

Structural Analysis of Zirconium Hydroxide Nitrate Monohydrates by X-Ray Powder Diffraction

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The crystal structures of α -Zr(OH)₂(NO₃)₂·1.65H₂O and β -Zr(OH)₂(NO₃)₂·H₂O were determined *ab initio* from laboratory X-ray powder diffraction data. The two zirconium hydroxide nitrates crystallize with triclinic unit cells ($P\bar{1}$) with the parameters: $a = 10.051(3)$ Å, $b = 10.357(3)$ Å, $c = 8.131(2)$ Å, $\alpha = 108.30(2)^\circ$, $\beta = 112.02(2)^\circ$, $\gamma = 79.75(3)^\circ$ for the α phase, and $a = 9.180(3)$ Å, $b = 10.465(4)$ Å, $c = 8.076(2)$ Å, $\alpha = 109.58(3)^\circ$, $\beta = 98.96(3)^\circ$, $\gamma = 80.43(3)^\circ$ for the β phase. An interpretation of the Patterson functions led to the location of two independent Zr atoms for the α and β forms. The light atom coordinates were determined from successive three-dimensional Fourier maps. The structure of α -Zr(OH)₂(NO₃)₂·1.65H₂O is built from edge sharing ZrO₈ trigonal dodecahedra, through double hydroxyl bridges, to form infinite neutral zigzag chains of chemical composition [Zr(OH)_{4/2}(NO₃)₂]_n, running along [011]. The 8-fold coordination of each Zr atom is completed by four oxygens from bidentate nitrate groups. They are involved in a complex hydrogen bonding network occurring between the chains via “free” water molecules. The loss of the weakly bonded water molecule leads to the β form without collapse of the 1D framework of the precursor. In the β variety, the 8-fold coordination is preserved for the two Zr atoms. However, the exact shapes of the polyhedra have not been precisely defined. © 1997 Academic Press

molecules (6), consists of isolated infinite linear macrocations [Zr(OH)_{4/2}(NO₃)(H₂O)₂]_n⁺, which are balanced by an equivalent amount of nitrate anions located between the chains. The 2D structure of Zr(OH)₃NO₃ (7) is built from neutral [Zr(OH)_{4/2}(OH)_{2/2}(NO₃)₂]_n layers resulting from the condensation of chains, formed by edge-sharing ZrO₈ trigonal dodecahedra, similar to those found in the 1D-type structure. In a previous powder diffraction study (3), we have also identified three modifications of Zr(OH)₂(NO₃)₂·H₂O (α , β , and γ). Among them, the α form, α -Zr(OH)₂(NO₃)₂·(1 + x)H₂O, is nonstoichiometric in water molecules, with $0 \leq x \leq 1$. The powder diffraction patterns of these three varieties were indexed on the basis of triclinic unit cells and attempts to solve *ab initio* the complete crystal structure were unsuccessful due to low resolution of the patterns arising from significant diffraction-line broadening. However, the atomic positions of the heavy atoms were proposed for the α and γ phases. From an increasing experience in structural analyses from powder data and the development of new approaches for structure solution, a new study of the powder diffraction patterns has been carried out. The present study deals with the structural investigation of zirconium hydroxide nitrate monohydrates.

INTRODUCTION

Similar to the variety of zirconium hydroxide sulfates reported in literature (1,2), the related family of hydroxide nitrates exhibits a number of phases, which have been clearly identified from temperature-dependent X-ray powder diffraction (TDXD) (3). These phases are generally obtained in a powder form and the application of the developments occurred in the past 10 years in *ab initio* structure determination (see, for example, Ref. (4)) has revealed an interesting crystal chemistry based on 1-dimensional (1D) and 2-dimensional (2D) structure types. The 1D structure of Zr(OH)₂(NO₃)₂·4.7H₂O (5), as well as that partially described for the stoichiometric phase with 4 water

EXPERIMENTAL CONSIDERATIONS

Materials

The commercial compound ZrO(NO₃)₂· n H₂O (S95623R) was supplied by Johnson Matthey. In a previous work (3), the chemical composition of the material was elucidated leading to the formula α -Zr(OH)₂(NO₃)₂·(1 + x)H₂O. Also, it was shown that the water content is dependent on the ambient hygrometric conditions. From the present structural study, the value of x for the powder sample investigated here was found to be 0.65, and this sample was stable at room temperature (20°C). As demonstrated by TDXD (3), β -Zr(OH)₂(NO₃)₂·H₂O can be obtained from the thermal transformation of the α phase in

nitrogen in the temperature range 30–55°C. Its thermal stability is greater in air and a sample of the β phase was prepared at 90°C. The third known modification of the monohydrated basic salt, γ -Zr(OH)₂(NO₃)₂·H₂O (3), was obtained from the decomposition, in air and under isothermal conditions at 24°C, of the commercial product ZrO(NO₃)₂·xH₂O (Aldrich Products, No. 29,349-3), whose exact chemical formula Zr(OH)₂(NO₃)₂·(4 + x)H₂O was established elsewhere (3, 5).

X-Ray Diffraction Data Collection

Powder diffraction data were collected with a Siemens D500 high-resolution powder diffractometer using the Bragg–Brentano geometry. Pure CuK α ₁ radiation ($\lambda = 1.540598 \text{ \AA}$) was produced with an incident beam curved-crystal germanium monochromator with asymmetric focusing (8). The alignment of the instrument was checked by means of the 00 l diffraction lines of fluorophlogopite mica standard material (NIST SRM 675); the error on the zero point was estimated less than 0.01°(2 θ). Powder specimens of the α and γ forms were mounted in a top-loaded sample holder and data were collected at 20 and 24°C, respectively. Slits in the incident beam were adjusted for a complete illumination of the sample at 12°(2 θ). No significant preferred orientation of the crystallites was detected from different preparations of the two samples in the sample holder. For the β phase, sensitive to humidity, the powder sample was mounted in an air-tight sample holder and data collection was carried out at 23°C. Each powder diffraction pattern was scanned in steps of 0.02°(2 θ), with fixed counting times (45 sec). After data collection, the stability of the X-ray source and, also, of the samples was checked by measuring again the first few lines of the patterns. The quality and resolution of the three diffraction patterns can be seen from the average FWHM of the lines at about 40°(2 θ), i.e., 0.12° for α -Zr(OH)₂(NO₃)₂·1.65H₂O, 0.13° for β -Zr(OH)₂(NO₃)₂·H₂O, and 0.24° for γ -Zr(OH)₂(NO₃)₂·H₂O. These values have to be compared with the instrumental resolution function (IRF) at the same angle, i.e., 0.065°(2 θ), obtained from

an annealed barium fluoride sample (8). The precise determination of peak positions was carried out by means of the Socabim fitting program PROFILE, available in the PC software package DIFFRAC-AT supplied by Siemens.

