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Crystal Structure Determination of $Zr(OH)_2(NO_3)_2 \cdot 4.7H_2O$ from X-Ray Powder Diffraction Data

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The crystal structure of $Zr(OH)_2(NO_3)_2 \cdot 4.7H_2O$ has been solved ab initio from X-ray powder data obtained from a conventional diffractometer. The unit cell was obtained by means of the successive dichotomy indexing method. This is triclinic, space group $P1$ with the following lattice parameters: $a = 9.541(1)$ Å, $b = 9.590(1)$ Å, $c = 6.753(1)$ Å, $\alpha = 98.64(1)°$, $\beta = 92.89(1)°$ and $\gamma = 118.60(1)°$, $Z = 2$. A total of 136 integrated intensities, unambiguously indexed, were used to generate a Patterson function from which the approximate heavy atom coordinates were derived. The remaining atoms were located by an interpretation of successive three-dimensional Fourier maps. The structure was refined by means of the Rietveld method ($R_F = 0.039$, $R_B = 0.063$, $R_p = 0.084$ and $R_{wp} = 0.108$). In accordance with the chemical analysis, the structure model shows that the most probable number of water molecules is 4.7. The structure of $Zr(OH)_2(NO_3)_2 \cdot 4.7H_2O$ consists of infinite and isolated chains of trigonal dodecahedra sharing edges. The zirconium atom is eightfold coordinated by four OH groups, two water molecules, and one bidentate nitrate group. The chains are held together by hydrogen bonds through additional water molecules and nitrate groups located between the chains.

Introduction

Determination of the structures of a number of zirconium hydroxide salts has revealed a variety of compounds with interesting structural chemistry. Basic sulfates have been studied extensively (*1*), but there is little reliable information concerning zirconium hydroxide nitrates. Indeed, only a brief report on the structure of a triclinic compound, $Zr(OH)_2(NO_3)_2 \cdot 4H_2O$, has been published (*2*), although several phases were identified from a study of the equilibrium diagram ZrO_2–HNO_3–H_2O (*3*). Among the reported phases, $ZrO(NO_3)_2 \cdot 5H_2O$, which has the same global chemical formula as those reported in Ref. (2), has a powder diffraction pattern which cannot be indexed by the unit cell parameters given for this compound. As part of our interest in the structural chemistry of metal hydroxide salts, we have studied the phase originally formulated $ZrO(NO_3)_2 \cdot 5H_2O$, whose water content is sometimes given as x, probably due to the low thermal stability of this phase. In other respects, in previous structural studies of basic metal nitrates for which only powders were available, we have shown that recent advances in conventional high resolution instrumentation and computational methods which have occurred in powder diffraction techniques can be used for structure characterization and, sometimes, for the solution of unknown crystal struc-

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tures (*4–8*). We present here the ab initio crystal structure determination of the phase $Zr(OH)_2(NO_3)_2 \cdot 4.7H_2O$ from X-ray powder diffraction data.

Experimental Considerations

Since the zirconyl nitrate hydrate, $ZrO(NO_3)_2 \cdot xH_2O$, obtained from Aldrich Products (No. 29,349-3) has the same powder diffraction pattern as that of the compound with $x = 5$ in Ref. (*3*), the powder sample studied by X-ray diffraction was taken from this commercially available compound. The zirconium content was determined by EDTA titration using xylenol orange as indicator. A 0.167-*g* sample was dissolved in dilute nitric acid to achieve a pH of approximately 2–3. A small amount (40 mg) of indicator was added and the solution was stirred magnetically. The solution was then titrated to a red color with a solution of 0.1 M thorium nitrate. The Zr content was found to be 27.4%, which is more than the theoretical value of 26.9% for the stoichiometric formula with 6 water molecules; this result corresponds to 5.7 water molecules. From the TG analysis it was difficult to obtain a precise value for x, due to the fact that weight loss is observed from the outset of the heating, which is an indication of the low thermal stability of this material and possible variations of the water content at room temperature. However, the total weight loss to obtain the oxide was found to be 62%, from which an x value of 5.2 can be calculated. The density of the sample was measured using the Archimedean method in CCl_4: the average value was $2.04 \text{ g} \cdot \text{cm}^{-3}$.

