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THE LAYER STRUCTURE OF Zr(OH)₃NO₃ DETERMINED ab initio USING CONVENTIONAL MONOCHROMATIC X-RAY POWDER DIFFRACTION

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Abstract—The structure of $Zr(OH)_3NO_3$ has been determined *ab initio* from X-ray powder diffraction data collected with a conventional diffractometer. The monoclinic unit cell parameters are a = 9.1146(9) Å, b = 6.7670(7) Å, c = 7.6137(9) Å, $\beta = 102.61(1)^\circ$, V = 458.28(6) Å³ and the space group is C2/m (Z = 4). Initial atomic coordinates were obtained by interpretation of the direct methods solution and a Fourier difference density map generated from 206 reflections. Seven atoms including one zirconium and one nitrogen atom were identified. The final Rietveld refinement carried out over the angular range $10-140^\circ$ (2θ) yielded the R factors, $R_F = 0.035$ and $R_{wp} = 0.117$. The structure consists of neutral [Zr(OH)_{4/2}(OH)_{2/2}(NO₃)]_n layers parallel to (001). Each layer results from the condensation of zigzag chains running along [010] formed by edge-sharing ZrO₈ trigonal dodecahedra. The bidentate nitrate groups are involved in a weak hydrogen bonding network between adjacent layers. The thermal behaviour of Zr(OH)₃NO₃, investigated by means of thermodiffractometry, is also described. The decomposition proceeds in two stages, including the formation of amorphous zirconia in the temperature range 200-240°C.

Keywords: C. ab initio calculations.

1. INTRODUCTION

Although extensive structural studies have been described for some zirconium hydroxide salts, notably hydroxide sulphates [1, 2], little work seems to have been devoted to the related basic nitrates. results Partial structural are known for $Zr(OH)_2(NO_3)_2.4H_2O$ [3] and the structure of $Zr(OH)_2(NO_3)_2.4.7H_2O$, solved *ab initio* from powder diffraction, was reported recently [4]. However, the large number of compounds identified from their powder diffraction pattern [5, 6] mirrors the complexity of the crystal chemistry of basic zirconium nitrates. Determination of new crystal structures would contribute to clarify this aspect of zirconium nitrate chemistry. In particular, the structure of the more basic phases would be of special interest. The purpose of the present study is to investigate the structure of a highly basic zirconium nitrate, Zr(OH)₃NO₃. From a general viewpoint, these compounds are most frequently obtained in a powder form, which is undoubtedly the main reason why there is only limited structural information available. The major recent advances in powder crystallography in solving ab initio crystal structures offer a powerful tool for investigating compounds

indexing and structure refinement, the ultra-high instrument resolution obtained with synchrotron radiations [7], as well as the high resolution of the diffractometers using conventional monochromatic X-ray sources [8] have played a central rôle in the development of modern structural characterization of powder materials. For instance, typical peak-widths lower than $0.03^{\circ}(2\theta)$ are obtained with synchrotron radiations [7, 9], while widths of $0.065^{\circ}(2\theta)$ at low angles have been reported with conventional monochromatic X-rays [8]. A similar value $[0.06^{\circ}(2\theta)]$ was also obtained with the K_{α} doublet [10]. Nevertheless, in this case the doubling of the diffraction lines resulting from the K_{α} doublet introduces an unnecessary scrambling of the pattern at high diffraction angles. The benefit of using conventional monochromatic X-rays has now been shown in a number of studies, e.g. Refs [2, 11-13]. The present paper illustrates again the power of laboratory monochromatic X-rays in structure investigations. It deals with the crystal structure of $Zr(OH)_3NO_3$, determined ab initio from powder diffraction, and a thermodiffractometric study of this new member of the basic zirconium nitrate class.

prepared in the polycrystalline form. In addition to the advent of a new methodology, for pattern

2. EXPERIMENTAL CONSIDERATIONS

A powder sample of Zr(OH)₃NO₃ was prepared from the commercial product supplied by Prolabo [No. 29304, 186] and formulated as $N_2O_7Zr.2H_2O$. From a high temperature X-ray diffraction (HTRXD) study of the commercial product, and by comparison with previous analyses on the thermal behaviour of zirconium hydroxide nitrates reported by Bénard et al. [6], it was easy to identify a mixture of two phases in an approximate ratio 3:2. An additional powder diffraction pattern registered at room temperature confirmed the presence of the two phases α -Zr(OH)₂(NO₃)₂.(1 + x)H₂O (0 < x < 1) [6] and $Zr(OH)_3NO_3$ [5]. Since the hydrated phase is soluble in water, the commercial product was washed thoroughly with distilled water. The remaining white polycrystalline product was filtered off, then washed with water and alcohol. From powder diffraction, it was seen that the phase $Zr(OH)_3NO_3$ was clean.