DATA ANALYSIS

Powder Pattern Indexing

The powder patterns of the three monohydrated zirconium basic salts have been already indexed by means of the computer program DICVOL91 (9) and the parameters of three conventional triclinic unit cells have been reported elsewhere (see Table 3 in Ref. (3)). In the course of the present study, new powder data were collected for the β and γ phases, and then indexed by means of DICVOL91, from which resulted the same solutions, but with a significant improvement of the figures of merit. After reviewing the complete data by means of the computer program NBS*AIDS83 (10), the parameters of the conventional unit cells are as follows:

$$\beta\text{-Zr(OH)}_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}: a = 9.180(3) \text{ \AA}, b = 10.465(4) \text{ \AA}, \\ c = 8.076(2) \text{ \AA}, \alpha = 109.58(3)^\circ, \beta = 98.96(3)^\circ, \gamma = 80.43(3)^\circ \\ [M_{20} = 30, F_{30} = 64(0.0112, 42)].$$

$$\gamma\text{-Zr(OH)}_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}: a = 7.421(2) \text{ \AA}, b = 8.348(3) \text{ \AA}, \\ c = 6.749(2) \text{ \AA}, \alpha = 108.94(3)^\circ, \beta = 98.81(3)^\circ, \gamma = 71.16(2)^\circ \\ [M_{20} = 49, F_{29} = 92(0.0085, 37)].$$

The powder data for the three compounds have been deposited with the ICDD (11). It is interesting to note that some apparent parametric analogies exist between the unit cells of all zirconium basic nitrates (Table 1). In order to display these crystallographic relationships, it has been found convenient to transform the conventional cell of γ -Zr(OH)₂(NO₃)₂·H₂O given above by the transformation matrix $[1\ 0\ 0 / \bar{1}\ 1\ 0 / 0\ 0\ 1]$ and to use the setting with unique axis c for the monoclinic unit cell of Zr(OH)₃NO₃ (7).

TABLE 1
Unit Cell Parameters of Six Zirconium Hydroxide Nitrates

Compound	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å ³)
Zr(OH) ₂ (NO ₃) ₂ ·4.7H ₂ O (5)	9.541(1)	9.590(1)	6.753(1)	98.64(1)	92.89(1)	118.60(1)	531.0(3)
Zr(OH) ₂ (NO ₃) ₂ ·4H ₂ O ^a (6)	7.408	9.894	6.741	97.45	99.78	93.71	480.9
γ -Zr(OH) ₂ (NO ₃) ₂ ·H ₂ O (3)	7.421(2)	9.206(2)	6.749(2)	99.84(3)	98.81(3)	120.88(3)	373.7(1)
Zr(OH) ₃ (NO ₃) (7)	7.6137(9)	9.1146(9)	6.7670(7)	90.0	90.0	102.61(1)	458.28(6)
α -Zr(OH) ₂ (NO ₃) ₂ ·1.65H ₂ O (3)	10.051(3)	10.357(3)	8.131(2)	108.30(2)	112.02(2)	79.75(3)	743.2(3)
β -Zr(OH) ₂ (NO ₃) ₂ ·H ₂ O (3)	9.180(3)	10.465(4)	8.076(2)	109.58(3)	98.96(3)	80.43(3)	716.7(3)

^aFrom single crystal diffraction data.

Table 1 displays the analogies between the four first cells, i.e., *b* and even more *c*, the direction of the chains in the three known structures (5–7), have the same order of magnitude. Also, striking similarities appear between the cells of α -Zr(OH)₂(NO₃)₂ · 1.65H₂O and β -Zr(OH)₂(NO₃)₂ · H₂O. Indeed, only *a* and β parameters are significantly changed during the loss of 0.65 water molecules. This preliminary analysis suggests that the same kind of zigzag chains (along *c*) could exist in the first four structures, which is already well verified for Zr(OH)₂(NO₃)₂ · 4.7H₂O and Zr(OH)₃NO₃, and that a second framework based on zirconium polyhedra should be present in the last two compounds. To shed light on all these crystallographic relationships, it would be of interest to know the structures of the polymorphic monohydrated α , β and γ phases. Since no single crystals were obtained, the three triclinic structures have been investigated with modern powder diffraction methods, assuming the centrosymmetric space group. Nevertheless, compared to the partial structure described elsewhere (3) for the γ phase, no additional information could be extracted from the new powder data set, a consequence of the significant diffraction line broadening reported above.

Structure Determination and Refinement

Integrated intensities were extracted by means of the program AJUST (12), based on a new recursive formula (13) for refining integrated intensities of partially overlapping reflections, according to the principles introduced first by Le Bail *et al.* (14). The extracted integrated intensities were used as input data in the program SHELXS-86 (15). Three-dimensional Patterson syntheses were generated from each powder data set. For both α -Zr(OH)₂(NO₃)₂ · 1.65H₂O and β -Zr(OH)₂(NO₃)₂ · H₂O, the vector sets were consistent with two independent heavy atoms leading to *Z* = 4. At this stage, it was interesting to see that the coordinates of Zr atoms were roughly the same in the two hydrated basic salts. The refinement of the Zr atomic positions in the two analyses led to a common crystal-structure model indicator *R_F* ≈ 0.25%. The subsequent stage in the *ab initio* structure determination from powder data was the location of the remaining light atoms (N and O). The procedure consisted in the calculation of successive Fourier maps by using the program SHELXL93 (16), alternating with Rietveld refinements carried out with the program FULLPROF (17). This critical operation was performed by increasing the angular range gradually. Nevertheless, it is well known that the success and precision of both structure solution and refinement depend on the number and resolution of diffraction lines in the selected range (i.e., the number of unambiguous data with regard to the complexity level of the structure and the number of atoms in the asymmetric unit). Since the quality of the X-ray powder diffraction patterns were not

the same for the α and β phases, the two structure determinations and refinements will be described separately:

(i) α -Zr(OH)₂(NO₃)₂ · 1.65H₂O. The unit cell of the α phase contains 25 independent atoms including two Zr atoms. It was possible to identify the four OH[−] bonded to the zirconium atoms and four symmetry independent bidentate NO₃ groups. The remaining oxygen atoms belong to “free” water molecules. The final cycle of the least-squares Rietveld refinement, based on 1364 reflections [8.5°–95°(2 θ)], involved 110 parameters including 94 structural parameters. The details of the Rietveld refinement are summarized in Table 2. Figure 1 shows the final Rietveld plot corresponding to the satisfactory residuals *R_F* = 0.043 and *R_{wp}* = 0.117. The final atomic positions and thermal parameters are given in Table 3. It should be noted that the thermal isotropic parameters for some light atoms were refined in blocs, taking into account their chemical function in the structure. The water molecule Ow3 exhibits a high temperature factor (≈ 5 Å²) compared to the two other “free” water molecules. The occupancy rate of Ow3 has been refined to 0.65. From a chemical point of view, this result is in accordance with the observed nonstoichiometry of the water molecules in the α phase (3). Selected bond lengths and angles are listed in Table 4.