A D500 Siemens powder diffractometer, using Bragg–Brentano geometry, was used for data collection. Pure Cu$K\alpha_1$ radiation (1.540598 Å) was produced with an incident beam curved-crystal germanium monochromator and asymmetric focusing (short focal distance 124 mm, long focal distance 216 mm). Complete illumination of the sample was effective from 12° (2θ). The alignment of the diffractometer was checked by means of standard reference materials. The zero error was measured as less than 0.01°(2θ). The instrumental resolution function (IRF) for this conventional powder diffractometer, with an incident-beam monochromator, has been discussed by Louër and Langford (*9*). The IRF has a minimum of 0.065° at about 40°(2θ) and has twice this value at 130°. Throughout the experiment the ambient temperature was maintained at 296 ± 1 K. Preliminary data collections from different preparations of the sample in the sample holder revealed that preferred-orientation effects of crystallites are negligible for this material. The powder diffraction pattern was scanned in steps of 0.02°(2θ) and fixed-time counting (56 sec) was employed. Finally, when all data had been collected, the stability of the intensity of the incident beam was checked by measuring again the first few lines of the pattern. A precise determination of peak positions and integrated intensities of Bragg components was carried out by means of the fitting program available in the PC software package DIFFRAC-AT (*10*). From the presentation of diffraction peaks by the Pearson VII function, it was seen that all peaks have a strong Gaussian character; in subsequent decomposition of clusters of lines, the selection of a Gaussian function led to better fitting results. The absolute error in the peak position of the first 20 lines of the pattern, used for indexing purposes was less than 0.03° (2θ).

Data Analysis

Indexing

The indexing of the powder diffraction data was performed by means of the successive dichotomy method (*11*), which is based on an exhaustive strategy in parameter-space. The program DICVOL91 (*12*), which

TABLE I

X-RAY POWDER DIFFRACTION PATTERN OF $Zr(OH)_2(NO_3)_2 \cdot 4.7H_2O$

$h\ k\ l$	$2\theta_{obs}$(°)	$2\theta_{calc}$(°)	d_{obs}(Å)	I/I_0
$1\ 0\ 0$	10.664	10.660	8.29	51
$\bar{1}\ 1\ 0$	10.757	10.766	8.22	100
$0\ \bar{1}\ 1$	15.428	15.407	5.74	2
$1\ 0\ 1$	18.311	18.290	4.841	2
$1\ 1\ 0$	18.532	18.516	4.784	20
$\bar{2}\ 1\ 0$	18.633	18.610	4.758	11
$0\ 1\ 1$	18.792	18.781	4.718	13
$\bar{1}\ \bar{1}\ 1$	20.651	20.638	4.298	11
$2\ 0\ 0$	21.424	21.413	4.144	11
$0\ 2\ 0$	21.531	21.520	4.124	5
$\bar{2}\ 2\ 0$	21.649	21.628	4.102	7
$\bar{2}\ 1\ 1$	22.483	22.467	3.951	1
$0\ \bar{2}\ 1$	23.017	23.011	3.861	9
$\bar{2}\ 0\ 1$	23.658	23.650	3.758	1
$\bar{1}\ 2\ 1$	24.658	24.655	3.607	2
$2\ \bar{2}\ 1$	24.852	24.834	3.580	2
$1\ 1\ 1$	25.007	24.999	3.558	5
$\bar{2}\ 2\ 1$	26.186	26.190	3.400	1
$0\ 0\ 2$ $0\ \bar{1}\ 2$	26.971	26.956 26.972	3.303	19
$1\ 0\ 2$	27.596	27.588	3.230	10
$2\ 1\ 0$	28.448	28.432	3.135	4
$\bar{3}\ 2\ 0$	28.674	28.661	3.111	17
$\bar{2}\ 3\ 0$	28.769	28.763	3.101	13
$\bar{1}\ \bar{2}\ 1$	28.943	28.942	3.082	1
$\bar{2}\ \bar{1}\ 1$	29.197	29.182	3.056	1
$\bar{1}\ \bar{1}\ 2$	29.651	29.647	3.010	5
$2\ \bar{3}\ 1$	30.326	30.321	2.945	2
$1\ 0\ 2$	30.474	30.470	2.931	4
$0\ 1\ 2$	31.075	31.061	2.876	4
$\bar{3}\ 2\ 1$	31.642	31.645	2.825	1
$\bar{2}\ 1\ 2$	32.187	32.203	2.779	<1
$0\ 3\ 0$	32.516	32.526	2.751	1
$3\ \bar{1}\ 1$ $\bar{3}\ 3\ 0$	32.696	32.681 32.692	2.737	2
$\bar{3}\ 0\ 1$ $\bar{2}\ 3\ 1$	33.298	33.297 33.310	2.689	3
$2\ \bar{1}\ 2$	33.715	33.700	2.656	1
$2\ 1\ 1$ $2\ \bar{2}\ 2$	33.764	33.761 33.784	2.652	1
$1\ 2\ 1$	34.065	34.076	2.630	1
$3\ \bar{3}\ 1$	34.693	34.707	2.584	3
$\bar{1}\ 2\ 2$	35.280	35.299	2.542	1
$\bar{2}\ \bar{1}\ 2$	35.659	35.665	2.516	2
$\bar{2}\ 2\ 2$	35.809	35.831	2.506	1
$1\ 1\ 2$	35.869	35.897	2.501	1
$1\ \bar{3}\ 2$	36.076	36.080	2.4877	1
$3\ 0\ 1$	36.930	36.944	2.4321	2
$2\ \bar{3}\ 2$	37.298	37.300	2.4089	4
$2\ 2\ 0$	37.515	37.540	2.3955	<1
$\bar{4}\ 2\ 0$	37.734	37.735	2.3821	3
$0\ 3\ 1$	37.843	37.811	2.3755	<1
$0\ 2\ 2$	38.111	38.091	2.3594	1
$2\ \bar{4}\ 1$	38.365	38.369	2.3443	1
$\bar{1}\ \bar{3}\ 1$	38.766	38.782	2.3210	1
$3\ 1\ 0$	39.092	39.103	2.3024	1
$\bar{4}\ 1\ 0$	39.206	39.213	2.2960	3
$1\ \bar{4}\ 1$	39.310	39.324	2.2901	1
$\bar{1}\ 4\ 0$ $\bar{4}\ 3\ 0$	39.460	39.446 39.463	2.2818	5
$\bar{3}\ 2\ 2$ $\bar{4}\ 2\ 1$	39.571	39.571 39.575	2.2756	3
$3\ \bar{2}\ 2$	39.920	39.931	2.2565	<1
$3\ \bar{4}\ 1$	40.530	40.538	2.2240	1
$0\ 0\ 3$	40.920	40.927	2.2037	2
$3\ \bar{1}\ 2$	41.353	41.362	2.1816	1

