

bring the observed structure factors of the layers $h0l$ to $h4l$ to the same scale.

The intensities were reduced to F_o by applying Lorentz, polarization and absorption factors. The absorption correction was accomplished using the formula proposed by Palm (1964). Structure factor calculations were performed on an IBM 360/40 computer using a program written by Meier & Gramlich (1968). Fourier syntheses (King & Van der Helm, 1963) were calculated on an IBM 1620 system. Full-matrix least-squares refinement was executed on a CDC 6500 electronic data processing system using the program *XFLS* by Busing, Martin & Levy (1967).

The final observed and calculated structure factors are listed in Table 1.

Crystal data

Zinc hydroxide nitrate is monoclinic with the following unit-cell dimensions (refined by least-squares calculations):

$$\begin{aligned} a &= 19.480(5) \text{ \AA} & \beta &= 93.28^\circ(2) \\ b &= 6.238(1) & V &= 669.2(2) \text{ \AA}^3 \\ c &= 5.517(1) \end{aligned}$$

(values in parentheses are standard deviations).

The calculated density for 2 formula units per cell is $d_x = 3.115(1) \text{ g.cm}^{-3}$ in agreement with the pycnometrically measured density $d = 3.02(3) \text{ g.cm}^{-3}$.

The crystal used for data collection was cut out of a rhomb-shaped specimen to a rectangular prism of the following dimensions: $0.07 \times 0.4 \times 0.1 \text{ mm}$. The linear absorption coefficient is 109.4 cm^{-1} .

The space group, as determined from Weissenberg and precession photographs, is either $C2$, Cm or $C2/m$. As the habit of the crystals is centrosymmetric the space group $C2/m$ was adopted; this choice was subsequently found to be correct.

Structure solution and refinement

Initially a Patterson synthesis was computed from the $h0l$ reflexions which revealed the positional parameters of the metal atoms. By two successive difference Fourier syntheses the positions of the hydroxide oxygen atoms and the nitrate groups were determined. A three-

dimensional structure factor calculation gave an R value of 20%. In all calculations the atomic scattering factors used for the neutral atoms were those listed in *International Tables for X-ray Crystallography* (1962). In a three-dimensional difference Fourier synthesis the oxygen atoms of the four water molecules were detected. By Fourier and difference Fourier methods the R value could be lowered to 10%. In the following least-squares refinement we first varied 20 positional parameters, 11 temperature parameters and 5 scale factors: the R value for 491 observed reflexions dropped to 7.8%. After the introduction of anisotropic temperature factors an R value of 6.4% was reached. In the last cycle 20 positional parameters and 46 temperature factors were varied. The function minimized was $\sum |F_c - s_q F_o|^2$ (s_q is a scale factor); the reflexions were given unit weights.

The final positional and thermal parameters are given in Tables 2 and 3.

Table 2. $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ positional parameters and their standard deviations

	x	y	z
Zn(1)	0.0000	0.5000	0.0000
Zn(2)	0.0000	0.2518(5)	0.5000
Zn(3)	0.0879(1)	0.0000	0.0079(4)
OH(1)	0.0622(4)	0.2512(20)	0.1882(13)
OH(2)	0.4402(7)	0.5000	0.3397(20)
OH(3)	0.4492(6)	0.0000	0.3091(21)
O(1)	0.2863(7)	0.5000	0.4974(29)
O(2)	0.1845(8)	0.5000	0.3090(25)
O(3)	0.3032(8)	0.0000	0.3014(28)
H ₂ O	0.3123(7)	0.5000	0.0125(25)
N	0.2206(9)	0.5000	0.4950(35)

Description of the structure

The structure of zinc hydroxide nitrate can be regarded as a variation of a hypothetical $\text{Zn}(\text{OH})_2$ structure in the $C6$ or CdI_2 -type group. One quarter of the zinc atoms are removed from the octahedral interstices of the sheet. Each occupied octahedron shares its edges with two unoccupied and four occupied octahedra. The resulting sheet is negatively charged: $[\text{Zn}_3^{\text{net}}(\text{OH})_8]^{2-}$. Tetrahedrally coordinated zinc atoms are located above and below the empty octahedron. Three corners of the tetrahedron are occupied by hydroxide ions belonging to the sheet described above, the fourth by a water