(ii) β -Zr(OH)₂(NO₃)₂ · H₂O. The quality of the powder diffraction data of β -Zr(OH)₂(NO₃)₂ · H₂O was lower than that of α -Zr(OH)₂(NO₃)₂ · 1.65H₂O. Although some light atoms (N, O) could be located without difficulty, part of the structure model was deduced from the apparent structural analogy with the α phase, i.e., both phases possess similar unit-cell parameters (Table 1) and heavy atom positions. The most ambiguous Fourier peaks corresponded to atoms belonging to nitrate groups. It is interesting to point out that only two of the three water molecules observed in α -Zr(OH)₂(NO₃)₂ · 1.65H₂O, are found in the β form (Ow1 and Ow2), so that only 24 atoms were taken

TABLE 2
Details of Rietveld Refinements for α -Zr(OH)₂(NO₃)₂ · 1.65H₂O and β -Zr(OH)₂(NO₃)₂ · H₂O

Compound	α -Zr(OH) ₂ (NO ₃) ₂ · 1.65H ₂ O	β -Zr(OH) ₂ (NO ₃) ₂ · H ₂ O
Space group		<i>P</i> $\bar{1}$
<i>Z</i>		4
No. of atoms	25	24
Wavelength (Å)		1.540598
Step scan increment (°2 θ)		0.02
2 θ range (°)	8.5–95	8–95
No. of reflections	1364	1315
No. of structure parameters	94	29
No. of profile parameters	16	16
<i>R_F</i>	0.043	0.083
<i>R_B</i>	0.052	0.147
<i>R_p</i>	0.085	0.133
<i>R_{wp}</i>	0.117	0.168

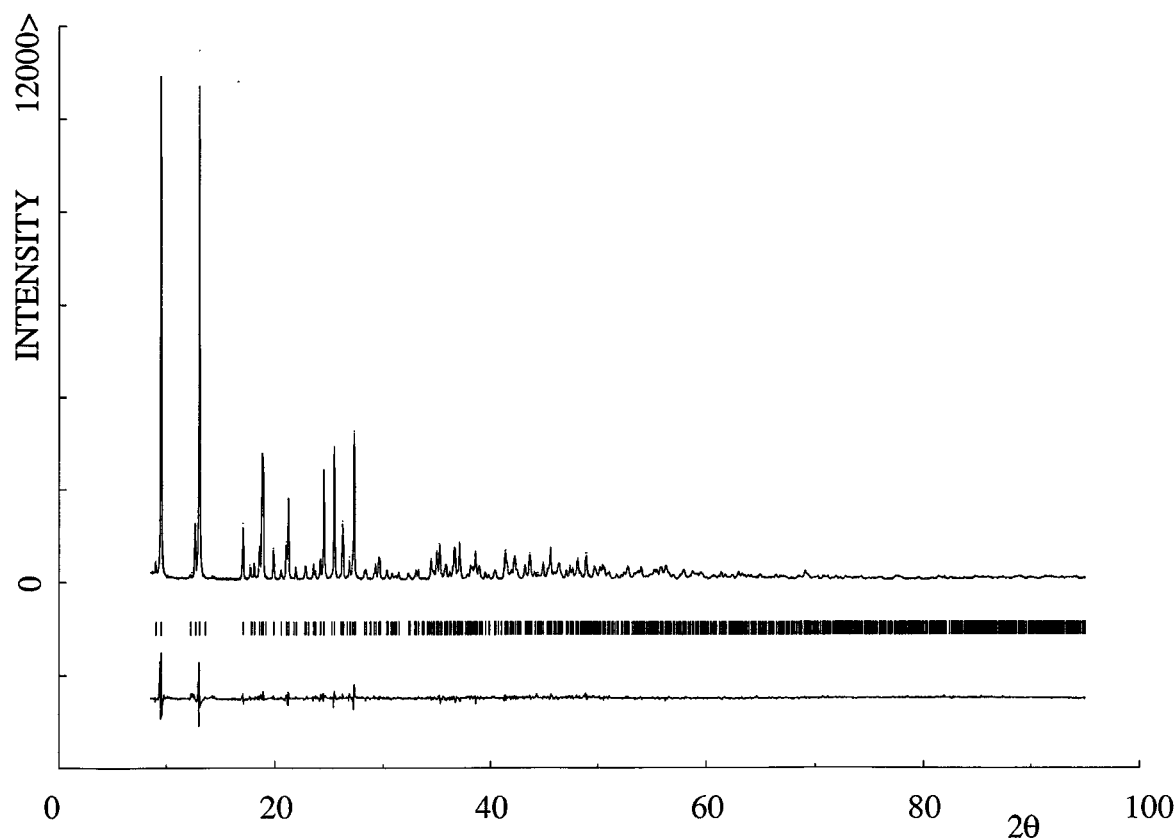


FIG. 1. Final Rietveld plot of α -Zr(OH)₂(OH)₂ · 1.65H₂O. The upper trace shows the observed data as dots, while the calculated pattern is represented by solid line. The lower trace is a plot of the difference: observed minus calculated. The vertical markers show positions calculated for Bragg reflections.

into consideration in the asymmetric unit cell of β -Zr(OH)₂(NO₃)₂ · H₂O. Due to the medium quality of the powder data, only 45 parameters, including 16 usual profile parameters, were refined in the final cycle of the Rietveld procedure, based on 1315 reflections [8° – $95^\circ(2\theta)$]. It was necessary to apply severe constraints on some structural parameters and only an overall temperature parameter was refined. In spite of these limitations in the structure refinement, the model proposed for β -Zr(OH)₂(NO₃)₂ · H₂O may be considered as chemically correct from the great analogy with the structure of α -Zr(OH)₂(NO₃)₂ · 1.65H₂O. The final cycle converged to reasonably low structure model and profile residuals $R_F = 0.083$ and $R_{wp} = 0.168$. Figure 2 exhibits the corresponding fit obtained between calculated and observed patterns. Final atomic parameters are reported in square brackets in Table 3, whereas selected bond distances and angles are given in Table 5.