tackles any system, including triclinic, was used for indexing the pattern. The first 20 lines were completely indexed on the basis of a triclinic cell with the parameters a = 9.761(2) Å, b = 9.588(2) Å, c = 6.749(2) Å, α = 81.40(2)°, β = 101.35(2)°, γ = 120.96(2)°, V = 530.2(5) Å^3. The reliability of the unit cell and indexing is indicated by the figures of merit M_{20} = 54 and F_{20} = 112(0.0059, 30). The quality of the data can also be evaluated by the average absolute magnitude of the discrepancy between observed and calculated 2θ values, i.e., $\Delta 2\theta$ = 0.0059°. The CDF-SRCH program (*13*) run on a PC computer was used to find the normalized unit cell parameters, which were used to interrogate the NIST Crystal Data base in order to search for an apparently isostructural material of known structure; no such structure was found. From the normalized parameters, the powder diffraction data were reviewed by means of the computer program NBS*AIDS83 (*14*). The 50 measured diffraction lines are indexed by this solution [a = 9.541(1) Å, b = 9.590(1) Å, c = 6.753(1) Å, α = 98.64(1)°, β = 92.89(1)°, γ =

118.60(1)°, $V = 531.0(3)$Å^3, $F_{30} = 55(0.0109, 50)$]. This cell corresponds to the reduced cell of that reported above. The list of observed and calculated peak positions is given in Table I. The experimental density, 2.04 g · cm^{-3}, is in better accordance with the calculated density, 2.092 g · cm^{-3}, for a chemical formula $ZrO(NO_3)_2 \cdot 5.7H_2O$ than with the value calculated for $ZrO(NO_3)_2 \cdot 6H_2O$ (2.126 g · cm^{-3}). The space group was assumed to be $P1$ and this was confirmed by the satisfactory refinement of the structure. At this stage, it is interesting to notice that the triclinic unit cell found (Table I) indexes the powder pattern reported for $ZrO(NO_3)_2 \cdot 5H_2O$ in Ref. (*3*). However, the quality of these data is rather low, as is shown by the corresponding figures of merit $M_{20} = 5$ and $F_{30} = 6(0.0292, 178)$. Also, it should be noted that the triclinic unit cell is significantly different from the cell reported by McWhan and Lundgren (*2*) for $Zr(OH)_2(NO_3)_2 \cdot 4H_2O$ (after transformation into the conventional unit cell, this is: a = 7.408 Å, b = 9.894 Å, c = 6.741 Å, α = 97.45°, β = 99.78°, γ = 93.71°, V = 480.90 Å^3), though some similarities may be detected in the values of the c parameter.