X-ray powder diffraction data were collected with a Siemens D500 high-resolution powder diffractometer. A strictly monochromatic Cu $K_{\alpha l}$ radiation $(\lambda = 1.540598 \text{ Å})$ was produced with an incidentbeam curved-crystal germanium monochromator with asymmetric focusing (short focal distance 124 mm, long focal distance 216 mm). The alignment of the diffractometer was checked by means of the 001 reflections of fluorophlogopite mica (NIST SRM 675) [14], and the zero error was estimated as less than $0.005^{\circ}(2\theta)$. The instrumental resolution function (IRF), obtained from an annealed barium fluoride sample, is characterized by a minimum of $0.065^{\circ}(2\theta)$ at about $40^{\circ}(2\theta)$ and has twice this value at $130^{\circ}(2\theta)$ [8]. Preliminary data collections revealed the stability of the product at room temperature and the absence of significant preferred orientation of the crystallites. The powder sample was mounted in a top-loaded sample holder and was completely illuminated at $12^{\circ}(2\theta)$. The diffraction pattern was scanned over the angular range $10-140^{\circ}(2\theta)$, with a step length of $0.02^{\circ}(2\theta)$. In order to improve the counting statistics at high angles, the counting times were 24 s step^{-1} to

 70° and 48 s step^{-1} from 70.02° to the end of the scan. Then, the full pattern was scaled to the lower scale. After data collection, the stability of the X-ray source was checked by recording the first lines of the pattern. The precise peak position of individual diffraction lines was determined by means of the Socabim fitting programe PROFILE, available in the PC software package DIFFRAC-AT supplied by Siemens. The interrogation of the ICDD PDF database [15], available in the program search/match of DIFFRAC-AT, did not reveal apparently isostructural phases.

The high-temperature X-ray diffraction (HTRXD) experiment was performed by using an INEL (CPS 120) curved position sensitive detector, which allows for a simultaneous recording of a powder pattern over a range of 120° , with a spatial resolution of $0.03^{\circ}(2\theta)$. It was used in a semi-focusing arrangement by reflection and strictly monochromatic $CuK_{\alpha l}$ radiation was selected by means of an incident-beam curved-crystal quartz monochromator with asymmetric focusing. The sample was stationary and a fixed angle of 6° between the incident beam and the surface of the sample was selected. Details about this system have been given elsewhere [16]. The sample was located in a monitored high-temperature device (Rigaku). The experiment was carried out under nitrogen gas with a heating rate of 20°C h⁻¹. To ensure satisfactory counting statistics an interval time of 1140 s between two successive patterns was selected, including a counting time of 1000 s.

3. DATA ANALYSIS

3.1. Thermal analysis of Zr(OH)₃NO₃

Figure 1 shows a three-dimensional representation of the successive powder diffraction patterns during the decomposition of anhydrous zirconium hydroxide nitrate, in the range 20–500°C. It shows that the decomposition of the precursor into tetragonal ZrO_2 occurs in two stages, without the formation of intermediate zirconium nitrate phases, as observed for two other precursors [6]. $Zr(OH)_3NO_3$ decomposes



Fig. 1. The HTRXD 3D plot for the thermal decomposition of Zr(OH)₃NO₃ under nitrogen gas (heating rate: 20°C h⁻¹, counting time for each pattern: 1000 s) (*: spurious diffraction line due to impurity).

between 200°C and 240°C into amorphous zirconia, which, in turn, transforms into crystalline ZrO₂ above 380°C. Results agree with the TG curve reported previously [5]. Moreover, from a comparison with the thermal behaviours of $Zr(OH)_2$ - $(NO_3)_2.(4+x)H_2O$ and α -Zr $(OH)_2(NO_3)_2.(1+x)$ - H_2O (0 < x < 1) studied under similar experimental conditions [6], it appears that $Zr(OH)_3NO_3$ has a higher thermal stability. Indeed, amorphous zirconia is obtained from 200°C, while for the two other precursors it is formed in the temperature ranges 160-200°C and 125-165°C, respectively [6]. It should be noted that the crystallization of amorphous zirconia takes place at the same temperature for the three precursors (380°C). This study shows that $Zr(OH)_3NO_3$ appears as thermally the most stable phase in the family of zirconium hydroxide nitrates.

