Zirconium Oxalates: Zr(OH)$_2$(C$_2$O$_4$)$_2$, (H$_{11}$O$_5$)$_2$[Zr$_2$(C$_2$O$_4$)$_5$(H$_2$O)$_4$], and MM'[Zr(C$_2$O$_4$)$_3$]·xH$_2$O with M and M' = Ammonium, Alkali Metal, and Hydroxonium Ion H$_{2n+1}$O$_n^+$ (n = 2, 3, 4)

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ABSTRACT: Crystallized powder of dihydroxide zirconium oxalate Zr(OH)$_2$(C$_2$O$_4$)$_2$ (ZrOx) was obtained by precipitation and the structure determined from powder X-ray data. The three-dimensional (3D) framework observed in (ZrOx) results from the interconnection of zirconium hydroxide chains $^{1}_1$[Zr(OH)$_2$]$^{2-}$ and zirconium oxalate chains $^{1}_1$[(Zr(C$_2$O$_4$)$_4$)$^{1+}$]. Single crystals of (H$_{11}$O$_5$)$_2$[Zr$_2$(C$_2$O$_4$)$_5$(H$_2$O)$_4$] (H$_2$Zr2OS) were obtained by evaporation. The structure contains dimeric anions [Zr$_2$(C$_2$O$_4$)$_5$(H$_2$O)$_4$]$^{2-}$ connected through hydrogen bonds to hydroxonium ions (H$_1$O$_3$)$^+$ to create a 3D supramolecular framework. The addition of ammonium or alkali nitrate led to the formation of single crystals of Na$_2$[Zr(C$_2$O$_4$)$_3$]·xH$_2$O (Na2ZrOx3), M(H$_2$O)[Zr(C$_2$O$_4$)$_3$]·H$_2$O, M = K (KHZrOx3), M = NH$_4$ (NH$_4$HZrOx3), M(H$_2$O)$_2$[Zr$_2$(C$_2$O$_4$)$_3$]$_{1.5}$[Zr(C$_2$O$_4$)$_3$]$_{1.5}$, M = Rb (RbHZrOx3), and M = Cs (CsHZrOx3). For the five compounds, the structure contains ribbons $^{1}_1$[(ZrOx)$_3$]$^{2-}$ formed by entities Zr(C$_2$O$_4$)$_4$ sharing two oxalates. In (Na2ZrOx3), the shared oxalates are in cis positions and the chain $^{1}_1$[Zr–Ox] is stepped with a Zr–Zr–Zr angle of 98.27(1)$^\circ$. In the other compounds, the shared oxalates are in trans positions and the chains $^{1}_1$[Zr–Ox] are corrugated with Zr–Zr–Zr angles in the range 140.34(1)–141.07(1)$^\circ$. In the compounds (MHZrOx3), the cohesion between the ribbons is ensured by the alkaline or ammonium cations and the hydroxonium ions (H$_1$O$_3$)$^+$ for M = K, NH$_4$, (H$_2$O)$_5$ for M = Cd or Cs. During the thermal decomposition of the alkaline-free zirconium oxalates (ZrOx), (H$_2$Zr2OS), and (NH4HZrOx3), the formed amorphous zirconia is accompanied by carbon; the oxidation of carbon at about 540 $^\circ$C to carbon dioxide is concomitant with the crystallization of the stabilized tetragonal zirconia.

INTRODUCTION

Zirconium-based oxalates play an important role in various domains. In chemistry, for example, the calcination of zirconium oxalate gels or molecular oxalate precursors was used for the preparation of nanosized powders, minispheres, or porous stabilized zirconium dioxide; a precursor of tetragonal yttria-stabilized zirconia (YSZ) was prepared by the oxalate method in an ethanol solution; the calcination of barium zirconium oxalate produced pure BaZrO$_3$ used as an inert crucible material for melt processing of YBCO superconductors or as nanopowders to induce artificial pinning centers in YBCO; the calcination of lead zirconium oxalate produced antiferroelectric lead zirconate PbZrO$_3$. In catalysis, the calcination of a Cu/Zr coprecipitate by a NaOH–Na$_2$C$_2$O$_4$ mixture solution produced a highly active and stable Cu/ZrO$_2$ catalyst for the partial oxidation of methanol to hydrogen for proton-exchange membrane fuel cell application. In biochemistry, zirconium oxalate increases the thermal and enzymatic stability of type I collagen. These potential applications have attracted many solid-state chemists to study the synthesis and the structure of many double or triple zirconium oxalates with monovalent and divalent cations. Almost all well-characterized double zirconium oxalates contain the tetrahedral anionic Zr(C$_2$O$_4$)$_4$ units, the charge being compensated by divalent cations in M$_2$Zr(C$_2$O$_4$)$_3$·nH$_2$O compounds with M = Ba, Sr, Ca, Pb, Cd, and (H$_2$en)CdZr(C$_2$O$_4$)$_3$·nH$_2$O (en = ethylene diamine) or by one divalent and two monovalent cations in M'$_2$MZr(C$_2$O$_4$)$_4$·4.4nH$_2$O compounds with M = Cd, M' = Na, K, NH$_4$, and M = Mn, M' = K or by four monovalent cations in M'$_2$Zr(C$_2$O$_4$)$_3$·nH$_2$O compounds obtained with M' = Na and K. Hybrid supramolecular architectures have been created by the assemblage of the Zr(C$_2$O$_4$)$_4$ units through...
organic dications with N−H donor functions or through H-bonds involving ditopic benzimidazolium or bisimidazolium-benzene monocations.

