

Ab Initio Structure Determination of New Mixed Zirconium Hydroxide Nitrates $ZrM(OH)_2(NO_3)_3$ ($M = K, Rb$) from X-Ray Powder Diffraction Data

P. Bénard-Rocherullé and D. Louër

Laboratoire de Chimie du Solide et Inorganique Moléculaire (UMR CNRS 6511), Groupe de Cristallographie, Université de Rennes I, Avenue du Général Leclerc, 35042 Rennes Cedex, France

Received July 19, 1999; accepted September 21, 1999

Two new mixed zirconium hydroxide nitrates $ZrM(OH)_2(NO_3)_3$ ($M = K, Rb$) have been synthesized through a wet chemical process. The two crystal structures have been solved *ab initio* from powder diffraction data collected with conventional monochromatic X-rays. $ZrK(OH)_2(NO_3)_3$ crystallizes with a monoclinic symmetry [$a = 16.569(3)$ Å, $b = 5.791(1)$ Å, $c = 9.813(2)$ Å, $\beta = 90.17(2)^\circ$, $P2_1/n$, $Z = 4$] and $ZrRb(OH)_2(NO_3)_3$ with an orthorhombic symmetry [$a = 10.126(3)$ Å, $b = 16.492(3)$ Å, $c = 5.855(2)$ Å, $Pbcn$, $Z = 4$]. The heavy atoms have been located from an interpretation of Patterson functions. The coordinates of the remaining light atoms have been determined from successive three-dimensional Fourier maps. The final Rietveld refinement indicators were $R_F = 0.042$, $R_p = 0.077$ ($M = K$) and $R_F = 0.064$, $R_p = 0.115$ ($M = Rb$). Like the structures of α - $Zr(OH)_2(NO_3)_2 \cdot 1.65H_2O$ and β - $Zr(OH)_2(NO_3)_2 \cdot H_2O$, the structures of the mixed basic zirconium nitrates are built from edge-sharing ZrO_8 polyhedra to form infinite neutral zigzag chains of chemical composition $[Zr(OH)_{4/2}(NO_3)_2]_n$. The main difference with respect to the hydrated phases is the nature of the cohesion in the structures based on ionic contacts involving intercalated K^+ or Rb^+ and NO_3^- species in the mixed compounds and on a complex hydrogen-bonding network in the hydrated phases. The crystal chemistry of the zirconium hydroxide nitrates is discussed and three structure types are identified. © 2000 Academic Press

trivalent metals, layered structures are again known with iron (9), and layers can also accommodate larger ions such as rare earth metals, e.g., neodymium, praseodymium, gadolinium, and lanthanum (10–13). Some interesting properties of nitrate hydroxides with layered structures have been described, e.g., ion exchange (9, 14, 15) and magnetic properties (15, 16). Due to the synthesis methods often used, such as also hydrolysis, many of these phases have been obtained only in powder form. It is then from the application of the modern developments in *ab initio* structure determination from powder diffraction data (see, for example, Ref. (17) that the crystal chemistry of these families of compounds could be elucidated. The impact of these advances in powder crystallography is particularly emphasized for the family of low-dimensional zirconium hydroxide nitrates, for which most structures were determined from powder diffraction data. All crystal structures are built from ZrO_8 trigonal dodecahedra. In $[Zr(OH)_2(NO_3)_2] \cdot 4.7H_2O$ (18) they form infinite isolated chains consisting of linear macrocations $[Zr(OH)_2(NO_3)_2(H_2O)_2]_n^{n+}$, which are balanced by an equivalent amount of intercalated nitrate anions, additional water molecules being located between the chains. In $[Zr(OH)_3(NO_3)_2] \cdot 1.65H_2O$ and β - $[Zr(OH)_2(NO_3)_2] \cdot H_2O$ (19) neutral zigzag chains are observed with water molecules located between the chains. Unlike these one-dimensional structures, $Zr(OH)_3NO_3$ (20) has a two-dimensional structure built from neutral layers, which result from the condensation of chains similar to those found in the one-dimensional phases. Since the structures are derived from simple basic principles and some structures are characterized by the presence of intercalated groups, it is reasonable to explore the possibility of obtaining new phases, particularly mixed compounds. The present study deals with such examples, i.e., the synthesis of two new mixed zirconium alkaline basic nitrates, $ZrM(OH)_2(NO_3)_3$ ($M = Rb, K$), and the determination *ab initio* of the crystal structures from powder diffraction data.

INTRODUCTION

The structural chemistry of basic nitrates exhibits various crystal-structure types with many metals. With divalent transition metals two-dimensional structures derived from the brucite-type are frequently observed, e.g., for zinc, nickel, copper (see Ref. (1) and references therein), and cadmium (2–4), while one-dimensional complexes have also been reported with zinc, cobalt, and manganese (5–7), and three-dimensional structures with cadmium (8). With

EXPERIMENTAL

Synthesis

The commercial compounds $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (whose correct chemical formula is in fact $\text{Zr}(\text{OH})_2(\text{NO}_3)_2 \cdot (1+x)\text{H}_2\text{O}$ (19)), $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, and RbNO_3 (99.99% purity) from Johnson-Matthey and pure KNO_3 and HNO_3 from Merck were used in the synthesis of $\text{ZrK}(\text{OH})_2(\text{NO}_3)_3$, whose chemical formula was revealed from the structure determination reported here. Half a gram of a mixture of hydrated zirconium hydroxide nitrate and KNO_3 with a Zr/K ratio 1/2 was dissolved in 20 ml diluted nitric acid (5.5 M). The solution was heated at 75°C and evaporated for 7 days. A white deposit was thus obtained. It was washed for a short time with concentrated HNO_3 (65%) to eliminate residual KNO_3 , then with alcohol before being dried at 40°C. An alternative synthesis method is the use of reactive $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$, obtained from slow precipitation by a 1 M ammoniac solution of a 0.1 M solution of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, mixed to a 1:2 molar ratio solution of KNO_3 and 20–30 ml of concentrated HNO_3 . The mixture was heated at 100°C for 3 days. The precipitate obtained was filtered off and washed with a minimum of nitric acid and, finally, with alcohol. The white powder was dried and kept at 40°C. A similar procedure was employed for the preparation of the rubidium compound by substituting RbNO_3 for KNO_3 .

