1	36.2	- 40.4
1	5	1	35.4	30.3
3	5	1	103.7	92.1
5	5	1	69.0	60.6
9	5	1	18.4	26.1
11	5	1	56.8	61.7
13	5	1	21.2	34.1
0	6	1	102.5	93.1
2	6	1	82.5	75.4
4	6	1	50.9	44.4
6	6	1	83.7	84.6
8	6	1	63.8	73.6
3	7	1	37.8	31.8
7	7	1	19.4	- 24.0
- 1	1	1	49.5	- 54.7
- 3	1	1	127.0	132.9
- 5	1	1	92.3	100.3
- 11	1	1	71.8	82.5
- 13	1	1	60.5	53.0
- 2	2	1	58.9	54.6
- 4	2	1	16.3	7.0
- 6	2	1	98.6	111.6
- 8	2	1	153.4	218.8
- 10	2	1	85.7	107.8
- 16	2	1	68.5	73.6
- 1	3	1	88.6	- 67.1
- 3	3	1	84.7	74.2
- 5	3	1	75.7	59.6
- 7	3	1	25.2	- 27.1
- 11	3	1	51.8	56.6
- 2	4	1	31.1	- 23.4
- 4	4	1	88.4	- 76.0
- 6	4	1	38.1	- 32.6
- 8	4	1	32.5	34.5
- 10	4	1	32.3	- 29.3
- 12	4	1	72.4	- 61.3
- 3	5	1	99.1	92.1
- 5	5	1	78.2	79.6
- 11	5	1	68.7	65.7
- 13	5	1	47.6	47.3
- 2	6	1	41.7	37.6
- 6	6	1	45.7	56.0
- 8	6	1	88.4	115.9
- 10	6	1	80.6	60.4
- 1	7	1	46.4	- 42.4
- 3	7	1	20.9	21.7
1	1	2	21.1	19.1
3	1	2	96.8	95.3
5	1	2	55.9	65.4
7	1	2	63.6	- 67.6
9	1	2	48.1	50.8
11	1	2	46.4	53.5
13	1	2	15.3	25.8
0	2	2	66.0	60.2
2	2	2	104.7	- 105.7
4	2	2	79.1	- 73.8
6	2	2	18.1	- 9.8
10	2	2	40.4	- 54.0
12	2	2	53.4	- 61.8
14	2	2	20.2	19.4
1	3	2	55.7	42.2
3	3	2	100.4	105.6
5	3	2	62.4	72.8
7	3	2	31.0	- 39.4
9	3	2	42.7	57.5
11	3	2	54.0	60.8
13	3	2	36.4	35.6
0	4	2	134.6	124.4
4	4	2	44.6	40.2
6	4	2	109.7	118.4
8	4	2	90.8	137.4
10	4	2	45.1	46.9
12	4	2	5.8	4.3
3	5	2	49.5	43.2
0	6	2	30.0	30.9
2	6	2	50.4	- 49.1
4	6	2	42.1	- 38.1
1	7	2	41.9	31.1
3	7	2	82.1	65.4
5	7	2	31.5	45.8
- 1	1	2	51.4	- 57.4
- 3	1	2	68.3	73.4
- 5	1	2	87.2	102.8
- 13	1	2	55.5	58.9
- 2	2	2	18.3	- 15.2
- 4	2	2	83.3	- 80.3
- 6	2	2	80.6	- 90.0
- 8	2	2	43.8	38.1
- 10	2	2	33.4	- 33.2
- 12	2	2	56.6	- 53.8
- 1	3	2	26.8	- 20.3
- 3	3	2	99.5	80.7
- 5	3	2	112.7	104.2
- 11	3	2	43.2	42.5
- 13	3	2	73.2	65.9
- 2	4	2	145.1	111.8
- 4	4	2	105.7	86.6
- 6	4	2	82.7	73.8
- 8	4	2	108.7	130.1
- 10	4	2	36.8	35.3
- 14	4	2	53.4	46.0
- 1	5	2	61.5	- 49.2
- 3	5	2	36.6	28.2
- 5	5	2	61.7	49.0
- 7	5	2	38.5	- 12.4
- 9	5	2	19.8	- 19.9