Structure Solution and Refinement

From the pattern decomposition, without reference to a structural model, 119 unambiguously indexed integrated intensities were obtained. In addition 17 unobserved reflections with small, but nonzero intensity, were added to this list. After being corrected for Lorentz-polarization effects, the 136 F_{obs} values were introduced in the SDP (*15*) crystallographic computing package to generate a Patterson map, from which the approximate position of the unique independent zirconium atom was derived. Calculations were performed on a MICROVAX 3100 computer. The approximate coordinates of the heavy atom were input to the Rietveld profile refinement method (R_F = 0.22). The program FULLPROF (*16*), based on the version DBW3.2S(8804) (*17*), which is a successor of the program described in Ref. (*18*), was used in this study. Successive Fourier maps, alternating with refinements, were calculated and gave the coordinates of 12 oxygen atoms. Among them it was possible to recognize the configuration of two nitrate groups, although the 2 nitrogen atoms were not seen clearly in the Fourier maps. Consequently, the coordinates of both nitrogen atoms were calculated geometrically. The approximate coordinates of the 15 independent atoms were used as a structural starting model in the Rietveld method. Although a Gaussian function was used in the initial stages of the study, a pseudo-Voigt function was finally selected to describe individual line-profiles, with a possible angular variation of the mixing parameter η. Integrated intensities were distributed over four FWHM on either side of a diffraction line. In order to describe the angular dependence of the peak full-width at half-maximum, the usual quadratic form in tan θ was used with initial values of the constants U, V, and W derived from the components obtained by pattern decomposition. Unit cell and instrument parameters were allowed to vary from time to time during the refinement process. The refinement, carried out in the range 12–92°(2θ), converged to the profile factors R_p = 0.111 and R_{wp} = 0.145. A final Fourier map was calculated and showed one residual peak with a height of 4.6 e · Å^{-3}. This peak, not bonded to the zirconium atom, could correspond to an additional water molecule. The least-squares refinement, including this atom, was therefore repeated, giving a significantly improved fit, as is shown by the value of the R-weighted profile indicator, R_{wp} = 0.106, whose numerator is the residual being minimized in the least-squares refinement. However, the value of the isotropic temperature factor of this atom was anomalously high (>10 Å^2). Consequently, its value was fixed to 6 (by analogy with similar nonbonded water molecules) and the refinement of the occupancy factor for this atom gave the value of 0.71(2), which is in exceptionally good agreement with the chemical analysis. At this stage of the refinement it became apparent that the compound was nonstoichiometric in water content. The final Rietveld refinement involved the following parameters: 64 atomic coordinates, including 15 isotropic temperature factors and 1 occupancy factor, 1 scale factor, 1 zero point parameter, 6 cell parameters, 3 half-width and 1 asymmetry parameters, 6 coefficients used to define the functional dependence of the background, and 2 parameters to describe the angular variation of the mixing factor η. The last variable to be refined was the preferred-orientation factor, which was found to be very small, in accordance with the preliminary studies reported above. During the last cycles of the refinement, the isotropic temperature factors of OH2 and Ow2 oscillated around zero, finally giving slightly negative values, which can be seen as physically acceptable within 3 e.s.d. It is well known that, in Rietveld refinement from X-ray data, the thermal parameters are very sensitive to the accuracy of data and particularly to the modeling of the background. The details of the refinement are given in Table II. Figure 1 shows the final fit obtained between calculated and observed patterns. This fit corresponds to satisfactory crystal-structure model indicators (R_F = 0.039, R_B = 0.063) and profile factors (R_p = 0.084, R_{wp} = 0.108). Final atomic parameters are given in Table III and selected bond distances and angles in Table IV.

TABLE II

DETAILS OF RIETVELD FULL-PROFILE REFINEMENT FOR $Zr(OH)_2(NO_3)_2 \cdot 4.7H_2O$

Space group	$P\bar{1}$
Z	2
Wavelength (Å)	1.5405981
2θ range (°)	12–92
Step scan increment (°2θ)	0.02
No. of reflections	896
No. of structural parameters	65
No. of profile parameters	19
No. of atoms	16
R_F	0.039
R_B	0.063
R_p	0.084
R_{wp}	0.108
"Expected" R_{exp}	0.037

Note. The R factors are defined as

$$R_F = \frac{\Sigma|I(\text{"obs"})^{1/2} - I(\text{calc})^{1/2}|}{\Sigma I(\text{"obs"})^{1/2}}$$

$$R_B = \frac{\Sigma|I(\text{"obs"}) - I(\text{calc})|}{\Sigma I(\text{"obs"})}$$

$$R_p = \frac{\Sigma|y_i(\text{obs}) - (1/c)y_i(\text{calc})|}{\Sigma y_i(\text{obs})}$$

$$R_{wp} = \left(\frac{\Sigma w_i[y_i(\text{obs}) - (1/c)y_i(\text{calc})]^2}{\Sigma w_i[y_i(\text{obs})]^2}\right)^{1/2}.$$