X-Ray Powder Diffraction

High-quality X-ray powder diffraction data were obtained with a Siemens D500 diffractometer using monochromatic $\text{CuK}\alpha_1$ X-rays ($\lambda = 1.5406 \text{ \AA}$) selected with an incident-beam-curved-crystal germanium monochromator with asymmetric focusing (short focal distance, 124 mm; long focal distance, 216 mm), whose performances have been reported elsewhere (21). The zero-point error was estimated to be lower than $0.01^\circ (2\theta)$. To minimize preferred orientation effects, the powders were mounted in a top-loaded sample holder (22). The diffraction patterns were scanned with a step length of $0.02^\circ (2\theta)$ over the angular ranges 8–140° (2θ) and 9–125° (2θ), with a counting time of 25 s step^{-1} , for $\text{ZrRb}(\text{OH})_2(\text{NO}_3)_3$ and $\text{ZrK}(\text{OH})_2(\text{NO}_3)_3$, respectively. After data collection, the stability of both the X-ray source and the samples were checked by recording again the first lines of each pattern. The extraction of the peak positions was performed with the Socabim fitting program PROFILE, available in the PC software package DIFFRAC-AT supplied by Siemens. The interrogation of the ICDD-PDF database (23) was carried out with the Socabim search/match program. No isostructural chemically related phase was found. DIAMOND (Version 2.1) from Crystal Impact was used for crystal structure drawings.

STRUCTURE DETERMINATION

Indexing

The powder diffraction patterns of the two basic salts were indexed with the program DICVOL91 (24). The first 20 peak positions, with an absolute error of $0.03^\circ (2\theta)$, were indexed on the basis of similar orthorhombic unit cells, characterized by the figures of merit $M_{20} = 22$ and $F_{20} = 40(0.0130, 39)$ for $\text{ZrK}(\text{OH})_2(\text{NO}_3)_3$ and $M_{20} = 23$ and $F_{20} = 35(0.0092, 63)$ for $\text{ZrRb}(\text{OH})_2(\text{NO}_3)_3$. Nevertheless, a monoclinic solution with similar parameters and a β angle close to 90° was also proposed for the potassium phase ($M_{20} = 29$, $F_{20} = 50(0.0067, 59)$). This last solution was initially rejected since the magnitude of the deviation from the orthorhombic cell was within the experimental error for the observed data. However, a careful examination of the individual angular error in the $(2\theta_{\text{obs}} - 2\theta_{\text{calc}})$ list obtained for the orthorhombic cell revealed a discrepancy of $0.04^\circ (2\theta)$ for one strong line (220), which is much greater than the precision usually obtained with the diffractometer, while the average angular discrepancy for the 20 lines was $0.013^\circ (2\theta)$. This subtle feature was an indication of a likely lower crystal symmetry for the potassium compound. This was confirmed from the fitting of a few diffraction lines in the pattern by using the pattern matching option available in the Rietveld program FULLPROF (25, 26). Figures 1a and 1b show the fit of two lines (including the 220 line at $21.045^\circ 2\theta$) obtained from the two unit cells. Clearly the best fit is obtained with the monoclinic symmetry. Nevertheless, no such evidence was obtained for the rubidium compound. The correctness of the orthorhombic cell ($\text{ZrRb}(\text{OH})_2(\text{NO}_3)_3$) and the monoclinic cell ($\text{ZrK}(\text{OH})_2(\text{NO}_3)_3$) was confirmed by reviewing the powder data available on the two patterns, using the program NBS * AIDS83 (27). The possible space groups $Pbcn$ and $P2_1/n$, respectively, were deduced from the systematic absences. The least-squares refined cell parameters and figures of merit, calculated with the extinction conditions, were:

$\text{ZrK}(\text{OH})_2(\text{NO}_3)_3$: $a = 16.569(3) \text{ \AA}$, $b = 5.791(1) \text{ \AA}$, $c = 9.813(2) \text{ \AA}$, $\beta = 90.17(2)^\circ$, and $V = 941.5(3) \text{ \AA}^3$ ($M_{20} = 43$, $F_{30} = 55(0.0076, 72)$).

$\text{ZrRb}(\text{OH})_2(\text{NO}_3)_3$: $a = 10.126(3) \text{ \AA}$, $b = 16.492(3) \text{ \AA}$, $c = 5.855(2) \text{ \AA}$, and $V = 977.7(3) \text{ \AA}^3$ ($M_{20} = 48$, $F_{30} = 58(0.0099, 52)$).

The powder diffraction data for the two phases have been submitted to the ICDD (23) for possible inclusion in the Powder Diffraction File. The unit cells found by DICVOL91 were used to interrogate the NIST-CDF database (23), in which no chemically related isostructural material with known structure was found. Consequently, the *ab initio* structure determinations of $\text{ZrK}(\text{OH})_2(\text{NO}_3)_3$ and $\text{ZrRb}(\text{OH})_2(\text{NO}_3)_3$ were undertaken, assuming the centrosymmetric space groups given above.