DESCRIPTION AND DISCUSSION

α -Zr(OH)₂(NO₃)₂ · 1.65H₂O

The structure of α -Zr(OH)₂(NO₃)₂ · 1.65H₂O consists of isolated infinite zigzag chains of edge sharing ZrO₈ poly-

hedra running along [011], with “free” water molecules located between the chains (Fig. 3). The chains are neutral with the chemical composition [Zr(OH)_{4/2}(NO₃)₂]_n. The arrangement within a chain may be described from an alternation of two distinct pairs of zirconium atoms bonded by double hydroxyl bridges according to the sequence [··· Zr1–(OH)₂–Zr1–(OH)₂–Zr2–(OH)₂–Zr2···] as illustrated in Fig. 4. The two Zr1O₈ and Zr2O₈ polyhedra have the OH2–OH3 edge in common, whereas the OH1–OH1^I and OH4–OH4^{II} edges bridge two Zr1O₈ and two Zr2O₈, respectively. The shortest Zr···Zr distances within a chain are 3.442 Å between two Zr1, 3.463 Å between two Zr2, and 3.478 Å between Zr1 and Zr2. This result indicates that the chains are homogeneous and, consequently, the geometric differences between the two independent ZrO₈ polyhedra must be small. In addition to the fact that Zr1 and Zr2 atoms have an eightfold coordination, they have a similar environment formed by ligands of two different chemical types, i.e., 4X and 4Y according to Hoard and Silvertown notation (18). In the present case, four oxygen atoms from hydroxyl groups [2 × OH1, OH2, OH3 for Zr1 and 2 × OH4, OH2, OH3 for Zr2] and four nitrate oxygens [O1, O2, O4, O5 for Zr1 and O7, O8, O10, O11 for Zr2]

TABLE 3
Fractional Atomic Coordinates and Thermal Isotropic Parameters with Their Standard Deviations for α -Zr(OH)₂(NO₃)₂ · 1.65H₂O and for β -Zr(OH)₂(NO₃)₂ · H₂O in Square Brackets

Atom	x	y	z	B _{iso} (Å ²)
Zr1	−0.0846(6) [−0.0865(9)]	0.1596(5) [0.1559(8)]	−0.0023(7) [0.006(1)]	2.4(2)
Zr2	0.1134(5) [0.1285(9)]	0.3818(4) [0.3715(9)]	0.4036(6) [0.358(1)]	1.1(1)
Ow1	−0.316(3) [−0.353(5)]	−0.134(2) [−0.066(4)]	0.029(4) [0.198(5)]	2.2(8)
Ow2	−0.187(3) [−0.206(5)]	−0.388(3) [−0.398(4)]	0.064(3) [0.113(6)]	0.5(8)
Ow3	0.473(5)	0.935(5)	0.814(6)	4.77(3)
OH1	−0.095(2) [−0.153(3)]	−0.031(3) [−0.009(2)]	0.036(3) [0.035(3)]	0.4(4) ^a
OH2	0.048(3) [0.066(3)]	0.325(3) [0.301(2)]	0.109(4) [0.105(3)]	0.4(4) ^a
OH3	−0.029(3) [−0.046(3)]	0.226(3) [0.250(2)]	0.302(4) [0.332(3)]	0.4(4) ^a
OH4	−0.021(3) [−0.061(3)]	0.553(3) [0.554(2)]	0.371(3) [0.378(3)]	0.4(4) ^a
N1	−0.132(4) [−0.141(2)]	0.108(4) [0.124(2)]	−0.368(5) [−0.328(3)]	1.6(9)
O1	−0.062(3) [−0.051(2)]	0.207(3) [0.204(2)]	−0.257(3) [−0.229(3)]	1.8(6) ^b
O2	−0.208(3) [−0.217(2)]	0.057(3) [0.068(2)]	−0.317(4) [−0.261(3)]	1.8(6) ^b
O3	−0.171(3) [−0.136(2)]	0.096(3) [0.082(2)]	−0.543(4) [−0.493(3)]	1.8(9)
N2	−0.346(5) [−0.363(2)]	0.305(4) [0.323(2)]	−0.005(7) [0.071(2)]	5.1(9)
O4	−0.257(3) [−0.261(2)]	0.341(3) [0.389(2)]	−0.047(4) [0.067(2)]	2.1(6) ^c
O5	−0.312(3) [−0.338(2)]	0.168(3) [0.239(2)]	0.001(4) [0.155(2)]	2.1(6) ^c
O6	−0.485(3) [−0.449(2)]	0.330(3) [0.295(2)]	−0.055(4) [−0.022(2)]	4.8(9)
N3	0.327(4) [0.336(3)]	0.213(4) [0.195(2)]	0.522(5) [0.414(2)]	0.9(9)
O7	0.314(3) [0.323(3)]	0.248(3) [0.243(2)]	0.376(4) [0.288(2)]	2.1(6) ^d
O8	0.244(3) [0.226(3)]	0.252(3) [0.205(2)]	0.618(4) [0.495(2)]	2.1(6) ^d
O9	0.441(3) [0.456(3)]	0.129(2) [0.123(2)]	0.566(4) [0.447(2)]	0.6(8)
N4	0.326(4) [0.322(2)]	0.560(4) [0.589(2)]	0.507(5) [0.405(3)]	2.8(9)
O10	0.251(3) [0.307(2)]	0.508(3) [0.499(2)]	0.349(4) [0.255(3)]	2.4(6) ^e
O11	0.281(3) [0.246(2)]	0.524(3) [0.592(2)]	0.625(4) [0.524(3)]	2.4(6) ^e
O12	0.392(4) [0.430(2)]	0.656(3) [0.658(2)]	0.570(5) [0.445(3)]	4.9(9)

Note. For α -Zr(OH)₂(NO₃)₂ · 1.65H₂O: ^{a,b,c,d,e} indicate that some B_{iso} factors have been constrained to vary in the same manner. Ow3 corresponds to the water molecule whose occupancy factor was found to be 0.65(3). For β -Zr(OH)₂(NO₃)₂ · H₂O: an overall B temperature factor has been refined.

are coordinated in the shape of a dodecahedron with triangular faces as shown in Fig. 5. The Zr1–O and Zr2–O distances spread in the respective ranges 2.11–2.37 Å and 2.05–2.38 Å. The corresponding mean values (2.24 and 2.22 Å) may be compared to those calculated for Zr(OH)₂(NO₃)₂ · 4.7H₂O (2.21 Å), Zr(OH)₂(NO₃)₂ · 4H₂O (2.21 Å), and Zr(OH)₃NO₃ (2.22 Å). In the structure of α -Zr(OH)₂(NO₃)₂ · 1.65H₂O, the eight Zr–OH distances are lower than 2.23 Å, whereas the remaining eight distances [Zr–O(NO₃)] are greater than 2.30 Å. Such bond lengths, with close values, are observed within similar ZrO₈ dodecahedral groupings and, also, in related eightfold configurations for Zr atoms, as the square antiprism (18–20) or the bicapped trigonal prism (1). The interatomic distances, Zr–O and O–O, describing the specific geometry of a triangular dodecahedron, are divided into six groups [*M–A*, *M–B*, *a*, *b*, *g*, and *m*] (see Table 4 and Fig. 5), in accordance with the notation of Hoard and Silverton for the $\bar{4}2m$ symmetry of the ideal Mo(CN)₈^{4−} coordination (18). This specific description allows the evaluation of the deviation from the ideal shape (18) and then makes easier the comparison between close dodecahedral coordinations, as those