Description of the Structure and Discussion

Perspective views of the crystal structure, along two directions, are shown in Figs. 2 and 3. The structure is built from infinite chains of edge-sharing ZrO8 polyhedra running close to the [001] direction. The zirconium atom is eightfold oxygen coordinated in the shape of a triangular dodecahedron as shown in Fig. 4. Scrutiny of the ligands shows that four oxygen atoms are bonded to only one zirconium atom, while the four other O atoms are linked to two Zr and are likely to have the same chemical nature (hydroxyl groups). This is an indication that the compound originally formulated $ZrO(NO_3)_2 \cdot 5.7H_2O$ is a hydroxy-complex, which must be written $Zr(OH)_2(NO_3)_2 \cdot 4.7H_2O$. The ligands of dodecahedra consist of four hydroxyl groups (2 × OH1–OH2) bridging two zirconium atoms, one bidentate nitrate group (O1–O2), and two water molecules (Owl–Ow2). The Zr–O distances range from 2.06 to 2.44 Å with a mean value of 2.21 Å, which compares well with the values reported in others hydroxy salts (*2, 19*). The four shortest bonds correspond to the

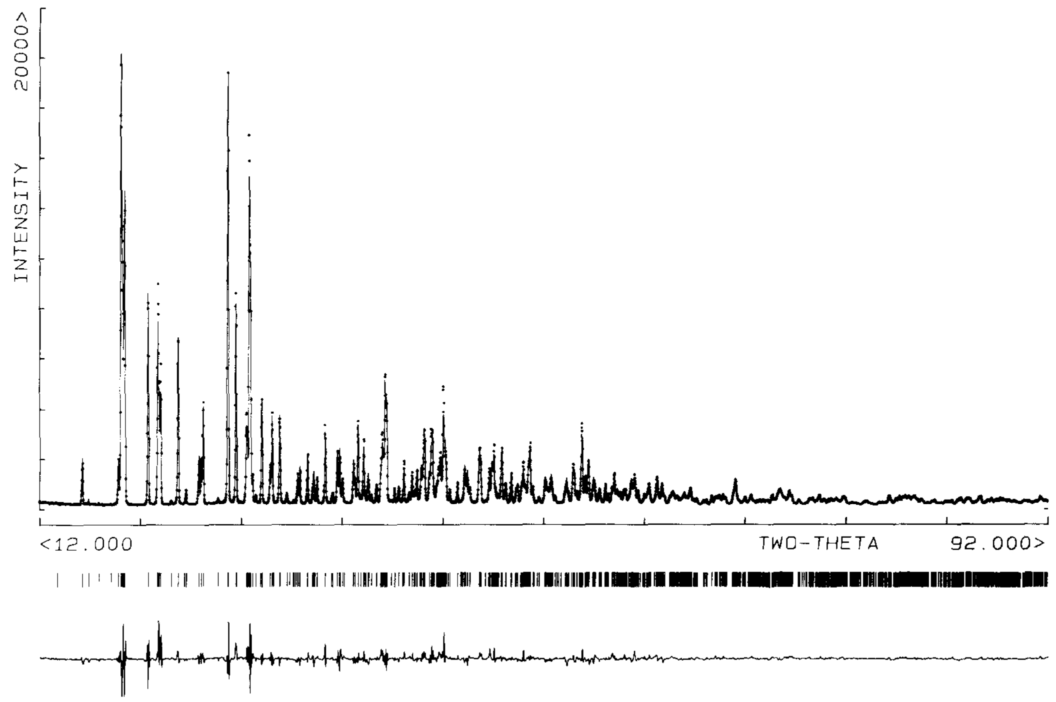

FIG. 1. The final Rietveld difference plot of $Zr(OH)_2(NO_3)_2 \cdot 4.7H_2O$ from the Siemens D500 dataset. The upper trace shows the observed data as dots, and the calculated pattern is shown by the solid line. The lower trace is a plot of the difference: observed minus calculated. The vertical markers show positions calculated for Bragg reflections.

Zr–OH contacts. As is to be expected, the Zr bonds to the double hydroxyl bridge are the strongest Zr–O bonds in the structure. Following Hoard and Silverton (*20*), the interatomic distances in the dodecahedron are divided into six groups, according to the ideal D_{2d} symmetry. The values for these groups, *M–A*, *M–B*, *a*, *b*, *g*, and *m*, are given in Table IV (see also Fig. 4). The average distances, 2.23 Å (type *M–A*), 2.18 Å (type *M–B*), 2.75 (type *a*), 3.18 Å (type *b*), 2.79 Å (type *g*), and 2.41 Å (type *m*) do not differ greatly from the values reported for zirconium sulfates (*21*). Apart from the O1–O2 (2.25 Å) distance in the nitrate group, the shortest O–O contacts in the ZrO8 polyhedron arise between hydroxyl groups (2.26, 2.33 Å) and are quite similar to the mean value of 2.34 Å found in $Zr_2(OH)_2(SO_4)_3 \cdot 4H_2O$ (*19*). The presence of the common edge between two dodecahedra and also three different ligands, with a constraint due to the bidentate nitrate group, influence the deviation of the dodecahedra from the ideal case.