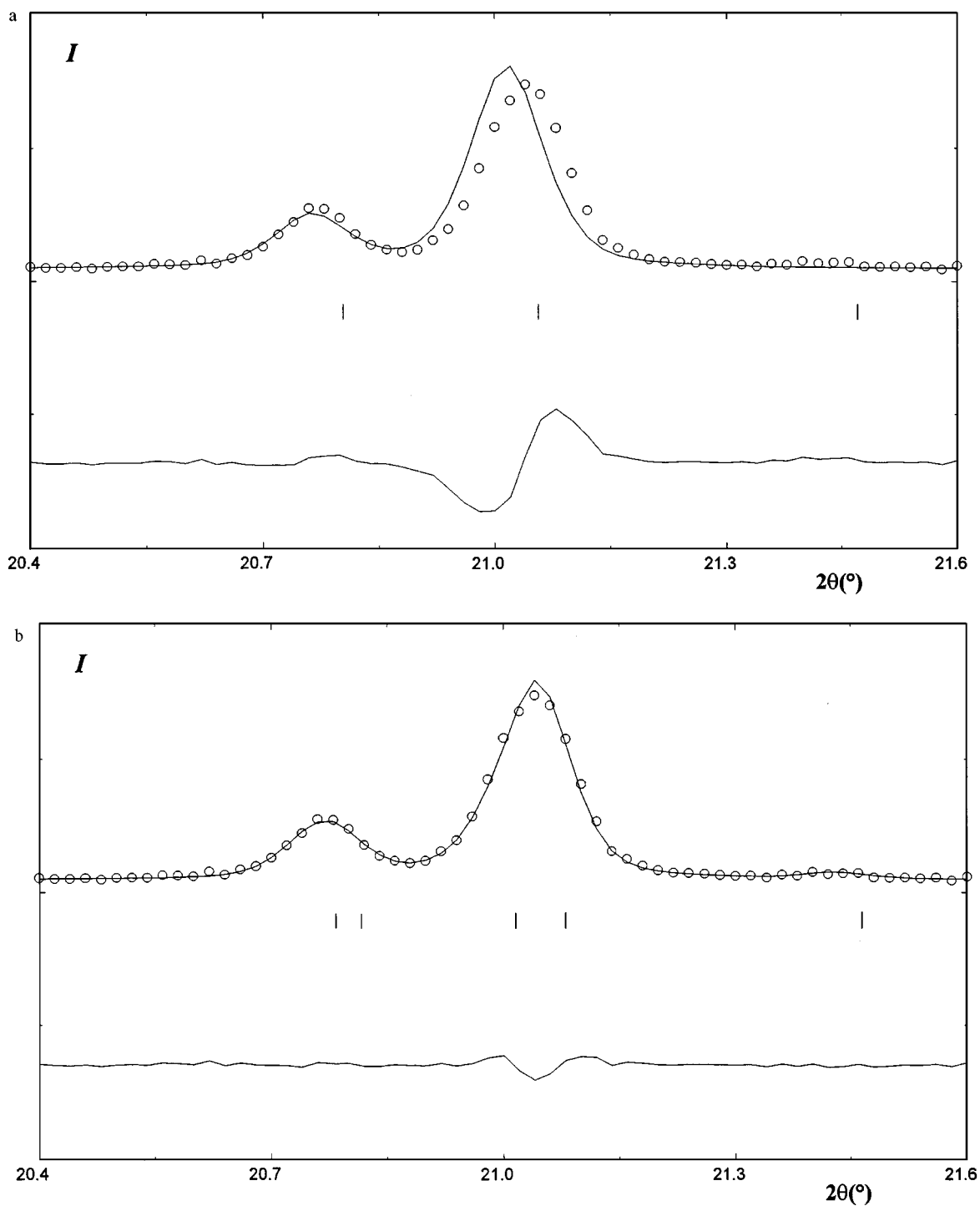


FIG. 1. Part of the pattern matching plots of $ZrK(OH)_2(NO_3)_3$ with (a) the orthorhombic (S.G. $Pbcn$) and (b) the monoclinic (S.G. $P2_1/n$) unit cells. The upper trace shows the observed data as empty circles, and the solid line is the calculated pattern. The lower trace is the plot of the difference (observed minus calculated). The vertical marks are the allowed space-group Bragg reflections.

Structure Solution and Refinement

Integrated intensities were extracted from the iterative pattern decomposition procedure available in the program

FULLPROF (26). A list of structure-factor moduli was obtained in the angular range $8-90^{\circ}$ (2θ). Patterson maps were calculated with the program SHELXS86 (28), yielding vectors consistent with a unique general location $4e$ for

Zr (0.44, 0.25, 0.50) and K (0.33, 0.24, 0.00) atoms in $\text{ZrK}(\text{OH})_2(\text{NO}_3)_3$, while a special position 4c for Zr (0.5, 0.441, 0.75) and Rb (0.5, 0.161, 0.25) was found in $\text{ZrRb}(\text{OH})_2(\text{NO}_3)_3$. The Rietveld refinements of these atomic positions led to crystal-structure model indicators R_F close to 0.20. Subsequently, from successive difference Fourier calculations, using the program SHELXL93 (29), the complete environment of the zirconium atoms in the two structures, including oxygen atoms from nitrate groups, was found. The location of the remaining atoms was revealed from somewhat laborious analyses of final difference Fourier maps from which the approximate geometry of nonbonded nitrate groups was recognized in the two structures. These additional anions ensure the neutrality of the crystal structures. Finally, a total of 16 independent atoms (1Zr, 1K, 3N, and 11O) was found in the unit cell of $\text{ZrK}(\text{OH})_2(\text{NO}_3)_3$, and 10 were found (1Zr, 1Rb, 2N, and 6O) in that of $\text{ZrRb}(\text{OH})_2(\text{NO}_3)_3$. The models were chemically sensible and provided a satisfactory trial structure model for a subsequent structure refinement. The two structures are based on the usual eightfold coordination of the Zr atom, which is bonded to another polyhedra through OH^- groups. Nitrate ions act as bidentate groups with respect to the metal atom, and the positive charge of the alkaline atoms is neutralized by free NO_3 groups. The two structure determinations are in accordance with the two chemical formulae $\text{ZrK}(\text{OH})_2(\text{NO}_3)_3$ and $\text{ZrRb}(\text{OH})_2(\text{NO}_3)_3$. As some spurious diffraction lines of KNO_3 or RbNO_3 were detected in the powder data, their patterns were also fitted in the final Rietveld refinements. The Rietveld refinements involved the usual profile parameters. The additional refined parameters were the scale factor and the atomic parameters, including isotropic atomic displacement parameters. Due to some instabilities observed during the refinements,