3.2. Ab initio structure determination of Zr(OH)₃NO₃

Indexing of the X-ray diffraction pattern was performed by the successive dichotomy method [17], using the PC version of DICVOL91 [18]. The first 20 lines were completely indexed on the basis of a monoclinic cell with the figures of merit $M_{20} = 64$ and $F_{20} = 100(0.0042, 48)$. This solution was used for reviewing the powder diffraction data available in the pattern by means of the computer program NBS*AIDS83 [19]. From this evaluation of data quality and refinement, the cell parameters are a = 9.1146(9) Å, b = 6.7670(7) Å, c = 7.6137(9) Å, $\beta = 102.61(1)^{\circ}$ and $V = 458.28(6) \text{ Å}^3$ $[M_{20} = 66;$ $F_{30} = 99(0.0087, 35)$]. Powder diffraction data are reported in the ICDD Powder Diffraction File, No. 45-1487. The possible space groups C2, Cm and C2/m were deduced from the systematic absences. It should also be noted that from the solution proposed by DICVOL91, an approximate indexing of the powder diffraction data of Zr(OH)₃NO₃ reported by Govorukhina et al. [5] can be proposed, with some angular discrepancies greater than $0.15^{\circ}(2\theta)$. The corresponding figures of merit $[M_{20} = 15; F_{30} =$ 10(0.0475, 65)] indicate the low quality of the data. Finally, the unit cell found by DICVOL91 was used to interrogate the NIST-CDF database [20], from which no chemically related isostructural material with known structure was found. Consequently, the ab initio structure determination of Zr(OH)₃NO₃ was undertaken from the X-ray powder diffraction data assuming the centrosymmetric space group C2/m, and this was confirmed by the satisfactory refinement of the structure.

Integrated intensities in the angular range $10-80^{\circ}(2\theta)$ were extracted by means of an iterative

Table 1. Details of Rietveld refinement for Zr(OH)₃NO₃

Space group	C2/m
Ż	4
Angular range (°2 θ)	10-140
Wavelength (Å)	1.5405981
Step scan increment ($^{\circ}2\theta$)	0.02
No. of reflections	475
No. of structural parameters	23
No. of profile parameters	17
No. of atoms	7
R _F	0.035
R _B	0.061
R _p	0.092
R_{wp}^{ν}	0.117

procedure for whole-pattern fitting [21] available in the Rietveld refinement program FULLPROF [22], based on the program described by Wiles and Young [23]. The 162 values of F_{obs} obtained with the 'pattern matching' option were used as input data for the Enraf-Nonius crystallographic structure computing package MolEN [24], running on a microvax computer. From the best solution obtained by means of the direct methods (program MULTAN) and the calculation of interatomic distances based on the first 10 peaks, six of them could be attributed to one Zr, one N and four O atoms, including two O from a nitrate group. After increasing the upper limit of the angular range, a subsequent difference Fourier map was generated from 206 reflections, and an additional peak corresponding to the missing nitrate oxygen atom was found. At this stage, it was seen that the formula $Zr(OH)_3NO_3$, given first by Govorukhina et al. [5], was correct. Indeed, one Zr atom is surrounded by six oxygens, each of them bridging two Zr atoms. Two oxygen atoms from a bidentate nitrate group complete the eightfoldcoordination sphere of Zr. The approximate coordinates of the seven independent atoms were used as a starting model in the Rietveld refinement method, and they were refined isotropically. The final refinement, carried out in the angular range $10-140^{\circ}(2\theta)$, involved the following parameters: 15 atomic coordinates and seven isotropic temperature factors, one scale factor, one zero-point, four cell dimensions, three half-widths, two parameters to describe the θ -dependent pseudo-Voigt profile shape function and one asymmetric factor. In addition, five coefficients were used to describe the functional dependence of the background. The last variable to be refined was the crystallite preferred-orientation factor. It was found to be close to zero, whatever the direction selected for the diffraction vector. Crystallographic details of the Rietveld refinement are listed in Table 1. Figure 2 displays the best agreement obtained between calculated and observed diffraction patterns. This fit corresponds to satisfactory crystal structure model



Fig. 2. The final Rietveld plot of $Zr(OH)_3NO_3$. The upper trace shows the observed data as dots, while 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. Note that the intensity scale is different for the high angle range.

indicators ($R_{\rm F} = 0.035$, $R_{\rm B} = 0.061$) and profile factors ($R_{\rm p} = 0.092$ and $R_{\rm wp} = 0.117$). The final atomic coordinates and thermal parameters are given in Table 2 and selected distances and angles in Table 3.

4. DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The structure of $Zr(OH)_3NO_3$ (Fig. 3) is built from

neutral layers, parallel to the (001) plane, with the overall composition $[Zr(OH)_{4/2}(OH)_{2/2}(NO_3)]_n$. From Fig. 4 it can be seen that a layer results from the condensation of zigzag chains, running along the [010] direction. It is of interest to note that zigzag chains, but isolated, have been observed in the structures of $Zr(OH)_2(NO_3)_2.4H_2O$ [3] and $Zr(OH)_2(NO_3)_2.4.7H_2O$ [4]. From the condensation of the chains within the layers of the structure of $Zr(OH)_3NO_3$ results pseudohexagonal windows

dard deviations for Zr(OH) ₃ NO ₃						
Atom	x	y	Z	$B_{\rm iso}$ (Å ²)		
Zr	0.1843(2)	0	0.4530(2)	1.04(4)		
OHI	-0.0600(8)	0	0.3360(9)	0.5(2)		
OH2	0.3480(9)	0.1957(7)	0.6215(6)	0.0(1)		
01	0.3669(9)	0	0.276(1)	1.3(2)		
O2	0.1472(9)	0	0.130(1)	1.9(2)		
O3	0.324(1)	0	-0.003(2)	4.8(4)		
N	0.284(2)	0	0.116(2)	6.8(5)		

6.8(5)

Table 2. Positional and thermal parameters with their stan-

formed by the edges of six ZrO₈ polyhedra (Fig. 4). The window size, defined by the shortest diagonal distance of the projected windows, is 2.52 Å. Two neighbouring zigzag chains are linked together through OH1-OH1^I hydroxyl bridges. As frequently

found in basic zirconium salts, the bonding units within a chain are double hydroxyl bridges. The chain is thus built up from double OH2-OH2 [OH2-OH2^{II}, OH2^{III}-OH2^{IV}] edge-sharing ZrO₈ polyhedra. Therefore, each zirconium atom is surrounded by six hydroxyl groups [4× OH2 and 2× OH1] and two additional O atoms from a bidentate nitrate group. The nitrate groups, located on both sides of a layer, lie on a mirror plane.

The coordination Zr-O is eightfold in the shape of an irregular dodecahedron with triangular faces. The Zr-O distances range from 2.133 to 2.411 Å. The two maxima, 2.361 and 2.411 Å, correspond to the Zr-O1 and Zr-O2 bonds, O1 and O2 coming from the nitrate group. It could be noted that the six remaining bonds,

Table 3	Selected	bond	distances	(Å)	and	angles	(°)	with	their	standard	deviations	for
Zr(OH) ₃ NO ₃												