As shown in Fig. 2, the structure consists of isolated infinite chains which may be considered as linear macrocations $[Zr(OH)_2(NO_3)(H_2O)_2^+]_n$ which are balanced by an equivalent amount of nitrate anions. These nitrate groups (N2, O4–6) and additional free water molecules (Ow3–5) are located between the chains; their distances to oxygen atoms of the ZrO8 coordination sphere are consistent with hydrogen bonds (Table IV), according to Baur's criteria (*22*). Two

TABLE III

POSITIONAL AND THERMAL PARAMETERS AND THEIR STANDARD DEVIATIONS FOR $Zr(OH)_2(NO_3)_2 \cdot 4.7H_2O$

Atom	x	y	z	B_{iso}(Å^2)
Zr	0.4473(2)	0.4432(2)	0.2359(3)	1.19(8)
OH1	0.413(1)	0.370(1)	0.524(2)	0.3(3)
OH2	0.592(1)	0.627(1)	0.078(1)	−0.2(3)
Ow1	0.311(1)	0.579(1)	0.241(2)	1.1(3)
Ow2	0.182(1)	0.241(1)	0.169(1)	−0.1(3)
O1	0.445(1)	0.185(1)	0.178(2)	2.9(4)
O2	0.673(1)	0.426(1)	0.247(2)	1.5(3)
O3	0.678(2)	0.205(2)	0.231(2)	5.8(5)
O4	−0.017(2)	0.159(1)	0.460(2)	3.6(4)
O5	0.825(2)	0.954(1)	0.213(2)	4.0(4)
O6	0.244(2)	0.043(2)	0.477(2)	4.1(5)
Ow3	0.431(1)	0.881(1)	0.283(2)	4.4(4)
Ow4	−0.050(1)	0.195(1)	−0.095(2)	5.8(5)
Ow5[a]	0.024(2)	0.501(2)	0.276(2)	6.0
N1	0.590(2)	0.263(2)	0.210(3)	4.6(6)
N2	0.848(2)	0.010(2)	0.394(3)	4.0(6)

[a] Ow5 corresponds to the water molecule whose occupancy factor was found to be 0.71(2) (B_{iso} was not refined).

TABLE IV

SELECTED BOND DISTANCES (Å) AND ANGLES (°) WITH THEIR STANDARD DEVIATIONS FOR $Zr(OH)_2(NO_3)_2 \cdot 4.7H_2O$

Within the ZrO_8 polyhedra[a]			
M–A		*M–B*	
Zr–OH1^{I}	2.06(1)	Zr–OH1	2.15(1)
Zr–OH2	2.13(1)	Zr–OH2^{II}	2.08(1)
Zr–Ow2	2.30(1)	Zr–Ow1	2.24(1)
Zr–O1	2.44(1)	Zr–O2	2.24(1)
a		*m*	
OH1^{I}–OH2	2.69(1)	OH1^{I}–OH1	2.33(2)
O1 –Ow2	2.81(2)	OH2^{II}–OH2	2.25(2)
		O1 –O2	2.25(2)
		Ow1 –Ow2	2.81(2)
b		*g*	
OH1 –O2	3.07(2)	OH1^{I} –Ow1	2.79(1)
OH1 –Ow1	3.39(1)	OH1^{I} –O2	2.77(2)
OH2^{II}–Ow1	3.18(1)	OH1 –Ow2	2.85(1)
OH2^{II}–O2	3.06(1)	OH1 –O1	2.84(2)
		OH2 –Ow1	2.81(2)
		OH2 –O2	2.76(2)
		OH2^{II}–O1	2.80(2)
		OH2^{II}–Ow2	2.73(2)
Within the NO_3 groups			
N1–O1	1.20(2)	O1–N1–O2	123(2)
N1–O2	1.35(2)	O1–N1–O3	124(2)
N1–O3	1.22(2)	O2–N1–O3	112(2)
N2–O4	1.37(2)	O4–N2–O5	116(2)
N2–O5	1.22(2)	O4–N2–O6	116(2)
N2–O6	1.25(2)	O5–N2–O6	128(2)
Possible hydrogen bonds			
Ow1–Ow3	2.51(2)	Zr–Ow1–Ow3	126.3(5)
Ow1–Ow5	2.50(2)	Zr–Ow1–Ow5	133.0(6)
Ow2–Ow4	2.59(2)	Zr–Ow2–Ow4	133.3(5)
Ow2–O4	2.74(2)	Zr–Ow2–O4	123.3(5)
Ow3–O3	2.96(2)	Zr–Ow2–O5	102.2(4)
OH1–O6	2.71(2)	Ow3–Ow1–Ow5	99.8(6)
OH2–O5	2.81(2)	Ow1–Ow3–O3	153.2(6)
		Ow4–Ow2–O4	91.8(5)

Note. Symmetry code: I, $1 - x, 1 - y, 1 - z$; II, $1 - x, 1 - y, -z$.