soft distance constraints were applied to the nitrate groups to keep the interatomic distances sensible, and light atoms (O, N) were constrained to have identical atomic displacement parameters. The conditions of the refinements are listed in Table 1. In spite of some difficulties arising from the moderate quality of the powder data and the number of parameters to be refined for the potassium compound, the final cycles converged to satisfactory structure models and profile residuals, $R_F = 0.042$ and $R_p = 0.077$ for $\text{ZrK}(\text{OH})_2(\text{NO}_3)_3$ and $R_F = 0.064$ and $R_p = 0.115$ for $\text{ZrRb}(\text{OH})_2(\text{NO}_3)_3$. Figures 2a and 2b show the final Rietveld plots for $\text{ZrK}(\text{OH})_2(\text{NO}_3)_3$ and $\text{ZrRb}(\text{OH})_2(\text{NO}_3)_3$, respectively. A better fit is obtained for the monoclinic phase. Final atomic positions and thermal atomic displacement parameters are given in Tables 2a and 2b. Selected bond distances and angles are reported in Tables 3a and 3b.

DESCRIPTION OF THE STRUCTURES

Figure 3 is a perspective view of the crystal structure of $\text{ZrK}(\text{OH})_2(\text{NO}_3)_3$ along $[010]$. The model may be described from one-dimensional units based on isolated chains of edge-sharing ZrO_8 polyhedra, running along the b axis at the approximate levels $x = 0.0$ (for $z = 0.0$) and $x = 0.5$ (for $z = 0.5$). Intercalated nitrate groups normal to (010) are located between the chains and each of them is associated with one K^+ cation, through ionic contacts (see $\text{K} \cdots \text{O7}$, O8 in Table 3a), making neutral the isolated chains. The shortest $\text{Zr} \cdots \text{Zr}$ distances are within the chain between two successive Zr atoms, which are bounded by double hydroxyl bridges according to a zigzag arrangement $[\cdots \text{Zr} - (\text{OH})_2 - \text{Zr} - (\text{OH})_2 - \text{Zr} - (\text{OH})_2 - \text{Zr} \cdots]$, as illustrated by the projection along $[001]$ in Fig. 4. Therefore, the eightfold coordination of the zirconium atom consists of four hydroxyl groups (OH1, OH2, and their pair deduced by symmetry-related operations, as indicated in Table 3a) and four bidentate nitrate O atoms, O1–O4. According to this description, the overall chemical composition of the neutral chain should be written as $[\text{Zr}(\text{OH})_{4/2}(\text{NO}_3)_2]_n$. In order to compare the structure of $\text{ZrK}(\text{OH})_2(\text{NO}_3)_3$ with that of $\text{ZrRb}(\text{OH})_2(\text{NO}_3)_3$, it is convenient to transform the cell of $\text{ZrRb}(\text{OH})_2(\text{NO}_3)_3$ given above by the transformation matrix $[0, 1, 0/0, 0, 1/1, 0, 0]$ (S.G. $Pbna$). The two structures are roughly equivalent, except that the plane of the nonbonded nitrate groups is parallel to the (a, c) plane in $\text{ZrRb}(\text{OH})_2(\text{NO}_3)_3$, while it is perpendicular in $\text{ZrK}(\text{OH})_2(\text{NO}_3)_3$. Apart from this difference, a similar structural description can be given for the two phases, with a well-defined zirconium coordination, and a complete chemical formulation $[\text{Zr}(\text{OH})_{4/2}(\text{NO}_3)_2]_n, n(M^+, \text{NO}_3^-)$ ($M = \text{K}, \text{Rb}$) may thus be proposed. The prevalent features in these structures are the eightfold coordination of zirconium atoms, the bidentate nitrate group, and the one-dimensional polymeric linkage through double

TABLE 1
Details of Rietveld Refinements for (a) $\text{ZrK}(\text{OH})_2(\text{NO}_3)_3$ and (b) $\text{ZrRb}(\text{OH})_2(\text{NO}_3)_3$

	Z	
	a	b
Wavelength (Å)	1.5406	
Step length ($^{\circ}2\theta$)	0.02	
Z	4	
Symmetry	monoclinic	orthorhombic
Space group	$P2_1/n$	$Pbca$
No. of atoms	16	10
2θ range ($^{\circ}$)	9–125	8–140
No. of reflections	1505	931
No. of structural parameters	54	26
No. of profile parameters	15	14
R_F	0.042	0.064
R_B	0.062	0.115
R_p	0.077	0.113
R_{wp}	0.099	0.153
R_{exp}	0.066	0.077