- 4	6	2	54.9	- 42.5
- 6	6	2	34.7	- 42.8
- 3	7	2	54.7	49.9
- 5	7	2	58.3	60.5
1	1	3	52.6	51.2
3	1	3	84.1	96.2
5	1	3	35.8	44.5
11	1	3	59.0	70.4
0	2	3	156.7	202.9
2	2	3	66.7	65.0
6	2	3	83.4	101.2
8	2	3	73.0	82.8
10	2	3	60.7	58,1
12	2	3	43.8	58.7
1	3	3	31.0	23.4
3	3	3	60.3	61.5
7	3	3	25.1	- 40.9
11	3	3	44.2	51.7
2	4	3	59.4	- 52.1
4	4	3	56.3	- 60.9
10	4	3	28.4	- 38.3
1	5	3	50.3	44.5
3	5	3	75.7	76.2
5	5	3	41.4	43.7
0	6	3	113.8	106.2
2	6	3	36.6	31.8
6	6	3	41.4	57.7
- 1	1	3	30.8	- 39.4
- 3	1	3	58.5	67.1
- 5	1	3	73.4	93.6
- 7	1	3	43.2	38.9
- 9	1	3	41.4	- 45.6
- 11	1	3	42.1	52.7
- 2	2	3	187.5	193.8
- 4	2	3	36.2	34.2
- 8	2	3	67.6	98.3
- 10	2	3	74.3	81.6
- 12	2	3	62.2	58.7
- 14	2	3	33.2	46.1
- 1	3	3	59.0	- 49.2
- 3	3	3	62.2	37.0
- 5	3	3	86.7	60.5
- 11	3	3	36.8	32.9
- 13	3	3	50.9	39.0
- 4	4	3	113.8	- 80.9
- 6	4	3	63.5	- 47.5
- 3	5	3	73.4	52.8
- 5	5	3	96.9	75.2
- 7	5	3	43.2	39.1
- 11	5	3	44.5	47.1
- 2	6	3	112.7	100.5
0	0	1	48.8	32.9
2	0	1	94.9	- 59.0
4	0	1	148.2	- 147.0
10	0	1	63.7	- 64.4
12	0	1	67.1	- 54.7
0	0	2	244.8	177.8
2	0	2	40.7	- 26.9
4	0	2	73.4	61.7
6	0	2	142.9	170.3
8	0	2	135.2	192.7
10	0	2	58.5	64.5
14	0	2	63.9	69.5
2	0	3	89.7	- 73.5
4	0	3	111.1	- 87.5
12	0	3	49.7	- 41.9
0	0	4	189.7	138.2
2	0	4	106.9	75.8
4	0	4	93.1	88.0
6	0	4	98.9	125.7
8	0	4	41.7	56.9
12	0	4	25.5	34.2
2	0	5	55.0	- 57.0
4	0	5	43.8	- 49.6
10	0	5	32.1	- 39.2
0	0	6	71.5	82.8
6	0	6	39.6	66.2
- 2	0	1	58.3	- 44.3
- 4	0	1	127.9	- 108.6
- 6	0	1	40.2	- 51.5
- 8	0	1	30.0	45.5
- 10	0	1	34.8	- 44.7
- 12	0	1	84.3	- 82.1
- 16	0	1	22.6	30.9
- 2	0	2	180.9	165.7
- 4	0	2	160.7	149.3
- 6	0	2	112.1	110.1
- 8	0	2	120.7	182.7
- 10	0	2	30.6	47.0
- 14	0	2	44.6	59.7
- 16	0	2	80.5	94.1
- 4	0	3	114.5	- 118.2
- 6	0	3	66.2	- 68.8
- 12	0	3	23.9	- 42.0
- 14	0	3	44.9	- 50.8
- 2	0	4	110.7	84.5
- 4	0	4	40.4	30.7
- 6	0	4	41.9	27.7
- 8	0	4	106.3	140.9
- 10	0	4	75.7	118.8
- 2	0	5	49.5	46.1
- 4	0	5	45.1	- 45.4
- 6	0	5	50.3	- 63.5
- 2	0	6	113.8	117.3
- 4	0	6	50.9	52.7