found in the structure of reported zirconium hydroxide nitrates (5–7) and other related basic salts (1, 21). As usual in zirconium hydroxide salts, the shortest Zr–O bonds are attributed to the strongest contacts where O≡OH[−]. From the average values of the *M–A* and *M–B* type distances, 2.22 and 2.26 Å for Zr1–O and 2.26 and 2.17 Å for Zr2–O, the characteristic bond-length ratio *M–A*/*M–B* may be calculated for the two dodecahedra encountered in α -Zr(OH)₂(NO₃)₂ · 1.65H₂O. It is 0.982 for the first, which is not significantly different from unity, the value deduced from the theoretical approach of the dodecahedron in the “hard sphere model” (18). It is also close to 1.008 observed in the true case of Zr(OH)₂SO₄ · 3H₂O (1). For the second dodecahedron, the value of 1.041 compares well with both the value 1.052 found in Zr(OH)₂CrO₄ (22) and the value 1.03 considered as a reference for the “most favorable” (MF) Zr dodecahedron (18). Moreover, the two ratios are more or less comparable with 1.023 and 1.025 obtained for Zr(OH)₂(NO₃)₂ · 4.7H₂O (5) and Zr(OH)₃NO₃ (7), respectively. In other respects, additional strong analogies occur with the two last compounds with regard to the four averaged nonequivalent edges (*m*, *a*, *b*, *g*) for each ZrO₈

TABLE 4
Selected Bond Distances (Å) and Angles (°) with Their
Standard Deviations for α -Zr(OH)₂(NO₃)₂·1.65H₂O

Within the ZrO ₈ polyhedra ^a			
M–A		M–B	
Zr1–OH1	2.12(3)	Zr1–OH1 ^I	2.10(3)
Zr1–OH2	2.11(3)	Zr1–OH3	2.22(3)
Zr1–O1	2.37(3)	Zr1–O2	2.37(3)
Zr1–O5	2.28(3)	Zr1–O4	2.34(3)
Av.	2.22	Av.	2.26
Zr2–OH2	2.14(3)	Zr2–OH3	2.10(3)
Zr2–OH4 ^{II}	2.23(2)	Zr2–OH4	2.05(3)
Zr2–O8	2.38(3)	Zr2–O7	2.27(3)
Zr2–O10	2.30(3)	Zr2–O11	2.27(3)
Av.	2.26	Av.	2.17
Zr(OH) ₃ NO ₃	2.248	Zr(OH) ₃ NO ₃	2.197
Zr(OH) ₂ (NO ₃) ₂ ·4.7H ₂ O	2.23	Zr(OH) ₂ (NO ₃) ₂ ·4.7H ₂ O	2.18
a (M = Zr1)		a (M = Zr2)	
OH1–O5	2.71(4)	OH2–O10	2.77(4)
OH2–O1	2.70(4)	OH4 ^{II} –O8	2.75(4)
Av.	2.705	Av.	2.76
Zr(OH) ₃ NO ₃	2.676		
Zr(OH) ₂ (NO ₃) ₂ ·4.7H ₂ O	2.75		
m (M = Zr1)		m (M = Zr2)	
OH2–OH3	2.51(4)	OH2–OH3	2.51(4)
OH1–OH1 ^I	2.44(4)	OH4–OH4 ^{II}	2.52(4)
O1–O2	2.14(4)	O7–O8	2.31(4)
O4–O5	2.15(4)	O10–O11	2.11(4)
Av.	2.31	Av.	2.36
Zr(OH) ₃ NO ₃	2.337		
Zr(OH) ₂ (NO ₃) ₂ ·4.7H ₂ O	2.41		
b (M = Zr1)		b (M = Zr2)	
O4–OH3	3.32(4)	O7–OH3	3.31(5)
O2–O4	3.16(4)	O7–O11	2.98(4)
OH1 ^I –OH3	3.38(4)	OH3–OH4	3.26(4)
OH1 ^I –O2	3.07(4)	OH4–O11	2.98(4)
Av.	3.23	Av.	3.13
Zr(OH) ₃ NO ₃	3.108		
Zr(OH) ₂ (NO ₃) ₂ ·4.7H ₂ O	3.18		
g (M = Zr1)		g (M = Zr2)	
OH2–OH1 ^I	2.92(4)	OH2–OH4	2.83(4)
OH3–OH1	2.86(4)	OH3–OH4 ^{II}	2.85(4)
OH2–O4	2.84(5)	OH2–O7	2.91(4)
OH3–O5	2.99(4)	OH3–O8	2.96(4)
OH1 ^I –O1	2.82(4)	OH4–O10	2.75(4)
OH1–O2	3.03(4)	OH4 ^{II} –O11	2.87(4)
O1–O4	2.96(4)	O7–O10	2.71(4)
O2–O5	2.97(4)	O8–O11	2.88(4)
Av.	2.92	Av.	2.84
Zr(OH) ₃ NO ₃	2.913		
Zr(OH) ₂ (NO ₃) ₂ ·4.7H ₂ O	2.79		
Within the NO ₃ groups			
N1–O1	1.25(5)	O1–N1–O2	119(7)
N1–O2	1.24(5)	O1–N1–O3	118(6)
N1–O3	1.30(5)	O2–N1–O3	117(6)
N2–O4	1.22(6)	O4–N2–O5	110(6)
N2–O5	1.41(5)	O4–N2–O6	130(9)
N2–O6	1.31(6)	O5–N2–O6	110(6)

TABLE 4—Continued

Within the NO ₃ groups			
N3–O7	1.31(5)	O7–N3–O8	127(7)
N3–O8	1.28(5)	O7–N3–O9	112(5)
N3–O9	1.32(5)	O8–N3–O9	121(7)
N4–O10	1.22(5)	O10–N4–O11	108(5)
N4–O11	1.38(5)	O10–N4–O12	132(9)
N4–O12	1.16(6)	O11–N4–O12	116(7)
Possible hydrogen bonds			
OH1 ... Ow1	2.60(4)	Zr1–OH1 ... Ow1	129(3)
OH2 ... Ow2	2.60(4)	Zr1–OH2 ... Ow2 ^I	124(3)
OH4 ... Ow2 ^{III}	2.62(3)	Zr2–OH4 ... Ow2 ^{III}	128(3)
Ow1 ... Ow3 ^{II}	2.66(6)	Ow2...Ow1...Ow3 ^{II}	138(5)
Ow1 ... Ow3 ^{IV}	2.35(5)	Ow2...Ow1...Ow3 ^{IV}	133(5)
Ow1 ... Ow2	2.77(5)	Zr1–O1 ... Ow2 ^I	101(2)
O1 ... Ow2 ^I	3.02(5)	Zr1–O4 ... Ow2 ^{III}	123(3)
O4 ... Ow2 ^{III}	2.79(4)	Zr1–O5 ... Ow3 ^{II}	139(5)
O5 ... Ow3 ^{II}	3.08(6)	Zr2–O7 ... Ow1 ^I	115(2)
O7 ... Ow1 ^I	3.13(4)	Zr2–O8 ... Ow2 ^V	105(2)
O8 ... Ow2 ^V	2.74(4)	Zr2–O10 ... Ow2 ^I	101(2)
O10 ... Ow2 ^I	3.05(4)		
O3 ... Ow3 ^{VI}	3.01(6)		
O12 ... Ow3	2.99(6)		
Ow3 ... Ow3 ^{VII}	2.77(6)		
Shortest Zr ... Zr distances			
Zr1 ... Zr1 ^I	3.442(8)	Zr2 ... Zr2 ^{II}	3.463(7)
Zr1 ... Zr2	3.478(7)		

Note. Symmetry code: I, $-x, -y, -z$; II, $-x, 1-y, 1-z$; III, $x, 1+y, z$; IV, $x-1, y-1, z-1$; V, $-x, -y, 1-z$; VI, $-x, 1-y, -z$; VII, $1-x, 2-y, 2-z$.