Table 3. Mean-square amplitudes of vibration ($\text{\AA}^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn(1)	32 (2)	28 (3)	22 (2)	0	1 (1)	0
Zn(2)	36 (1)	26 (2)	22 (1)	0	2 (1)	0
Zn(3)	31 (1)	26 (2)	25 (1)	0	2 (1)	0
OH(1)	25 (4)	43 (8)	14 (3)	1 (6)	4 (2)	1 (4)
OH(2)	35 (6)	34 (11)	13 (3)	0	-4 (4)	0
OH(3)	16 (5)	30 (10)	20 (6)	0	0 (3)	0
O(1)	24 (8)	60 (15)	55 (10)	0	8 (7)	0
O(2)	29 (7)	42 (14)	36 (8)	0	-3 (6)	0
O(3)	38 (9)	127 (20)	36 (9)	0	16 (7)	0
H ₂ O	31 (7)	64 (16)	34 (6)	0	-3 (6)	0
N	37 (10)	40 (20)	47 (12)	0	7 (8)	0

molecule. The complex sheet so formed is positively charged, $[\text{Zn}_5^{\text{Oct}}(\text{OH})_8\text{Zn}_1^{\text{Tet}}(\text{H}_2\text{O})_2]^{2+}$. These sheets are stacked so that the second sheet is shifted along [010] by an amount $b/2$. The nitrate anions are located between the sheets and lie in a plane normal to them. The nitrate groups do not directly coordinate the zinc atoms: the symmetry D_{3h} is therefore almost preserved. In addition, the sheets are held together by hydrogen bonds: two oxygen atoms of the nitrate group are hydrogen bonded with water, the third forms a bond with two hydroxide ions of the sheet. Two views of the structure are given in Fig. 1(a) and (b). The bond lengths and angles are presented in Table 4.

Table 4. *Interatomic distances and bond angles in $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$*

(a) Coordination octahedron around Zn(1)	
Zn(1)–OH(1 ^I)	2.193 (12) Å
Zn(1)–OH(1 ^{II})	2.193 (12)
Zn(1)–OH(1 ^V)	2.193 (12)
Zn(1)–OH(1 ^{VI})	2.193 (12)
Zn(1)–OH(3 ^{III})	2.020 (11)
Zn(1)–OH(3 ^{IV})	2.020 (11)
∠ OH(3 ^{III})–Zn(1)–OH(1 ^I)	83.4 (0.5)°
∠ OH(1 ^I)–Zn(1)–OH(1 ^{II})	89.9 (0.5)
(b) Coordination octahedron around Zn(2)	
Zn(2)–OH(1 ^I)	2.160 (12) Å
Zn(2)–OH(1 ^V)	2.160 (12)
Zn(2)–OH(2 ^{III})	2.118 (11)
Zn(2)–OH(2 ^{IV})	2.118 (11)
Zn(2)–OH(3 ^{III})	2.089 (11)
Zn(2)–OH(3 ^{IV})	2.089 (11)
Mean value	2.122 (6)
∠ OH(1 ^I)–Zn(2)–OH(2 ^{III})	89.2 (0.5)°
∠ OH(1 ^I)–Zn(2)–OH(3 ^{III})	82.6 (0.5)
∠ OH(2 ^{IV})–Zn(2)–OH(3 ^{IV})	96.1 (0.5)
(c) Coordination tetrahedron around Zn(3)	
Zn(3)–OH(1 ^I)	1.937 (12) Å
Zn(3)–OH(1 ^{II})	1.937 (12)
Zn(3)–OH(2 ^{IV})	1.963 (11)
Zn(3)–H ₂ O(1 ^V)	1.953 (11)
Mean value	1.947 (6)
∠ OH(1 ^I)–Zn(3)–OH(1 ^{II})	108.0 (0.6)°
∠ OH(1 ^{II})–Zn(3)–OH(2 ^{IV})	115.8 (0.6)
∠ OH(1 ^I)–Zn(3)–H ₂ O(1 ^V)	108.5 (0.6)
∠ OH(2 ^{IV})–Zn(3)–H ₂ O(1 ^V)	99.6 (0.6)
(d) Nitrate group	
N–O(1 ^I)	1.277 (23) Å
N–O(2 ^I)	1.209 (25)
N–O(3 ^{IV})	1.242 (23)
Mean value	1.243 (12)
∠ O(1 ^I)–N–O(2 ^I)	122.9 (1.9)°
∠ O(1 ^I)–N–O(3 ^{IV})	114.6 (1.9)
∠ O(2 ^I)–N–O(3 ^{IV})	122.5 (1.9)
(e) Hydrogen bonds	
H ₂ O(1 ^I)–O(1 ^I)	2.751 (23) Å
H ₂ O(1 ^I)–O(3 ^{IV})	2.758 (23)
OH(1 ^I)–O(2 ^I)	2.891 (23)
OH(3 ^I)–O(3 ^I)	2.842 (23)