[a] Notations according to Hoard and Silverton (*20*).

kinds of nitrate groups are present in the structure, one is nonbonded to the zirconium atom (N2, O4–6) while the other acts as a bidentate ligand (N1, O1–3). It should be noted that the spread in N–O distances from 1.20 to 1.37 Å (Table IV) is not explained by the statistical error calculated from the estimated standard deviation derived from the Rietveld method. However, because it is usually recognized that this later is underestimated, it is likely that the range of N–O distances is mainly due to some inaccuracy in the refinement from powder data. In other respects, it is usual to consider a nitrate group as an unsymmetrically bidentate ligand when the distances from the metal atom to both coordinated oxygens differ by more than 0.2 Å (*23*). In the present study, it is not possible to draw conclusions about this feature, because the distances Zr–O1 and Zr–O2 are 2.44(1) and 2.24(1) Å, respectively. However, it can be noted that the longer N–O distance (N–O2

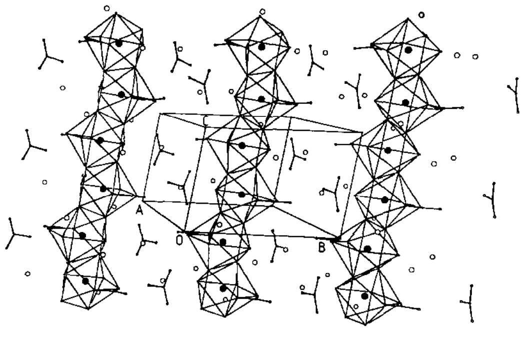

FIG. 2. ORTEP view of the structure of $Zr(OH)_2(NO_3)_2 \cdot 4.7H_2O$ along [100] showing the direction of the infinite chains. Full circles represent the zirconium atoms and open circles correspond to free water molecules.

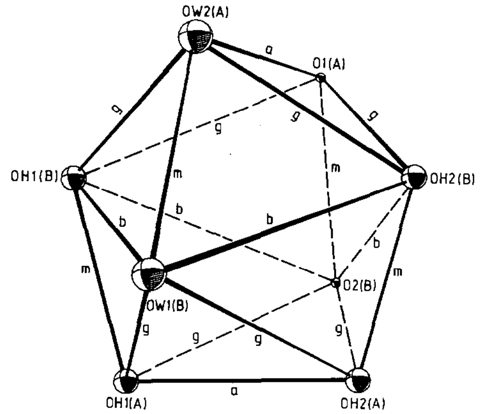

FIG. 4. Coordination sphere of oxygen atoms around zirconium atom in $Zr(OH)_2(NO_3)_2 \cdot 4.7H_2O$. The O–O distances are indicated according to the common notation used by Hoard and Silverton (*20*) to characterize a trigonal dodecahedron.

= 1.35 Å) corresponds to the shortest Zr–O(N) contact. The third oxygen atom O3 is weakly hydrogen-bonded to a water molecule (O3–Ow3 = 2.96 Å). From this study, it follows that a more descriptive formula for this compound would be $[Zr(OH)_2(NO_3)(H_2O)_2](NO_3) \cdot 2.7H_2O$.

The precision reached in this study can be discussed in terms of a comparison with similar examples, e.g., the results of Rietveld refinements for two cadium hydroxide nitrates reported recently (*6*, *8*). Two criteria of precision are often used: the R-factors, commonly calculated during the course of a Rietveld refinement, and the estimated standard deviation (e.s.d.) values of atomic coordinates. For a comparison of refinements from different powder diffraction data, it has been shown (*5*) that the R-profile values, as defined in Table II (R_{wp} and R_p), are not appropriate because they are strongly dependent on the background intensity. Comparison is then only possible by means of the Bragg and structure factor values R_B and R_F. These quantities are, respectively, 0.083 and 0.056 for $Cd_5(OH)_8(NO_3)_2 \cdot 2H_2O$ (*8*), 0.059 and 0.049 for $Cd_3(OH)_5NO_3$ (*6*), and 0.063 and 0.039 for $Zr(OH)_2(NO_3)_2 \cdot 4.7H_2O$, which indicates that the best fit between observed and calculated data was obtained in the case of the zirconium compound. In other respects, the second criteria can be the e.s.d. values of the light atom coordinates (*24*). Again, the same sequence is obtained, since σ(O,N) values are in the ranges 0.019–0.041 Å (mean value: 0.027 Å) for $Cd_5(OH)_8(NO_3)_2 \cdot 2H_2O$, 0.010–0.040 Å (mean value: 0.024 Å) for $Cd_3(OH)_5NO_3$ and 0.007–0.020 Å (mean value: 0.013 Å) for $Zr(OH)_2(NO_3)_2 \cdot 4.7H_2O$. These values demonstrate that a higher precision has been obtained for the zirconium hydroxide ni-