^aNotation according to Hoard and Silverton (18).

polyhedron ranged according the sequence $m < a < g < b$ [$m = a < g < b$ in the MF case (18)]. It can be stated that the shorter O–O bonds in such Zr polyhedra occur over the trapezoid m edges (see Fig. 5), i.e., those which are responsible for the polymerization through the OH–OH bridges and those involving a chemical function such as the bidentate nitrate group. It would not be reasonable to emphasize too much these last structural features, since they should have to be interpreted in terms of ligand coulombic repulsions and σ and π bondings. In spite of the medium accuracy arising from X-ray powder diffraction data with low resolution, it is worth noting that the present results are in good accordance with previous studies based on crystal (2, 6) or powder (1, 5, 7) diffraction data.

According to the classification of the coordination modes suggested by Addison *et al.* (23), the four unequivalent nitrate groups act as bidentate groups. It is usual to consider a nitrate group as an unsymmetrically bidentate ligand when the distances from the metal to both coordinated oxygen atoms differ more than 0.2 Å. Although this criteria is verified for each nitrate group in this study (see Table 4), it is not sufficient to range them in the classification proposed by Leclaire (24). It should be pointed out that the maximum

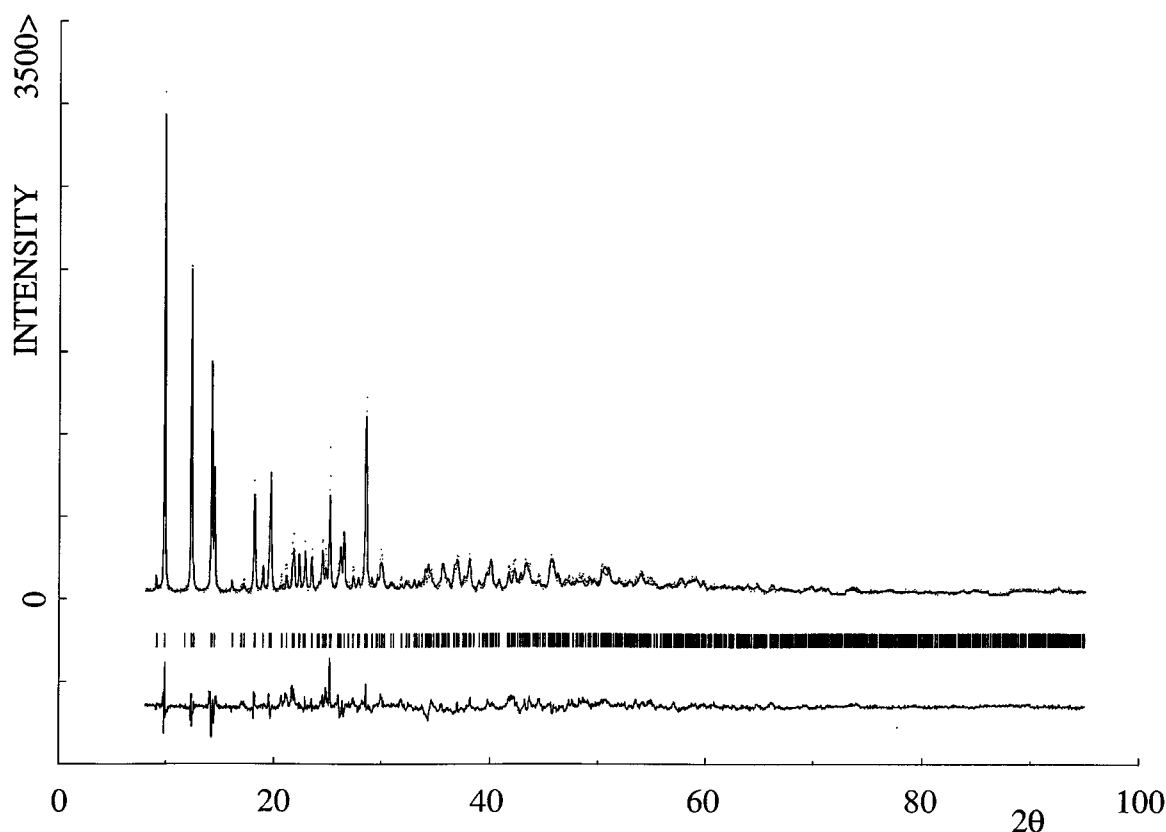


FIG. 2. Final Rietveld plot of β -Zr(OH)₂(OH)₂ · H₂O. The upper trace shows the observed data as dots, while the calculated pattern is represented by solid line. The lower trace is a plot of the difference: observed minus calculated. The vertical markers show positions calculated for Bragg reflections.

discrepancy between two N–O distances is close to 0.25 Å and the O–N–O angles are, in general, significantly far from 120°. However, half the nitrate are almost regular, i.e., N1O₃ and N3O₃ with bond lengths and angles in the ranges (1.24–1.30 Å, 117°–119°) and (1.28–1.32 Å, 112°–127°), respectively.

Although the hydrogen atoms were not located in this powder work, the hydrogen bonding scheme was clearly suggested by an examination of the O...Ow bonds, as well as the Zr–O...Ow and Ow...Ow...Ow angles, where O≡Ow, OH, O(NO₃). All of them agree with the criteria required for such bonds (25). As shown in Table 4, a complex hydrogen-bonding network between the chains, made up through the “free” water molecules, serves to hold the Zr chains together. The role of the nitrate and hydroxyl oxygens, except OH3, in propagating the 1D structure by participation in hydrogen bonding is far from negligible. It is interesting to note that Ow2 is largely more involved than Ow3 and even more than Ow1 in this scheme. Also, the hydrogen bond lengths from Ow2 are, in average, shorter. These features are consistent with the low isotropic *B* value for Ow2. It is clear that this water molecule plays a crucial role in contributing to the stability of the 1D structure.