Astonishingly, little is known about single zirconium oxalates. The first accessible report of the study on zirconium oxalate is from Venable and Baskerville in 1896. The authors did not succeed in the preparation of the neutral oxalate Zr(C₂O₄)₂ but obtained by precipitation the basic oxalate noted Zr(C₂O₄)₂·Zr(OH)₄ and by crystallization the acid oxalate, Zr(C₂O₄)₂·H₂C₂O₄·8H₂O. They also prepared double acid oxalates with

Table 1. Crystal Data and Structure Refinement Parameters for Zr(OH)₂(C₂O₄) (ZrOx) and (H₁₁O₅)₂[Zr₂(C₂O₄)₅(H₂O)₄] (H₂Zr₂Ox₅)

|                | ZrOx Zr(OH)₂(C₂O₄) | H₂Zr₂Ox₅ (H₁₁O₅)₂[Zr₂(C₂O₄)₅(H₂O)₄] |
|----------------|---------------------|--------------------------------------|
| CCDC number    | 2011396             | 2011397                              |
| empirical formula | C₂O₄H₂Zr₁       | C₁₁O₅H₄₂Zr₂                        |
| formula weight | 213.3              | 876.78                              |
| temperature/K  | 293                | 296                                  |
| crystal system | Monoclinic         | triclinic                           |
| space group    | C₂/c               | P1                                  |
| a/Å            | 12.813(4)          | 6.9269(3)                           |
| b/Å            | 5.8882(14)         | 10.4427(6)                          |
| c/Å            | 6.7088(13)         | 10.6447(6)                          |
| α/deg          | 90                 | 78.421(2)                           |
| β/deg          | 118.25(2)          | 86.155(2)                           |
| γ/deg          | 90                 | 89.945(2)                           |
| volume/Å³      | 445.9(2)           | 752.56(7)                           |
| Z              | 4                  | 1                                   |
| p₁₂₁ g/cm³     | 3.177              | 1.935                               |
| µ/mm⁻¹         | 20.01              | 0.821                               |
| F(000)         | 408                | 442                                 |
| radiation      | Cu Kα              | Mo Kα                               |
| 2θ range for data collection/deg | 5–110 (stepsize 0.02) | 3.90–51.88 |
| index ranges   |                     | 19,393                               |
| reflections collected | 5614/39/9        | 2914/15/253                         |
| independent reflections | 2914 [Rint = 0.0389, Rap = 0.0581] |  |
| data/restraints/parameters | 5614/39/9        | 2914/15/253                         |
| goodness-of-fit on F² | 4.45                | 1.045                               |
| final R indexes [I ≥ 2σ (I)] | R₁ = 0.0417 wR₂ = 0.0600 | R₁ = 0.0282 wR₂ = 0.0529 |
| final R indexes [all data] | R₁ = 0.0417 wR₂ = 0.0600 | R₁ = 0.0378 wR₂ = 0.0566 |
| largest diff. peak/hole/e Å⁻³ | 1.01/−1.82          | 0.55/−0.40                         |