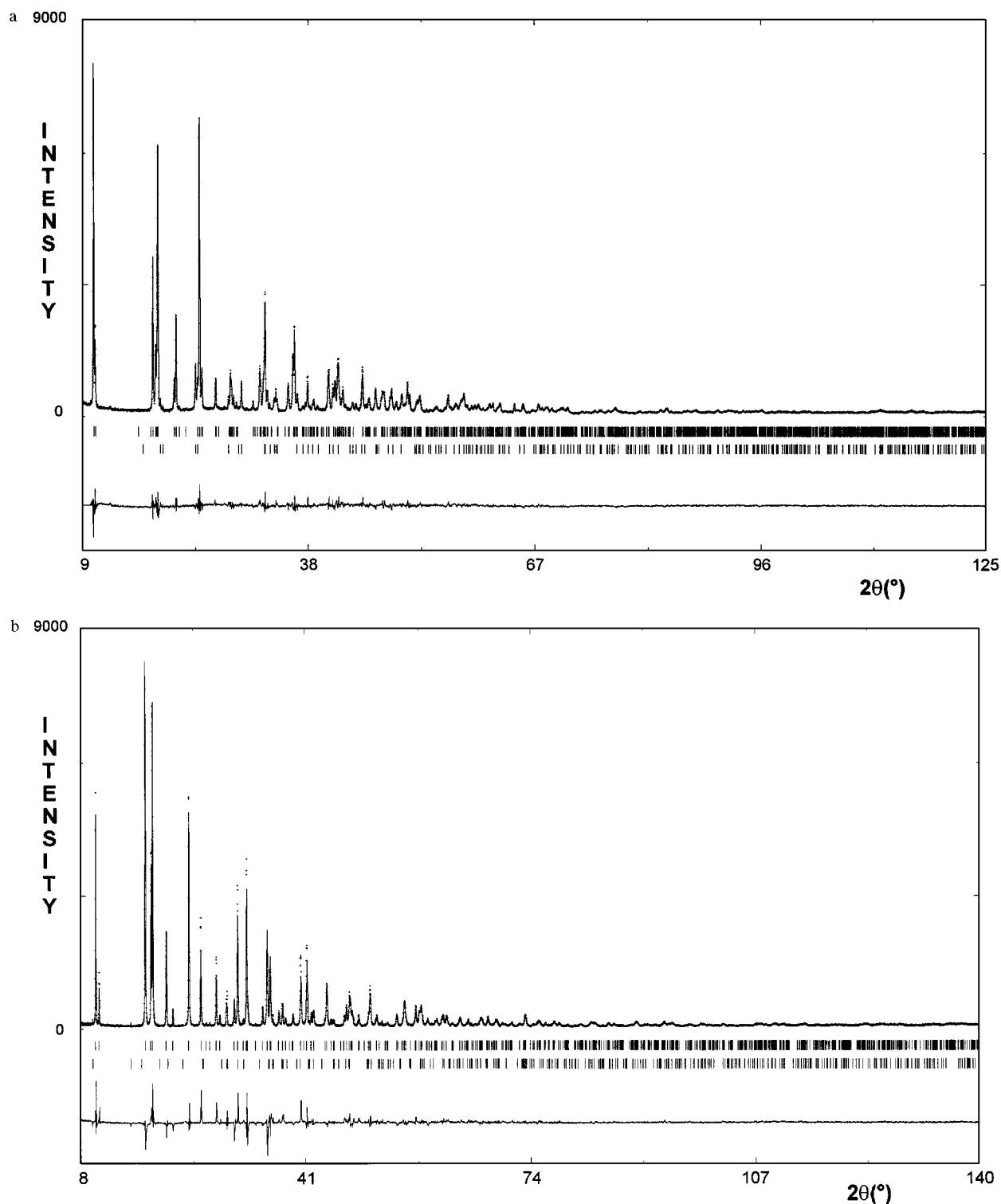


FIG. 2. Final Rietveld plots for the two mixed zirconium hydroxide nitrates (including spurious phases, KNO_3 and $RbNO_3$, lower vertical marks) for (a) $ZrK(OH)_2(NO_3)_3$ and (b) $ZrRb(OH)_2(NO_3)_3$.

OH–OH bridges. They clearly show the structural relationship between these new phases and the simple zirconium basic nitrates (18–20).

The Zr–O bond lengths in $ZrK(OH)_2(NO_3)_3$ and $ZrRb(OH)_2(NO_3)_3$ spread in the respective ranges 2.07–2.34 Å (mean value, 2.24 Å) and 2.06–2.26 Å (mean

TABLE 2a
Fractional Atomic Coordinates and Isotropic Atomic Displacement Parameters for ZrK(OH)₂(NO₃)₃

Atom	x	y	z	B _{iso} (Å ²)
Zr	0.4418(1)	0.252(1)	0.5058(4)	1.09(6)
K	0.3319(3)	0.244(3)	−0.000(1)	3.06(2)
OH1	0.481(1)	0.514(4)	0.379(2)	0.6(2) ^a
OH2	0.493(1)	−0.028(4)	0.633(2)	0.6(2) ^a
O1	0.3691(9)	0.249(3)	0.708(1)	0.6(2) ^a
O2	0.3647(9)	0.213(3)	0.307(1)	0.6(2) ^a
O3	0.336(1)	0.503(4)	0.555(1)	0.6(2) ^a
O4	0.329(1)	0.010(3)	0.484(1)	0.6(2) ^a
O5	0.272(1)	0.508(5)	0.751(2)	4.8(4) ^b
O6	0.264(1)	−0.042(4)	0.289(2)	4.8(4) ^b
O7	0.6283(8)	0.210(3)	0.018(2)	2.2(3) ^c
O8	0.558(1)	0.458(2)	−0.104(2)	2.2(3) ^c
O9	0.541(1)	0.091(2)	−0.131(2)	2.2(3) ^c
N1	0.583(1)	0.256(3)	−0.087(2)	2.2(3) ^c
N2	0.323(2)	0.425(5)	0.675(2)	4.8(4) ^b
N3	0.316(2)	0.064(5)	0.356(2)	4.8(4) ^b

^{a,b,c} Some parameters were allowed to vary in the same manner.

value, 2.17 Å). These values can be easily compared with the distances within the ZrO₈ polyhedra found in other zirconium nitrate phases, e.g., Zr(OH)₂(NO₃)₂·4H₂O (2.12–2.37 Å; mean value, 2.21 Å) (30) and Zr(OH)₂(NO₃)₂·4.7H₂O (2.06–2.44 Å; mean value, 2.21 Å) (18), Zr(OH)₂(NO₃)₂·1.65H₂O (2.05–2.38 Å and 2.11–2.37 Å; mean values, 2.22 and 2.24 Å) (19), Zr(OH)₃NO₃ (2.13–2.41 Å; mean value, 2.20 Å) (20). In spite of the modest precision obtained in the present investigation, it is worth noting that the results agree well with the previous studies on the zirconium basic salts from X-ray powder diffraction. It is also interesting to see the small changes within the Zr–O distances for both ZrK(OH)₂(NO₃)₃ and ZrRb(OH)₂(NO₃)₃, in comparison with those found in the hydrated zirconium hydroxide,

TABLE 2b
Fractional Atomic Coordinates and Isotropic Atomic Displacement Parameters for ZrRb(OH)₂(NO₃)₃

Atom	x	y	z	B _{iso} (Å ²)
Zr	0.5	0.4413(2)	0.75	1.76(7)
Rb	0.5	0.1615(2)	0.25	4.0(1)
OH	0.371(1)	0.486(1)	0.009(5)	4.3(2) ^a
O1	0.694(1)	0.3758(7)	0.739(3)	4.3(2) ^a
O2	0.5460(9)	0.3428(8)	0.953(2)	4.3(2) ^a
O3	0.723(1)	0.2700(9)	0.005(3)	4.3(2) ^a
O4	0	0.6540(6)	0.75	4.3(2) ^a
O5	0.1064(8)	0.5412(6)	0.850(2)	4.3(2) ^a
N1	0.664(1)	0.3261(9)	0.914(3)	4.3(2) ^a
N2	0	0.5801(7)	0.75	4.3(2) ^a

^{a,b,c} Some parameters were allowed to vary in the same manner.