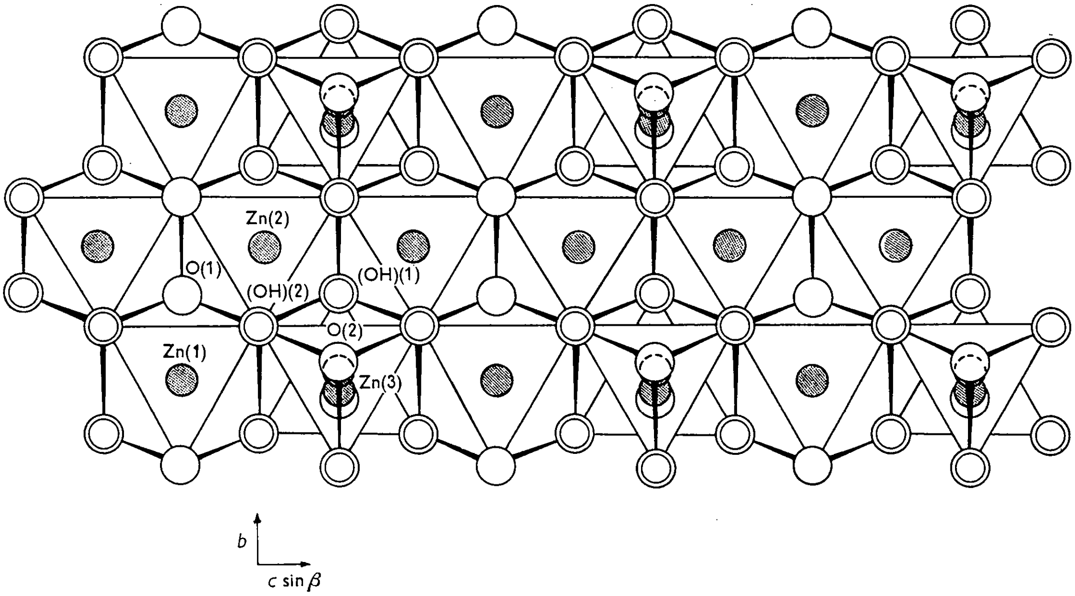

Fig. 2. A single oxy-hydroxy-zinc sheet of hydrozincite, $Zn_5(OH)_6(CO_3)_2$ viewed along [100].

octahedral edge to form a sheet with holes parallel to (100). These holes are distributed on a 6·3 × 5·4 Å rectangular net. Two $Zn(3)(OH)_3O$ tetrahedra, occurring above and below this sheet, join the octahedral chains further together by sharing a corner each of two Zn(1) octahedra occurring in neighboring chains and a common corner of two Zn(2) octahedra (Fig. 2). The fourth corner of the Zn(3) tetrahedron is shared by a carbonate group.

The bond distances and angles are listed in Table 3. The Zn(1) coordination octahedron is quite regular with an average Zn–OH (or O) distance 2·10 Å and (OH)(2)–Zn(1)–(OH)(2) (or O(1)) angle varying from 81·7° to 98·3°. In the Zn(2) octahedron, on the other hand, the Zn–O (or OH) distances range from 2·04 to 2·16 Å and (OH)–Zn(2)–(OH) (or O) angle varies from 79·6° to 95·7°. The tetrahedral Zn(3)–OH distances average 1·98 Å, while Zn(3)–O(2) is 1·85 Å. The significantly short Zn(3)–O(2) distance is reasonable, since O(2) has a charge deficiency of 1/6, assuming it gets a charge contribution of 2/4 from Zn(3) and 4/3 from C.