Table 4 (cont.)

Symmetry code:

$$\begin{array}{llll} \text{I} = & x & y & z \\ \text{II} = & x & -y & z \\ \text{III} = & x - \frac{1}{2} & y - \frac{1}{2} & z \end{array} \quad \begin{array}{llll} \text{IV} = & \frac{1}{2} - x & \frac{1}{2} - y & -z \\ \text{V} = & -x & y & -z \\ \text{VI} = & -x & -y & -z \end{array}$$

Discussion of the structure

The structure of zinc hydroxide nitrate is closely related to those of zinc hydroxide chloride $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ (Nowacki & Silverman, 1961; refined by Allmann, 1968), and zinc hydroxide carbonate (hydrozincite), $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ (Ghose, 1964), in so far as these compounds contain zinc in octahedral and tetrahedral coordination. The ratio of octahedral to tetrahedral zinc is always 3:2.

The three compounds differ in that the carbonate group in hydrozincite coordinates both the octahedral and the tetrahedral zinc atoms, whereas in zinc hydroxide chloride the chloride ion takes part in the tetrahedral coordination of zinc. On the other hand in $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ the nitrate group coordinates neither the tetrahedral nor the octahedral metal atoms.

The mean octahedral Zn–O distance of 2.13 Å is comparable with the value of 2.16 Å in zinc hydroxide chloride, 2.10 Å in hydrozincite, 2.07 Å in $\text{Zn}(\text{OH})_2 \cdot \text{ZnSO}_4$ (Iitaka, Oswald & Locchi, 1962) and 2.10 Å in $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Ferrari, Braibanti, Manotti Lanfredi & Tiripicchio, 1967).

The Zn(1)–OH(1) distance is significantly longer than the Zn(1)–OH(3) distance. This difference is due to the fact that the OH(3) ions are exclusively coordinated to Zn(1) and Zn(2) whereas OH(1) is coordinated to Zn(3) as well. Therefore OH(1) is pulled out of the layer (100) in the direction of Zn(3), and the Zn(1)–OH(1) distance is increased.

The occurrence of strongly distorted octahedra with considerable variation in the distances between the central atom and its neighbours is fairly common in the crystal chemistry of zinc, see *e.g.* $\text{Zn}(\text{OH})_2 \cdot \text{ZnSO}_4$ (Iitaka, Oswald & Locchi, 1962) or $\beta\text{-Zn}(\text{OH})\text{Cl}$ (Forsberg & Nowacki, 1959).

The distance between the centre of the empty octahedron and the oxygen atoms is 2.22 Å, which is significantly larger than the Zn–O distance in the occupied octahedron. This is readily understood on the basis of an ionic model and electrostatic repulsion of the oxygen atoms involved in the empty octahedron. The Zn–O distance in the tetrahedron with an average value of 1.95 Å is similar to those found in $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ (1.94 Å), $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ (1.95 Å) and $\text{Zn}(\text{OH})_2 \cdot \text{ZnSO}_4$ (2.02 Å).