Zr(OH)₂(NO₃)₂·4.7H₂O. This feature can be explained by the fact that, in the two mixed compounds, there are only two kinds of oxygen, with different chemical functions in the polyhedron, (i.e., oxygen atoms from hydroxyl groups and from bidentate nitrate ions), whereas the eightfold Zr coordination in Zr(OH)₂(NO₃)₂·4.7H₂O includes one more oxygen type, water oxygen atoms characterized by a stretching of the Zr–O bond lengths. In ZrK(OH)₂(NO₃)₃, a shortening of the Zr–OH distances is observed. The corresponding average value (2.15 Å) agrees with the values obtained for eightfold coordinated zirconium in various basic nitrates and sulfates, e.g., 2.14 Å for Zr(OH)₂(NO₃)₂·4.7H₂O (18), 2.14 Å for Zr(OH)₂(NO₃)₂·1.65H₂O (19), 2.17 Å for Zr(OH)₃NO₃ (20), 2.14 Å for Zr(OH)₂SO₄·H₂O (31), and 2.11 Å for both Zr(OH)₂SO₄·3H₂O (32) and ZrK₃OH(SO₄)₃·2H₂O (33). Due to the moderate precision achieved in the present study, it is not reasonable to emphasize these structural features too much or to discuss the ZrO₈ polyhedron shape (triangular dodecahedron, square antiprism, or bicapped trigonal prism) in terms of Hoard and Silverton's notations (34).

Two kinds of nitrate groups are present in the structures, i.e., nitrates nonbonded to the zirconium atom and nitrates acting as bidentate ligands (see Tables 3a and 3b). However,

TABLE 3a
Selected Bond Distances (Å) and Angles (°) with their Standard Deviations for ZrK(OH)₂(NO₃)₃

Within the ZrO ₈ polyhedra			
Zr–OH1	2.07(2)	Zr–OH1 ^I	2.17(2)
Zr–OH2	2.21(2)	Zr–OH2 ^{II}	2.17(2)
Zr–O1	2.32(2)	Zr–O2	2.34(2)
Zr–O3	2.33(2)	Zr–O4	2.33(2)
Within the NO ₃ groups			
N1–O1	1.31(3)	O1–N1–O3	114(2)
N1–O3	1.28(2)	O1–N1–O5	124(3)
N1–O5	1.23(3)	O3–N1–O5	122(3)
N2–O2	1.27(3)	O2–N2–O4	115(2)
N2–O4	1.32(2)	O2–N2–O6	125(3)
N2–O6	1.25(3)	O4–N2–O6	120(3)
N3–O7	1.30(2)	O7–N2–O8	116(2)
N3–O8	1.25(2)	O7–N2–O9	119(2)
N3–O9	1.26(2)	O8–N2–O9	118(2)
Shortest K...O contacts			
K...O1 ^{III}	2.92(2)	K...O6 ^{IV}	2.89(2)
K...O2	3.06(2)	K...O7 ^V	2.71(3)
K...O4 ^{IV}	3.09(2)	K...O8 ^{VI}	2.70(2)
K...O5 ^{III}	3.04(3)	K...O9 ^V	3.14(2)
Shortest Zr...Zr distances			
Zr...Zr ^I	3.455(9)	Zr...Zr ^{II}	3.496(9)

Note. Symmetry codes: I, 1 – x, 1 – y, 1 – z; II, 1 – x, – y, 1 – z; III x, y, z – 1; IV, 0.5 – x, 0.5 + y, 0.5 – z; V, 1 – x, – y, – z; VI, 1 – x, 1 – y, – z.

TABLE 3b
Selected Bond Distances (Å) and Angles (°) with their Standard Deviations for $ZrRb(OH)_2(NO_3)_3$

	Within the ZrO_8 polyhedra		
Zr–(OH ^I , OH ^{II})	2.13(2)	Zr–(OH ^{IV,V})	2.26(2)
Zr–(O1, O1 ^{III})	2.24(1)	Zr–(O2, O2 ^{III})	2.06(1)
	Within the NO_3 groups		
N1–O1	1.34(3)	O1–N1–O2	103(2)
N1–O2	1.24(2)	O1–N1–O3 ^I	133(2)
N1–O3 ^I	1.23(2)	O2–N1–O3 ^I	124(2)
N2–O4	1.22(1)	O4–N2–(O5, O5 ^{VI})	116(1)
N2–(O5, O5 ^{VI})	1.38(1)	O5–N2–O5 ^{VI}	125(1)
	Shortest K ... O contacts		
Rb ... (O1 ^{VII} , O ^{VIII})	3.15(1)	Rb ... (O4 ^{IX} , O4 ^X)	2.925(4)
Rb ... (O3, O3 ^{II})	3.21(2)	Rb ... (O5 ^{XI} , O5 ^{XII})	3.25(1)
	Shortest Zr ... Zr distances		
Zr ... Zr ^{XIII}	3.504(2)		

Note. Symmetry codes: I, $x, y, 1 + z$; II, $1 - x, y, 0.5 - z$; III, $1 - x, y, 1.5 - z$; IV, $x, 1 - y, 0.5 + z$; V, $1 - x, 1 - y, 1 - z$; VI, $-x, y, 1.5 - z$; VII, $1.5 - x, 0.5 - y, z - 0.5$; VIII, $x - 0.5, 0.5 - y, 1 - z$; IX, $x + 0.5, y - 0.5, z - 1$; X, $0.5 + x, y - 0.5, z$; XI, $0.5 - x, y - 0.5, z - 1$; XII, $0.5 + x, y - 0.5, 1.5 - z$; XIII, $x, 1 - y, 1 - z$.

due to the lack of precision on oxygen atomic positions, no definitive conclusion can be stated about the distances behavior within the intercalated nitrate groups.