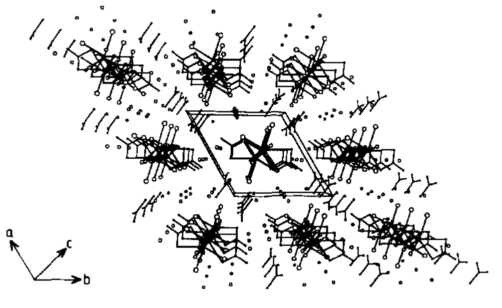

FIG. 3. ORTEP view of the structure of $Zr(OH)_2(NO_3)_2 \cdot 4.7H_2O$ along [001].

trate. This is likely to be the consequence of better powder diffraction data, particularly the lack of a residual preferred orientation effect of the crystallites.

To conclude, the crystal structure of the zirconium hydroxyde nitrate $Zr(OH)_2(NO_3)_2 \cdot 4.7H_2O$ has been solved ab initio from X-ray powder data, obtained from a conventional diffractometer. Clearly, as previously shown for this kind of material (*8*), the accuracy of the results of the refinement cannot rival the precision obtained with single-crystal techniques, but the description of the structure is satisfactory for most chemical purposes. The crystal structure of this compound is characterized by chains and nonbonded nitrate groups and water molecules, which could suggest specific chemical reactions.

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References

1. P. L. Squattrito, P. R. Rudolf, and A. Clearfield, *Inorg. Chem.* **26,** 4240 (1987).

2. D. B. McWhan and G. Lundgren, *Acta Crystallogr. Sect. A* **16,** 36, (1963).

3. O. A. Govorukhina, V. N. Brusentsova, T. N. Vasil'eva, N. L. Mikhailova, S. D. Nikitina, R. I. Schchegoleva, and V. A. Musloboev, *Zh. Neorg. Khim.* **34,** 3159 (1989).

4. D. Louër and M. Louër, *J. Solid State Chem.* **68,** 292 (1987).

5. L. Eriksson, D. Louër, and P.-E. Werner, *J. Solid State Chem.* **81,** 9 (1989).

6. J. Plevert, M. Louër, and D. Loür, *J. Appl. Crystallogr.* **22,** 470 (1989).

7. M. Louër, D. Louër, A. Lopez Delgado, and O. Garcia Martinez, *Eur. J. Solid State Inorg. Chem.* **26,** 241 (1989).

8. P. Benard, M. Louër, and D. Louër, *Powder Diffraction* **6,** 10 (1991).

9. D. Louër and J. I. Langford, *J. Appl. Crystallogr.* **21,** 430 (1988).

10. J. Nusinovici and A. Rehfeldt-Oskierskin, *in* "Collected Abstracts of Powder Diffraction Meeting", Toulouse (France), July 1990, p. 315.

11. D. Louër and M. Louër, *J. Appl. Crystallogr.* **5,** 271 (1972).

12. A. Boultif and D. Louër, *J. Appl. Crystallogr.* (1991), in press.

13. "NIST Crystal Data File" (1988). JCPDS-ICDD, Swarthmore, PA.

14. A. D. Mighell, C. R. Hubbard, and J. K. Stalik, "NBS*AIDS80: A FORTRAN Program for Crystallographic Data Evaluation". Nat. Bur. Stand. (U.S.) Tech. Note 1141 (1981). [NBS*AIDS83 is an expanded version of NBS*AIDS80]

15. B. A. Frenz. *The Enraf-Nonius CAD-4 SDP. Frenz and Associates, Inc., College Station, TX, and Enraf-Nonius, Delft (1986).*

16. J. Rodriguez-Carvajal, *in* "Collected Abstracts of Powder Diffraction Meeting", Toulouse (France), July 1990, p. 127.

17. D. B. Wiles, A. Sakthivel, and R. A. Young, Program DBW3.2S (1987).

18. D. B. Wiles and R. A. Young, *J. Appl. Crystallogr.* **14,** 149 (1981).

19. D. B. McWhan and G. Lundgren, *Inorg. Chem.* **5,** 284 (1966).

20. J. L. Hoard, and J. V. Silverton, *Inorg. Chem.* **2,** 235 (1963).

21. I. J. Bear and W. G. Mumme, *Acta Crystallogr. Sect. B* **25,** 1572 (1969).

22. W. H. Baur and A. A. Khan, *Acta Crystallogr. Sect. B* **26,** 1584 (1970).

23. C. C. Addison, N. Logan, S. C. Wallwork, and C. D. Garner, *Q. Rev.* **25,** 289 (1971).

24. J. C. Taylor, *Aust. J. Phys.* **38,** 519 (1985).