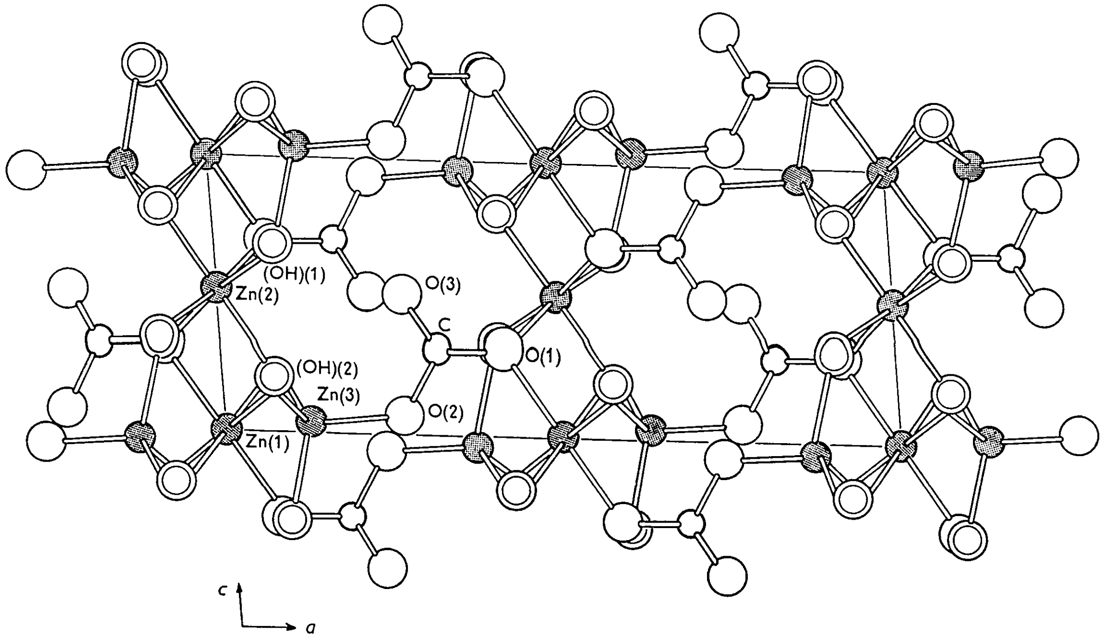

Fig. 3. Projection of the structure of hydrozincite, $Zn_5(OH)_6(CO_3)_2$ along [010].

Table 3. *Interatomic distances and angles in hydrozincite*, $Zn_5(OH)_6(CO_3)_2$

(I)	x, y, z
(II)	$\bar{x}, \bar{y}, \bar{z}$
(III)	$x, \bar{y}, z$
(IV)	$\bar{x}, y, \bar{z}$
(V)	$-\frac{1}{2}+x, \frac{1}{2}+y, z$
(VI)	$\frac{1}{2}-x, \frac{1}{2}-y, \bar{z}$
(VII)	$\frac{1}{2}+x, \frac{1}{2}-y, z$
(VIII)	$\frac{1}{2}-x, \frac{1}{2}+y, \bar{z}$
(IX)	$x, 1-y, z$
(X)	$\bar{x}, y, 1-z$
(XI)	$\frac{1}{2}-x, \frac{1}{2}-y, 1-z$