The nitrate group has almost D_{3h} symmetry, the differences in the N–O bond lengths not being significant. The almost complete preservation of D_{3h} symmetry can be clearly seen in the infrared spectra: the strong doubly-degenerated asymmetric N–O stretching frequency ν_3 of the nitrate group near 1380 cm^{-1} is not

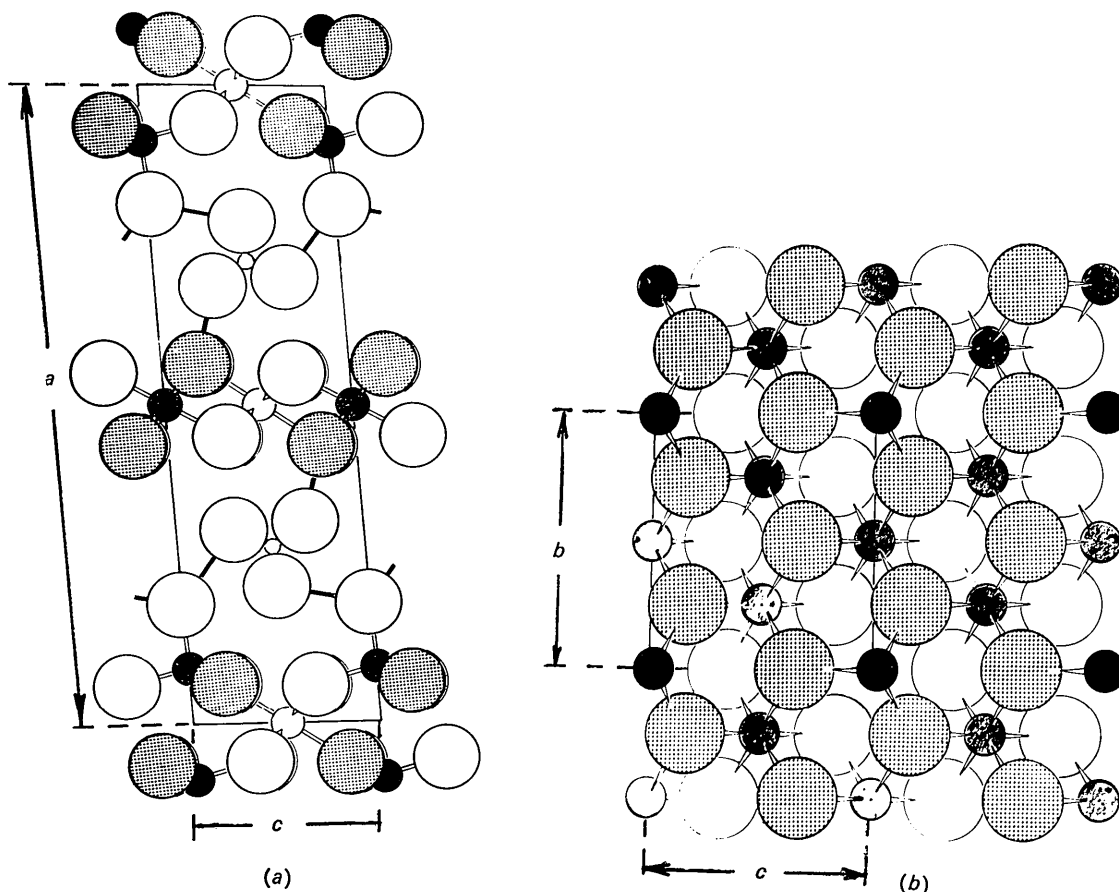
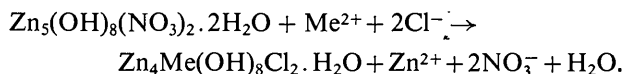


Fig. 1. $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$. Partial projections (a) along b , (b) normal to the b, c plane; nitrate groups omitted. Small circles are nitrogen, medium circles zinc and large circles oxygen atoms. Shaded circles represent atoms above the plane of projection.

split and the forbidden, totally symmetric ν_1 mode (1020 cm^{-1}) can hardly be detected in the spectra.

As the nitrate oxygen atoms are not directly bonded to any metal atoms, the nitrate groups may be replaced by chlorine ions merely by immersing the crystals in solutions of metal chlorides:



The crystal structure of the product is very similar to the structure of zinc hydroxide chloride, $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$. A discussion of this topotactic reaction and the infrared and ultraviolet spectra will shortly be published elsewhere.

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