The unique alkaline cations (Rb^+ or K^+) are perfectly ordered in the structures and form ionic contacts with lengths less than 3.15 Å for K^+ and 3.25 Å for Rb^+ with nitrate oxygen atoms bonded or nonbonded to the Zr atom (Tables 3a and 3b). The alkaline atoms appear as eightfold coordinated. The shortest $Rb \cdots O$ and $K \cdots O$ distances occur with the oxygen from the free nitrate group, and the longest ones involve the oxygen from the free nitrate group, and the longest ones involve the oxygen atoms of the bidentate nitrate groups. In particular, the $K \cdots O$ contacts could be compared with those reported for the structure of $ZrK_3OH(SO_4)_3 \cdot 2H_2O$ (33). It is clear that the K^+ , as well as the Rb^+ , cations ensure the interconnection between the neutral and linear chains and, then, play a major role in contributing to the stability of the structures.

DISCUSSION

Two new zirconium basic nitrates have been synthesized and their crystal structures have been solved *ab initio* from powder diffraction data, using conventional X-rays. Although the precision of these studies is modest, due to the combined effects of diffraction line broadening, the degree of line-overlap, residual preferred orientation, and impurity phases (ca. 5%), the structure models are complete and, thus, can be interpreted in terms of the structural building

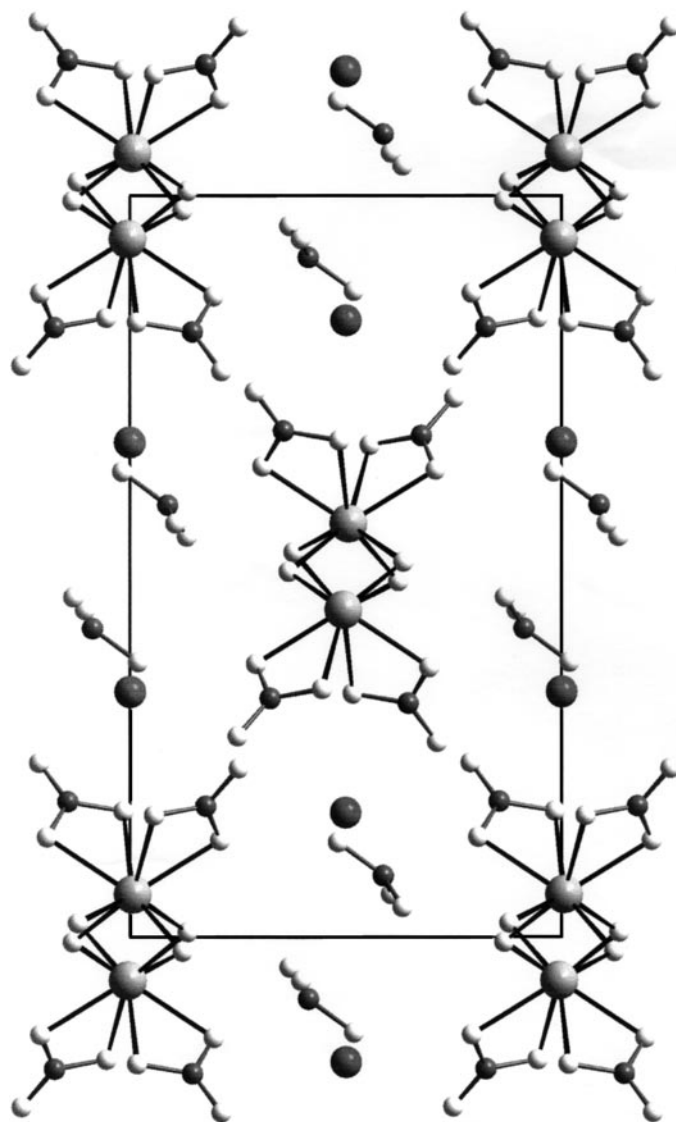


FIG. 3. View of the structure of $ZrK(OH)_2(NO_3)_3$ along the b axis (a vertical and c horizontal). The large black circles are N atoms; the small black circles are K atoms; the large gray circles are Zr atoms; and the small gray circles are O atoms.

principles already known for the zirconium hydroxide nitrates family. Indeed, it is possible to summarize the different structure types, from both the dimensionality of the structures and the overall composition of the chains or layers, as follows:

Type I: 1D macrocations formulated as $(Zr(OH)_{4/2}(NO_3)(H_2O)_2)_n$, balance by an equivalent number of nitrate groups. Representative examples are $Zr(OH)_2(NO_3)_2 \cdot 4H_2O$ (30) and $Zr(OH)_2(NO_3)_2 \cdot 4.7H_2O$ (18).

Type II: 1D neutral chains $(Zr(OH)_{4/2}(NO_3)_2)_n$, found in α - $Zr(OH)_2(NO_3)_2 \cdot 1.65H_2O$, in β - $Zr(OH)_2(NO_3)_2 \cdot H_2O$ (19), and in the structures reported here for $ZrK(OH)_2(NO_3)_3$ and $ZrRb(OH)_2(NO_3)_3$.