Within the Zn(1) octahedron

Zn(1)(I)–(OH)(2)(I)	2·10 Å
Zn(1)(I)–(OH)(2)(II)	2·10
Zn(1)(I)–(OH)(2)(III)	2·10
Zn(1)(I)–(OH)(2)(IV)	2·10
Zn(1)(I)–O(1)(V)	2·12
Zn(1)(I)–O(1)(VI)	2·12
(OH)(2)(I) –(OH)(2)(III)	3·09
(OH)(2)(II) –(OH()2)(IV)	3·09
(OH)(2)(III)–(OH)(2)(II)	2·86
(OH)(2)(IV)–(OH)(2)(I)	2·86
O(1)(V)–(OH)(2)(I)	2·76
O(1)(V)–(OH)(2)(II)	3·19
O(1)(V)–(OH)(2)(III)	2·76
O(1)(V)–(OH)(2)(IV)	3·19
(OH)(2)(I) –Zn(1)(I)–(OH)(2)(III)	94·4°
(OH)(2)(III)–Zn(1)(I)–(OH)(2)(II)	85·6
(OH)(2)(II) –Zn(1)(I)–(OH)(2)(IV)	94·4
(OH)(2)(IV)–Zn(1)(I)–(OH)(2)(I)	85·6
O(1)(V)–Zn(1)(I)–(OH)(2)(I)	81·7
O(1)(V)–Zn(1)(I)–(OH)(2)(III)	81·7
O(1)(V)–Zn(1)(I)–(OH)(2)(II)	98·3
O(1)(V)–Zn(1)(I)–(OH)(2)(IV)	98·3

Within the Zn(2) octahedron

Zn(2)(I)–(OH)(1)(V)	2·10 Å
Zn(2)(I)–(OH)(1)(XI)	2·10
Zn(2)(I)–O(1)(V)	2·16
Zn(2)(I)–O(1)(XI)	2·16
Zn(2)(I)–(OH)(2)(I)	2·04
Zn(2)(I)–(OH)(2)(XI)	2·04
O(1)(XI)–(OH)(1)(XI)	3·15
O(1)(XI)–O(1)(V)	2·76
O(1)(V) –(OH)(1)(V)	3·15
(OH)(1)(XI)–(OH)(1)(V)	2·94
(OH)(2)(I) –O(1)(XI)	3·04
(OH)(2)(I) –(OH)(1)(XI)	3·04
(OH)(2)(I) –O(1)(V)	2·76
(OH)(2)(I) –(OH)(1)(V)	2·93
(OH)(1)(XI)–Zn(2)(I)–O(1)(XI)	95·7°
O(1)(XI)–Zn(2)(I)–O(1)(V)	79·6
O(1)(V) –Zn(2)(I)–(OH)(1)(V)	95·7
(OH)(1)(V)–Zn(2)(I)–(OH)(1)(XI)	88·8
(OH)(2)(I) –Zn(2)(I)–(OH)(1)(XI)	94·4
(OH)(2)(I) –Zn(2)(I)–O(1)(V)	92·9
(OH)(2)(I) –Zn(2)(I)–(OH)(1)(V)	90·2
(OH)(2)(I) –Zn(2)(I)–O(1)(V)	82·2

Within the Zn(3) tetrahedron

Zn(3)(I)–(OH)(2)(I)	1·99 Å
Zn(3)(I)–(OH)(2)(IX)	1·99
Zn(3)(I)–(OH)(1)(VI)	1·98
Zn(3)(I)–O(2)(I)	1·85
(OH)(1)(VI)–(OH)(2)(I)	3·27
(OH)(1)(VI)–(OH)(2)(IX)	3·27
(OH)(1)(VI)–O(2)(I)	3·04
(OH)(2)(I) –O(2)(I)	3·16
(OH)(2)(IX)–O(2)(I)	3·16
(OH)(2)(I) –(OH)(2)(IX)	3·21
(OH)(2)(I) –Zn(3)(I)–(OH)(2)(IX)	107·9°
(OH)(2)(I) –Zn(3)(I)–O(2)(I)	110·9
(OH)(2)(I) –Zn(3)(I)–(OH)(1)(VI)	111·1
(OH)(1)(VI)–Zn(3)(I)–O(2)(I)	105·0
(OH)(1)(VI)–Zn(3)(I)–(OH)(2)(IX)	111·1
(OH)(2)(IX)–Zn(3)(I)–O(2)(I)	110·9