Within the ZrO ₈ polyhedra [†]									
M_A M_B									
Zr-OH1 Zr-OH2 Zr-OH2 ^{III} Zr-O2 Av.	2.209(8) 2.186(5) 2.186(5) 2.411(9) 2.248	$ \begin{array}{c} Zr-OH1^{I} \\ Zr-OH2^{II} \\ Zr-OH2^{IV} \\ Zr-OI \\ Av. \end{array} $	2.159(7) 2.133(5) 2.133(5) 2.361(9) 2.197						
$Zr(OH)_2(NO_3)_2.4.7H_2O$	2.23	$Zr(OH)_2(NO_3)_2.4.7H_2O$	2.18						
a OH2-OH2 ^{III} OH1-O2 Av. Zr(OH) ₂ (NO ₃) ₂ .4.7H ₂ O	2.641(7) 2.71(1) 2.676 2.75	m OH1-OH1 ¹ OH2-OH2 ¹¹ OH2 ¹¹¹ -OH2 ^{11V} O1-O2 Av. Zr(OH) ₂ (NO ₃) ₂ .4.7H ₂ O	2.50(1) 2.388(6) 2.388(6) 2.07(1) 2.337 2.41						
b OH1 ¹ -OH2 ^{II} OH1 ^I -OH2 ^{IV} OH2 ^{II} -O1 OH2 ^{IV} -O1 Av. Zr(OH) ₂ (NO ₃) ₂ .4.7H ₂ O	3.231(7) 3.231(1) 2.984(9) 2.984(9) 3.108 3.18	g OH1 ¹ -OH2 OH1-OH2 ^{III} OH1-OH2 ^{II} OH1-OH2 ^{IV} OH2-O1 OH2 ^{II} -O1 OH2 ^{II} -O2 OH2 ^{IV} -O2 Av. Zr(OH) ₂ (NO ₃) ₂ .4.7H ₂ O	3.018(8) 3.018(8) 2.789(7) 3.055(8) 3.055(8) 2.788(8) 2.788(8) 2.913 2.79						
	Within the NO ₃ groups								
N-01 N-02 N-03	1.28(2) 1.27(2) 1.05(2)	01-N-02 01-N-03 02-N-03	108(2) 125(3) 127(3)						
Possible hydrogen bonds									
Interlayer OH1-O3 ^V OH2-O3 ^{V1}	3.09(1) 3.20(1)	$Zr-OH1O3^{V}$ $Zr-OH2O3^{VI}$	150(2) 127.0(7)						
Intralayer OH2–O1 ^{VII}	2.866(9)	$Zr-OH2O1^{VII}$	125.5(5)						
Shortest ZrZr distances									
Within a chain ZrZr ^(II,IV)	3.599(9)	between chains $Zr \dots Zr^{I}$	3.58(3)						

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

†Notations according to Hoard and Silverton [25].



Fig. 3. Projection of the crystal structure of $Zr(OH)_3NO_3$ looking along [010], in terms of infinite layers with the composition $[Zr(OH)_{4/2}(OH)_{2/2}(NO_3)]_n$. Filled circles represent the Zr atoms.



Fig. 4. Projection of the crystal structure of $Zr(OH)_3NO_3$ along [001], showing the arrangement within a layer of edge-sharing ZrO_8 polyhedra. Filled circles represent the Zr atoms.



Fig. 5. Coordination sphere of oxygen atoms around Zr atom in $Zr(OH)_3NO_3$. The 18 O-O edges and eight vertices are indicated according to the notations used by Hoard and Silverton [25] to characterize the ideal $\bar{4}2m$ triangular dodecahedron.

which link the Zr atom to hydroxyl groups, are significantly shorter, with close lengths in the range 2.133-2.209 Å. The complete Zr-O range compares well with the distances found in the structure of $Zr(OH)_2(NO_3)_2.4H_2O(2.12-2.37 \text{ Å})$, while a slightly greater spread is found in Zr(OH)₂(NO₃)₂.4.7H₂O (2.06-2.44 Å). Nevertheless, the mean Zr-O value (2.22 \AA) calculated for $Zr(OH)_3NO_3$ is quite in accordance with the value (2.21 Å) obtained for the two other basic nitrates. It is interesting to note that in zirconium hydroxide sulphates the average Zr-O value is 2.19 Å [2]. In Fig. 5, the eight sites and 18 O-O edges are labelled according to the nomenclature of Hoard and Silverton [25] used for the maximum symmetry $\overline{4} 2m$ of the Mo(CN)⁴⁻ coordination polyhedron. In Table 3 are indicated the average values of M-A and M-B, a, b, m and g bond lengths for $Zr(OH)_3NO_3$, together with the values found in $Zr(OH)_2(NO_3)_2.4.7H_2O$. It can be seen that the M-A/M-B ratio is greater than unity in the two examples, 1.023 and 1.025 respectively. Also, the four unequivalent edge lengths are ranged according to the sequence m < a < g < b. These results are in satisfactory agreement with the geometric features found for the 'most favourable' coordination polyhedra [M-A/M-B = 1.03; a = m < g < b] [25]. Moreover, these three bond lengths ratios are intermediate between the values 1.008 and 1.052 found in $Zr_2(OH)_2(SO_4)_3.4H_2O$ [26] and $Zr(OH)_2CrO_4$ [27], in which the same Zr configuration is observed. A factor Zr-O(A)/Zr-O(B) > 1 indicates that the Zr-O(A) bonds are more strongly influenced by strains incident to formation of the network. These effects are more important for the two zirconium hydroxide nitrates and even more for the chromate.