Moreover, it is also important to point out that Ow3, considered as the first water molecule which leaves the structure of α -Zr(OH)₂(NO₃)₂ · 1.65H₂O, is not connected to Ow2. Ow3 is weakly bonded to the chains via nitrate oxygens (2.99, 3.01, 3.08 Å), which is consistent with a high temperature factor for Ow3. The shortest O...O distances (2.35 Å) occurring between two “free” water molecules, Ow1 and Ow3, may be considered as a strong bond, but it is of less importance for the stability of this 1D structure.

The precision achieved in this study can be discussed from the e.s.d.’s on light-atom coordinates (26). On the basis of the 23 corresponding atoms in the asymmetric unit of α -Zr(OH)₂(NO₃)₂ · 1.65H₂O, σ (O,N) spreads in the range (0.020–0.057) with an average value 0.034. These results can be compared with those obtained for Zr(OH)₂(NO₃)₂ · 4.7H₂O since the chemical formula and the contrast between atoms are similar. The two compounds differ by the unit cell dimensions (see Table 1) and the content of the cells (16 atoms for Zr(OH)₂(NO₃)₂ · 4.7H₂O and 25 for Zr(OH)₂(NO₃)₂ · 1.65H₂O). A higher precision was clearly obtained for the less complex structure, Zr(OH)₂(NO₃)₂ · 4.7H₂O, since σ (O, N) were in the range (0.007–0.020 Å) with an average e.s.d. of 0.013 Å.

TABLE 5
Selected Bond Distances (Å) and Angles (°) with Their Standard Deviations for β -Zr(OH)₂(NO₃)₂·H₂O

Within the ZrO ₈ polyhedra ^a							
Zr1–OH1	2.02(3)	Zr1–OH1 ^I	2.46(3)	Zr2–OH2	1.95(2)	Zr1–OH3	2.15(3)
Zr1–OH2	2.11(3)	Zr1–OH3	2.47(2)	Zr2–OH4 ^{II}	2.17(2)	Zr1–OH4	2.34(3)
Zr1–O1	2.20(2)	Zr1–O2	2.27(2)	Zr2–O8	2.35(2)	Zr1–O7	2.08(2)
Zr1–O5	2.65(2)	Zr1–O4	2.63(2)	Zr2–O10	2.66(2)	Zr1–O11	2.57(2)
Av.	2.35	Av.			2.28		
Within the NO ₃ groups							
N1–O1	1.26(3)	O1–N1–O2	120(5)	N3–O7	1.26(3)	O7–N3–O8	120(4)
N1–O2	1.26(3)	O1–N1–O3	120(5)	N3–O8	1.26(3)	O7–N3–O9	120(4)
N1–O3	1.26(3)	O2–N1–O3	120(5)	N3–O9	1.26(3)	O8–N3–O9	120(5)
N2–O4	1.26(3)	O4–N2–O5	120(4)	N4–O10	1.26(3)	O10–N4–O11	120(4)
N2–O5	1.26(3)	O4–N2–O6	120(5)	N4–O11	1.26(3)	O10–N4–O12	120(4)
N2–O6	1.01(3)	O5–N2–O6	106(3)	N4–O12	1.26(3)	O11–N4–O12	120(5)
Shortest Zr...Zr distances							
Zr1...Zr1 ^I	3.36(1)	Zr1...Zr2	3.53(1)	Zr2...Zr2 ^{II}	3.68(1)		

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

β -Zr(OH)₂(NO₃)₂·H₂O

The crystal structure of β -Zr(OH)₂(NO₃)₂·H₂O derives directly from that of α -Zr(OH)₂(NO₃)₂·1.65H₂O, except that the water molecule Ow3 is here absent. It was also demonstrated that the departure with temperature of the excess of 0.65 water molecule does not cause the collapse of the basic framework. Nevertheless, great modifications in the bond lengths are observed. From a structural point of view, the approximate model obtained for β -Zr(OH)₂(NO₃)₂·H₂O from powder diffraction may be viewed as a 1D network based on zigzag chains running along [011] built up from ZrO₈ polyhedra of two types (Zr1O₈ and Zr2O₈) sharing double hydroxyl edges. As in

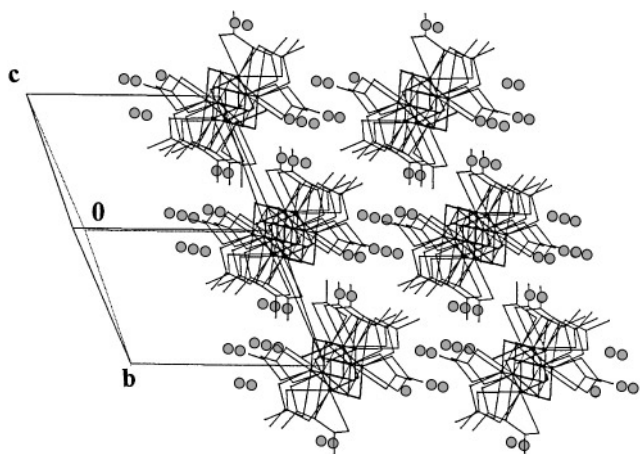


FIG. 3. View of the crystal structure of α -Zr(OH)₂(OH)₂·1.65H₂O along [0 1 1] showing the direction of the infinite chains. Full circles represent the free water molecules.

α -Zr(OH)₂(NO₃)₂·1.65H₂O, the polyhedron around Zr1 shares one edge with another Zr1 and one more edge with one Zr2. Bidentate nitrate groups complete the eightfold coordination of each Zr atom. As already said, several

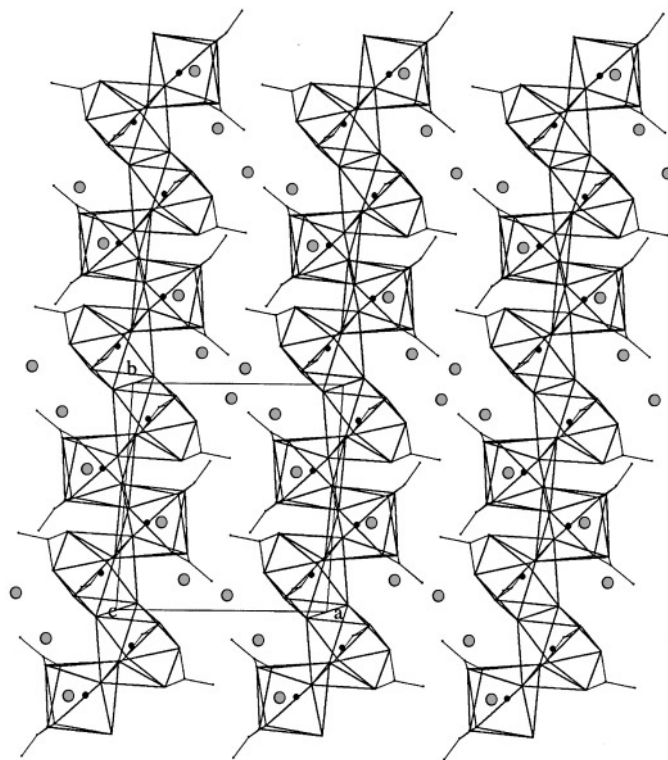


FIG. 4. Projection of the crystal structure of α -Zr(OH)₂(OH)₂·1.65H₂O along [0 0 1] in terms of edge-sharing dodecahedra with triangular faces around zirconium atoms. Small full circles represent the zirconium atoms and large full circles the water molecules.