Within the carbonate group

C(I)–O(1)(I)	1·35 Å	O(1)(I)–O(2)(I)	2·39 Å
C(I)–O(2)(I)	1·44	O(2)(I)–O(3)(I)	2·33
C(I)–O(3)(I)	1·27	O(3)(I)–O(1)(I)	2·31

O(1)(I)–C(I)–O(2)(I)	118·2°
O(1)(I)–C(I)–O(3)(I)	123·9
O(2)(I)–C(I)–O(3)(I)	117·9

Zinc–zinc distances

Zn(1)(I)–Zn(2)(I)	3·18 Å	Zn(3)(V)–Zn(3)(I)	3·50 Å
Zn(1)(I)–Zn(3)(I)	3·60	Zn(2)(I) –Zn(2)(III)	3·29
Zn(2)(I)–Zn(3)(I)	3·53	Zn(2)(I) –Zn(2)(IX)	2·99

Zinc–carbon distances

Zn(2)(V) –C(I)	3·03 Å
Zn(3)(I) –C(I)	2·88
Zn(3)(VI)–C(I)	3·76

Hydrogen bond distances and angles

(OH)(1)(I) –O(3)(XI)	2·78 Å
(OH)(2)(I) –O(3)(XI)	2·90
(OH)(2)(III)–O(3)(XI)	2·90
(OH)(1)(I) –O(3)(XI)–(OH)(2)(I)	114·0°
(OH)(1)(I) –O(3)(XI)–(OH)(2)(III)	114·0
(OH)(2)(I) –O(3)(XI)–(OH)(2)(III)	64·4
(OH)(2)(I) –O(3)(XI)–C(XI)	94·6
(OH)(2)(III)–O(3)(XI)–C(XI)	94·6
(OH)(1)(I) –O(3)(XI)–C(XI)	145·8

The tetrahedral Zn–O bond in hydrozincite is predominantly covalent and the average bond distance (1·95 Å) is significantly smaller than the average octahedral Zn–O bond distance (2·10 Å). The Zn–O bond distances in structures containing zinc in both octahedral and tetrahedral coordination are shown in Table 4. It should be noted that in $Zn(OH)_2.ZnSO_4$, γ-$Zn_3(PO_4)_2$ and $Zn_5(OH)_6(CO_3)_2$ the average octahedral Zn–O bond distance (2·09 Å) is much smaller than the sum of Pauling's octahedral radii (2·14 Å). It is possible that in these compounds the octahedral Zn–O bond also has some covalent character.

Bonding of the carbonate group

The carbonate groups lie on the mirror planes at y equal to 0 or $\frac{1}{2}$ and hence normal to the zinc sheets. They bind the complex sheets together in a three-

Table 4. *Zinc–oxygen bond lengths in compounds containing zinc in both octahedral and tetrahedral coordination*

Substance	Octahedral to tetrahedral zinc ratio	Average octahedral Zn–O	Average hetrahedral Zn–O	References
$Zn_2Mo_3O_8$	1 : 1	$2{\cdot}14_5$ Å	$1{\cdot}92_5$ Å	McCarroll, Katz & Ward (1957)
$Zn_5(OH)_8Cl_2.H_2O$	3 : 2	$2{\cdot}16_5$	2·02	Nowacki & Silverman (1961)
$Zn(OH)_2.ZnSO_4$	1 : 1	2·07	$2{\cdot}01_5$	Iitaka, Locchi & Oswald (1962)
γ $Zn_3(PO_4)_2$	1 : 2	2·10	2·04	Calvo (1963)
$Zn_5(OH)_6(CO_3)_2$	3 : 2	2·10	1·95	This paper

dimensional network by sharing a corner of the Zn(3) tetrahedron occurring away from the sheet and a corner of the Zn(1) octahedron occurring in the sheet next above; the third corner is hydrogen bonded to one (OH)(1) and two (OH)(2) groups (Fig. 3).