1351

For the basic chromate, the distortions are the consequence of a complex three-dimensional network based on infinite macrocations $[Zr_3(OH)_6(CrO_4]_n^{4n+}]$ linked by CrO_4^{2-} groups [27]. In the case of $Zr_2(OH)_2(SO_4)_3.4H_2O$, the structure consists of dimers $Zr_2(OH)_6^{2+}$ connected by sulfate groups [26]. A M-A/M-B ratio greater than unity can be interpreted, for the Zr complexes, in terms of ligand repulsions and weak π -bonding involving the d_{xy} orbital. For $Zr(OH)_3NO_3$, the *m* distances (mean 2.337 Å) are all shorter than the *a* distances (mean 2.676 Å) though the overall average value (2.506 Å) is close to that of 2.57 Å observed for the 'most favourable' model [25]. Therefore, the main distortions in the Zr polyhedron are localized in the two trapezoïds (see Fig. 5). They arise from the double hydroxyl bridges $[2 \times OH2(A) - OH2(B)]$ involved in a $M-(OH)_2-M$ zigzag chain and the hydroxyl bridges [OH1(A)-OH1(B)] between neighbouring chains. Also, it should be noted that the bidentate character of the nitrate group introduces additional constraints. The fourth *m* distance [d(O1-O2) =2.07 Å] is significantly short with respect to the mean (m = 2.337 Å). A comparable average value т edges (2.41 Å) was reported for for $Zr(OH)_2(NO_3)_2.4.7H_2O$ [4]. The difference is probably due to the replacement of the two OH1 groups by O atoms from two individual water molecules [d(Ow1 - Ow2) = 2.81 Å].

The nitrate group acts as a bidentate ligand with regard to the zirconium polyhedron. Because the bond distances from the nitrogen to the twofold coordinated oxygen atoms [O1 and O2] are nearly equal (1.27 and 1.28 Å), and significantly longer than the third N-O3 distance (1.05 Å), the nitrate group in $Zr(OH)_3NO_3$ may be considered as symmetric. This is also consistent with the comparable angles O1-N-O3 and O2-N-O3 (125 and 127°) observed between the bonded O atoms and the terminal O3 atom. 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 oxygen atoms differ by more than 0.2 Å [28]. In the present study, the two comparable Zr-O1 [2.361(9)Å] and Zr-O2 [2.411(9) Å] bond lengths are consistent with this criteria. Therefore, although the precision of distances is modest, the bidentate nitrate group in Zr(OH)₃NO₃ can be considered as belonging to the type II_{2b} from the class I of the classification of the coordination mode of nitrate proposed by Leclaire [29]. The rôle of the nitrate groups in propagating the layer structure by participation in hydrogen bonding is limited, except in the [001] direction through the O3 atom. The shortest O3^V-OH1 interlayer distance is 3.09 Å (Table 3), which corresponds to a

weak hydrogen bond [30]. Since the second distance $O3^{IV}$ —OH2 is long (3.20 Å), it is likely that van der Waals interactions contribute to hold together adjacent layers. The large thermal parameter observed for the terminal O3 oxygen is also consistent with the weak bonding of adjacent layers. Finally, it should be noted that the shorter O1^{VII}—OH2 distance (2.866 Å) agrees well with the presence of intralayer hydrogen bonds, which strengthen the layer stability.

In conclusion, the ab initio structure determination of Zr(OH)₃NO₃ from laboratory monochromatic X-ray diffraction data has shown the effectiveness of the powder diffraction method in the structural investigation of basic zirconium hydroxide nitrates, when single crystals are not available. This highly basic compound is the first example of a layered compound reported for basic zirconium nitrates, for which only chain structures have been described. An interesting feature is the framework of the layers based on the condensation of individual chains with the same geometry as those found in the known structures of the family. Moreover, the Zr-Zr distance (3.599 Å) within a zigzag chain in the layer structure is slightly greater than the distances found in the chain structures (3.562 Å [3] and 3.57 Å [4]), and the nearest to the value found in the decomposition product, tetragonal zirconia (3.64 Å). This present study sheds new light on the structural variation in the complex chemistry of basic hydroxide nitrates.

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