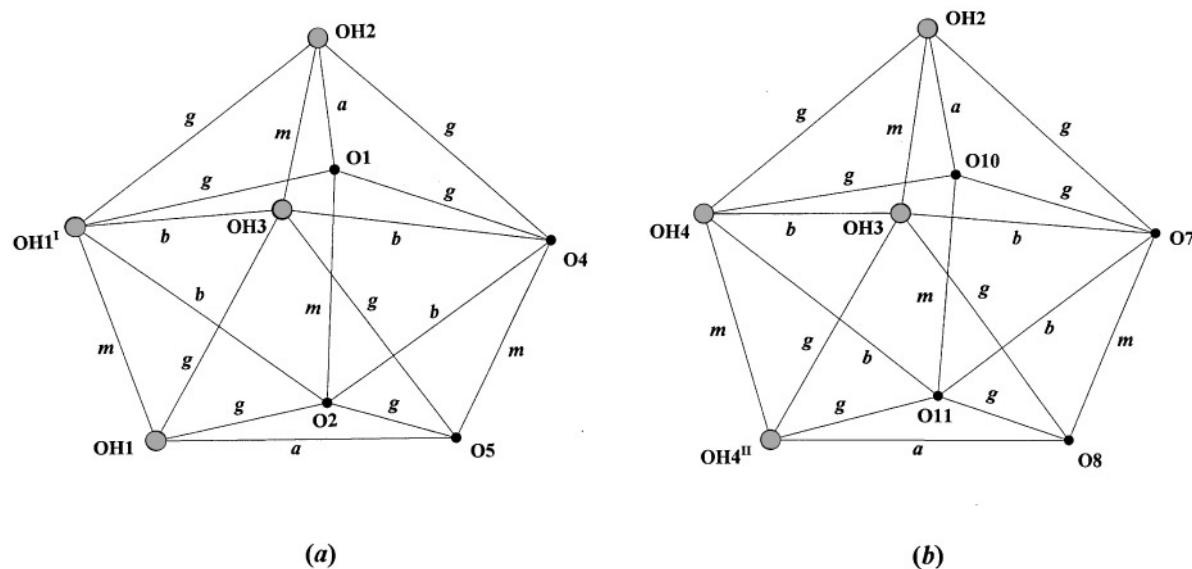


FIG. 5. Coordination polyhedron of oxygen atoms around (a) Zr1 and (b) Zr2 atoms in α -Zr(OH)₂(OH)₂·1.65H₂O. The 18 O–O edges and eight vertices are indicated according to the notations used by Hoard and Silverton (18) to characterize the ideal $\bar{4}2m$ triangular dodecahedron.

constraints have been applied on structural parameters; consequently, no definitive conclusion can be made about the true shape of the ZrO₈ groups, the distances and angles within the polyhedra appearing poorly indicative. They are far from those observed in the α phase and more scattered. The Zr1–O and Zr2–O bond lengths spread in the respective ranges 2.02–2.65 Å (mean value: 2.35 Å) and 1.95–2.67 Å (mean value: 2.28 Å). The variability of the Zr–O distances undoubtedly is caused by inaccuracies in the oxygen positions. Similar distortions must be noted about the O–O distances within the polyhedra. The geometry is in accordance neither with the ideal dodecahedral Mo(CN)₈⁴⁻ type (18) nor with both the square antiprism and the bicapped trigonal prism shapes.

CONCLUSION

The crystal structures of α -Zr(OH)₂(NO₃)₂·1.65H₂O and β -Zr(OH)₂(NO₃)₂·H₂O have been solved *ab initio* from laboratory X-ray powder diffraction; however, the accuracy of the second model is less accurate due to the combined effect of diffraction line broadening and a high number of atoms in the asymmetric unit. Similarities between the two 1D structures, based on neutral chains of ZrO₈ polyhedra, have been clearly established. From a structural point of view, it deserves to be noted that all the zirconium basic nitrates reported to date have double hydroxyl bridges as bonding unit in the polymeric linkage, as already found in the related well known family of sulfates. The other edges of the Zr polyhedron are formed from O bidentate nitrates and O water molecules or additional O hydroxyl groups as, for

example, in the neutral layer structure of Zr(OH)₃NO₃. Contrary to the basic salts such as Zr(OH)₂X₂·7H₂O (X=Cl, Br) (20, 27) described from a tetranuclear [Zr₄(OH)₈(H₂O)₁₆]⁸⁺ complex and more than in the sulfate or chromate systems there is the strongest tendency to form linear Zr–OH species in the hydroxide nitrates family. In addition, one of the predominant features of this family is both the 8-fold coordination for the heavy atom and the symmetry of a dodecahedron [Mo(CN)₈⁴⁻] for the ZrO₈ polyhedron. Finally, the shortest nonbonded Zr···Zr distances may be an indication about the cohesion within a chain of ZrO₈ polyhedra. The mean value of 3.46 Å observed in α -Zr(OH)₂(NO₃)₂·1.65H₂O appears remarkably shorter than those found in all known zirconium basic salts (3.55–3.60 Å) (1, 7, 21). Concerning the nitrates, a relation between the nature of the chains and the mean Zr···Zr intra-bond lengths can be established: the shortest distances are observed in the neutral chains of 1D structures (3.46 Å for α -Zr(OH)₂(NO₃)₂·1.65H₂O and 3.52 Å for β -Zr(OH)₂(NO₃)₂·H₂O), the 1D structures of Zr(OH)₂(NO₃)₂·4.7H₂O and Zr(OH)₂(NO₃)₂·4H₂O built from linear macrocations exhibit higher values, 3.562 and 3.57 Å, respectively, and, finally, the distance in the direction of the chains in the layer structure of Zr(OH)₃NO₃ is still higher (3.599 Å).

To conclude, it is worth noting that zirconium hydroxide nitrates form a family with a variety of structures, mainly 1D, but also 2D in the case of Zr(OH)₃NO₃ whose structure is formed from the condensation of the chain units found in the 1D structures. This family of compounds illustrates beautifully the significant progress that occurred in powder

diffraction in the past 10 years (4). Five years ago almost nothing was known about the chemistry and crystal chemistry of zirconium hydroxide nitrates. From the application of temperature-dependent powder diffraction and the powerful methods for solving *ab initio* crystal structures from powder data, a wealth of information on the crystal chemistry of basic zirconium nitrates has been obtained.

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