The O–O–O angle varies from 118·2° to 123·9° and the C–O distance 1·27 to 1·44 Å. The deformation of the carbonate group apparently depends on its environment as shown in Fig. 4. The C–O(2) distance is the longest, 1·44 Å, since O(2) is bonded covalently to Zn(3) and hence is drawn away from C. The O(1) oxygen atom is bonded to an octahedral zinc atom and so the C–O(1) bond is intermediate in length, namely 1·35 Å. The shortest C–O(3) distance, 1·27 Å involves oxygen O(3), which is not bonded to any zinc, but is hydrogen bonded to one (OH)(1) and two (OH)(2) groups.

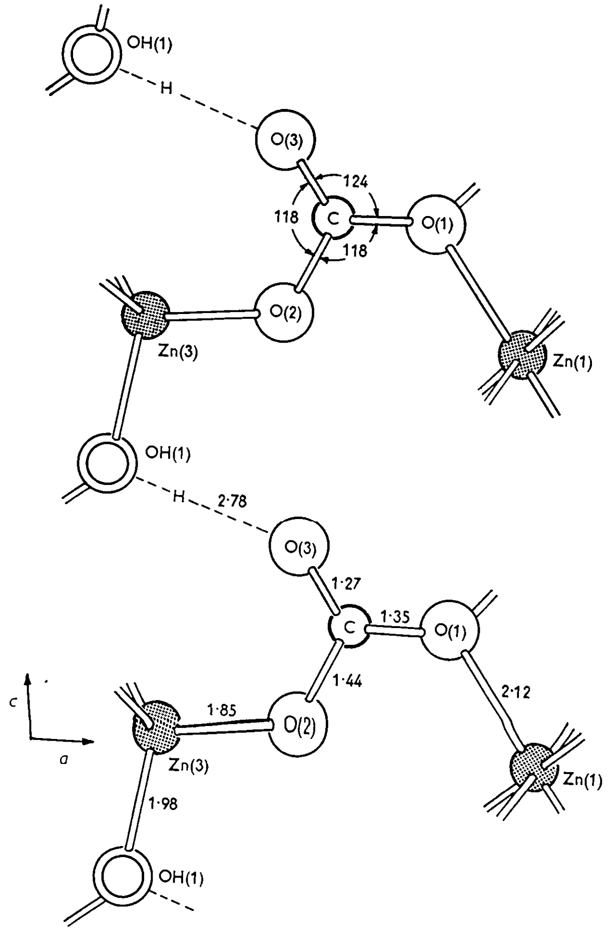

Fig. 4. A three-dimensional section through the structure of hydrozincite, $Zn_5(OH)_6(CO_3)_2$ at $y = \frac{1}{2}$, showing the bonding of the carbonate group. (O–H)(2) · · · O(3) bonds not shown.

Hydrogen bonding

The infrared spectrum of hydrozincite shows a single band in the $3\,\mu$ region. This band is due to two unresolved peaks at 3225 cm^{-1} and 3290 cm^{-1}. The infrared spectral evidence thus indicates that both OH groups are involved in the hydrogen bonding. The hydrogen bond between (OH)(1) and O(3) (2·78 Å) is of the usual order of magnitude, while those between (OH)(2) and O(3) (2·90 Å) are somewhat longer. Hence the infrared absorption peaks at 3225 cm^{-1} and 3290 cm^{-1} should be assigned to (O–H)(1) · · · O(3) and (O–H)(2) · · · O(3) bond stretchings respectively. The arrangement of the three hydrogen bonds and the C–O(3) bond around O(3) is distorted tetrahedral.

Comparison with related structures

The complex sheet structure found in hydrozincite is very similar to the structure of $Zn_5(OH)_8Cl_2.H_2O$ (Nowacki & Silverman, 1961). In the latter structure octahedral and tetrahedral zinc occur in the same ratio, the tetrahedral coordination around zinc being completed by a chlorine atom. In this structure the holes in the octahedral zinc layer are distributed on a rhombic 6·4 × 6·4 Å net. The electrically neutral sheets are packed rhombohedrally, being held together by weak O–H · · · Cl bonds.