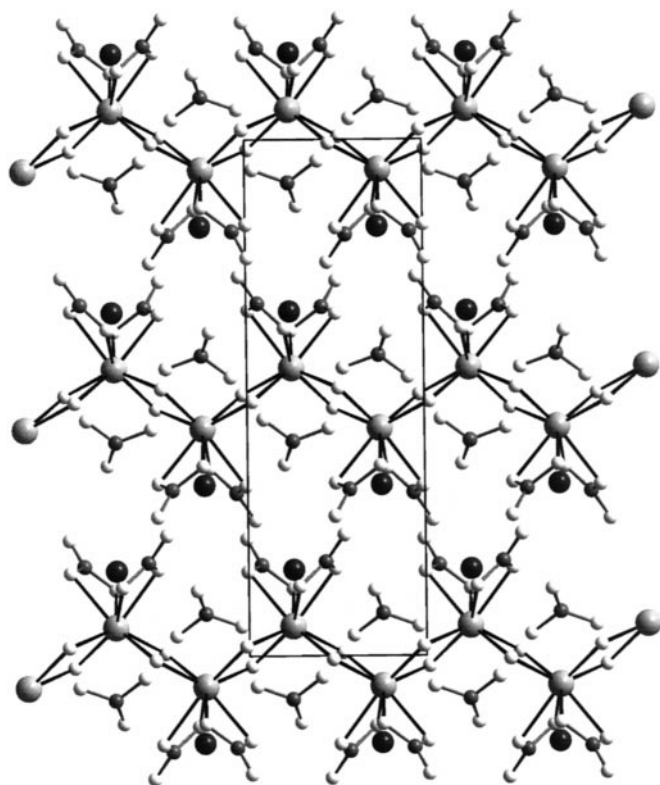


FIG. 4. View of the structure of $\text{ZrK}(\text{OH})_2(\text{NO}_3)_3$ along the c axis (a vertical and b horizontal) showing chain-like arrangements (parallel to the b axis) of the ZrO_8 polyhedra through double hydroxyl bridges.

Type III: 2D neutral layers $(\text{Zr}(\text{OH})_{4/2}(\text{OH})_{2/2}(\text{NO}_3))_n$, reported for $\text{Zr}(\text{OH})_3(\text{NO}_3)$ (20).

With regard to this classification, the structures of the two new compounds $\text{ZrK}(\text{OH})_2(\text{NO}_3)_3$ and $\text{ZrRb}(\text{OH})_2(\text{NO}_3)_3$, contain 1D units, as in the two varieties of $\text{Zr}(\text{OH})_2(\text{NO}_3)_2 \cdot (1+x)\text{H}_2\text{O}$ ($x = 0$ and $x = 0.65$), and therefore they belong to Type II. Moreover, the magnitude of the cohesion within the typical chains of ZrO_8 polyhedra may be discussed through the $\text{Zr} \dots \text{Zr}$ distances between the bridged Zr atoms. As already reported for known zirconium basic salts containing $[\text{Zr}(\text{OH})_2]_n^{2n+}$ chains (18, 19, 20, 32, 35), the common values for $\text{Zr} \dots \text{Zr}$ intrabond lengths spread in the range 3.55–3.60 Å, except for α - $\text{Zr}(\text{OH})_2(\text{NO}_3)_2 \cdot 1.65\text{H}_2\text{O}$ and β - $\text{Zr}(\text{OH})_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, in which shorter average values (3.46 and 3.52 Å) are found. It is interesting to note that this is also true for the two mixed compounds (see Tables 3a and 3b); then, this feature must be a characteristic of Type II. This observation may be related to the closeness of the chains in structures of Type II. In the same way, it is of interest to compare the density calculated for the phases (Table 4). The smaller values are obtained for the 1D structures (Type I) with linear and positive chains while the neutral layers structure of $\text{Zr}(\text{OH})_3\text{NO}_3$ (Type III)

TABLE 4
Calculated Density ($\text{g} \cdot \text{cm}^{-3}$) for Zirconium Hydroxide Nitrates

Compound	Type	Density
$\text{Zr}(\text{OH})_2(\text{NO}_3)_2 \cdot 4.7\text{H}_2\text{O}$ (18)	I	2.088
$\text{Zr}(\text{OH})_2(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (30)	I	2.210
α - $\text{Zr}(\text{OH})_2(\text{NO}_3)_2 \cdot 1.65\text{H}_2\text{O}$ (19)	II	2.493
β - $\text{Zr}(\text{OH})_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (19)	II	2.477
$\text{ZrK}(\text{OH})_2(\text{NO}_3)_3$	II	2.493
$\text{ZrRb}(\text{OH})_2(\text{NO}_3)_3$	II	2.695
$\text{Zr}(\text{OH})_2\text{NO}_3$ (20)	III	2.950

exhibits the higher value ($2.95 \text{ g} \cdot \text{cm}^{-3}$). The structures with neutral zigzag chains (Type II) show intermediate values, around $2.48 \text{ g} \cdot \text{cm}^{-3}$, for α - $\text{Zr}(\text{OH})_2(\text{NO}_3)_2 \cdot 1.65\text{H}_2\text{O}$, β - $\text{Zr}(\text{OH})_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, and $\text{ZrK}(\text{OH})_2(\text{NO}_3)_3$. The deviation from this mean, observed for $\text{ZrRb}(\text{OH})_2(\text{NO}_3)_3$, is related to the atomic weight of Rb in comparison with that of K. In fact, the major difference between the two mixed compounds and the two modifications of the hydrated phases arises from the cohesion of the structures, based on a hydrogen-bonding scheme between chains in the two hydrated basic salts and on ionic contacts involving K^+ and Rb^+ and NO_3^- species located between the chains in the mixed compounds. Also interesting is the behavior of the phases in water, which is likely related to the characteristics of the crystal structures. Indeed, Type II phases are highly soluble, while Type I compounds are poorly soluble and the Type III compound is insoluble.

To conclude, the crystal structure of the two new zirconium compounds extends the structural classification of zirconium basic nitrates to mixed phases, from common structural building principles. The study demonstrates again how rich the basic nitrate families are, whatever the values (II, III, IV) of the metal involved in the phases.

ACKNOWLEDGMENT

The authors are indebted to Professor M. Louër for helpful discussions. They are also grateful to G. Marsolier and L. Pelloquin for their technical assistance in powder-diffraction data collection and chemical synthesis, respectively.

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