Copper octahedral chains, similar to the one described above, formed of one Cu(1) and two Cu(2) octahedra sharing four and three edges alternately, are found also in lindgrenite, $Cu_3(MoO_4)_2(OH)_2$ (Calvert & Barnes, 1957) and pseudomalachite, $Cu_5(PO_4)_2(OH)_4$ (Ghose, 1963). In lindgrenite, chains of $Cu(OH)_2O_4$ octahedra are joined in a three dimensional network by tetrahedral MoO_4 groups. In pseudomalachite, where the metal to oxygen ratio is the same as that in hydrozincite, chains of one $Cu(OH)_2O_4$ and two $Cu(OH)_3O_3$ octahedra alternate with a second type of chain composed of $Cu(OH)_2O_4$ octahedra sharing opposite square-edges forming a sheet. These sheets are bonded together by tetrahedral PO_4 groups.

The bonding of the carbonate group in hydrozincite can be compared to the situation found in callaghanite, $Cu_2Mg_2CO_3(OH)_6$ (Brunton, Steinfink & Beck, 1958). In callaghanite two oxygen atoms are at 1·41 Å from the carbon atom and are shared with two magnesium atoms. The third oxygen is closer to the carbon atom, namely 1·29 Å and is shared by hydrogen bonds 2·64 Å in length with two H_2O molecules. It is very likely that the C–O(3) bond in hydrozincite as well as the C–O(*c*) bond in callaghanite (1·29 Å) have some double bond character. In contrast to these two cases, the three oxygens of the carbonate group in azurite, $Cu_3(OH)_2(CO_3)_2$ (Gattow & Zemann, 1958) are bonded to three copper atoms each and the C–O bond distances are 1·24, 1·27 and 1·30 Å.

The structure of aurichalcite $(Cu, Zn)_5(OH)_6(CO_3)_2$ is closely related to that of hydrozincite and presumably contains complex sheets, composed of (Cu, Zn) octahedra and Zn tetrahedra, bonded through the carbonate groups. The stacking sequence of the sheets however may be different, since the *a* axis of aurichalcite is approximately twice that of hydrozincite. The structure of aurichalcite is under investigation.

Synthetic basic zinc carbonates

Three different modifications of basic zinc carbonates have been prepared (Sahli, 1952), of which two are stacking-ordered and -disordered phases of hydrozincite. The compositions of these preparations are not constant, the disordered phase in general containing less CO_2 and more OH than the ordered phase. Ageing of the disordered phase with CO_2 converts it to the ordered phase. These facts can be readily explained on the basis of the structure. Since the carbonate groups hold the complex sheets together, replacement of some carbonate groups by OH ions will facilitate random mistakes in the layer sequence giving rise to the disordered phase. Ageing with CO_2 in effect reconstitutes the structure.

Frondel (1951) mentions some natural hydrozincites, yielding few broad powder lines, which correspond to the strongest powder lines of well crystallized hydrozincite. These are nothing but the stacking-disordered phases of hydrozincite, like the synthetic CO_2-deficient disordered phases.

Synthetic basic zinc carbonates always contain some water, most of which is adsorbed on the surface. However, a part may be structural, the water molecules being located in channels running parallel to [001] in between rows of carbonate groups.

The author is indebted to Prof. W. Feitknecht and Dr H. R. Oswald for laboratory facilities and discussions, to Prof. W. Neff and Dr R. Hüsser, Institut für angewandte Mathematik for the use of the Bull Gamma AET computer, and to the IBM, Extension Suisse, Zürich, for their cooperation and the donation of free computing time on the IBM 650 computer. Prof. C. Frondel of Harvard University and Mr Paul E. Desautels, U.S. National Museum, Washington, D.C., kindly provided specimens of hydrozincite. This research has been supported by the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung.

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