Figure 1. In (ZrOx), the zirconium atom is coordinated by four OH and two bidentate oxalates (a) with a trigonal pyramidal overall environment (M is the middle of the C−C bond) (b) giving a square antiprism ZrO₈ polyhedron (c) and a (3D) framework (d) that can be deconstructed in two intersecting ribbons ¹[Zr(OH)₂]₁²⁻ (e) and ¹[Zr(C₂O₄)]₁²⁻ (f).
sodium, Zr(C\textsubscript{2}O\textsubscript{4})\textsubscript{2}·3Na\textsubscript{2}C\textsubscript{2}O\textsubscript{4}·H\textsubscript{2}C\textsubscript{2}O\textsubscript{4}·5H\textsubscript{2}O, and potassium, [Zr(C\textsubscript{2}O\textsubscript{4})\textsubscript{2}]·(K\textsubscript{2}C\textsubscript{2}O\textsubscript{4})\textsubscript{2}·H\textsubscript{2}C\textsubscript{2}O\textsubscript{4}·8H\textsubscript{2}O. The precipitation of the basic oxalate (Zr(C\textsubscript{2}O\textsubscript{4})(OH)\textsubscript{2})\textsubscript{2} under acidic conditions was confirmed by Kobayashi et al. and the amorphous hydroxide Zr(OH)\textsubscript{2} precipitates under neutral conditions.\textsuperscript{30,31} In 1931, Gable reported the preparation of anhydrous oxalate Zr(C\textsubscript{2}O\textsubscript{4})\textsubscript{2} by precipitation from a methanol solution.\textsuperscript{32} In fact, the obtained compound was later identified as Zr(C\textsubscript{2}O\textsubscript{4})\textsubscript{2}·2CH\textsubscript{3}OH and the tetrahydrate Zr(C\textsubscript{2}O\textsubscript{4})\textsubscript{2}·4H\textsubscript{2}O was also prepared from methanol solution but without precautions to exclude humidity.\textsuperscript{33} However, except the structure of a compound formulated Zr(OH)\textsubscript{2}(C\textsubscript{2}O\textsubscript{4})·H\textsubscript{2}O,\textsuperscript{34} no other structure determination of simple zirconium oxalate has been reported.

In this paper, we report the structures of the basic oxalate Zr(OH)\textsubscript{2}(C\textsubscript{2}O\textsubscript{4})\textsubscript{2} determined from powder X-ray diffraction pattern and of the acidic oxalate (H\textsubscript{11}O\textsubscript{5})\textsubscript{2}[Zr\textsubscript{2}(C\textsubscript{2}O\textsubscript{4})\textsubscript{5}(H\textsubscript{2}O)\textsubscript{4}] determined from single-crystal X-ray data. The introduction of a monovalent cation (Na\textsuperscript{+}, K\textsuperscript{+}, NH\textsubscript{4}\textsuperscript{+}, Rb\textsuperscript{+}, Cs\textsuperscript{+}) in the reagent solution gives a series of zirconium oxalates with three different structures determined from single-crystal X-ray data and built on zirconium-oxalate chains.

In general, the decomposition of oxalates, whether they are of transition metals, lanthanides, or even actinides are the subject of numerous studies motivated by their role as precursors of transition metals, lanthanides, or even actinides are the subject of numerous studies motivated by their role as precursors of numerous studies motivated by their role as precursors of numerous studies motivated by their role as precursors of numerous studies motivated by their role as precursors of numerous studies motivated by their role as precursors of numerous studies motivated by their role as precursors of numerous studies motivated by their role as precursors of numerous studies motivated by their role as precursors of numerous studies motivated by their role as precursors of numerous studies motivated by their role as precursors of numerous studies motivated by their role as precursors of numerous studies.
ZrO₂ polyhedron (2.16(4) and 2.13(4) Å), the OH–OH bridge distance (2.48(5) Å), the Zr–Zr distance (3.511(5) Å), and the Zr–Zr–Zr (145.7(5)°) angle are comparable to the distances observed in other zirconium di-hydroxide salts with eight-coordinated zirconium (Table S1). The other Zr–O distances observed within the ZrO₂ polyhedron involving oxygen from oxalate ligands are longer (2.33(5) and 2.39(4) Å). These distances are in agreement with those calculated in the hydroxide oxalate anion [(ZrOH(C₂O₄)₃)₂]° built from two crystallographic independent [ZrOH(C₂O₄)₃]° entities connected by two bridging OH groups observed in the complex Na₆[ZrOH-(C₂O₄)₃]°·7H₂O. The average Zr–O value (2.25 Å) is in agreement with the sum of the ionic radii (r₂⁺ + r_OH = 2.16 Å). The bond-valence sum for Zr calculated using Brese and O'Keeffe data with b = 0.37 Å is 3.48 vu.

The structure of a compound Zr(OH)₂(C₂O₄)·0.5H₂O determined from single-crystal X-ray data has been reported; the refined structure perfectly matches that of SrC₂O₄·0.5H₂O. The structure of (H₁₁O₅)₂[Zr₂(C₂O₄)₅(H₂O)₄] (H₂Zr₂Ox₅). Its description as a pseudosquare rather than a tetrahedron is more appropriate (the sides of the trigonal prism and belonging to the bicapped 4-4 trigonal bipyramidal overall environment of Zr, and the zirconium-oxygen ions through hydrogen bonds involving oxalate oxalate ions O5, O7, O9, O10, O11, and O12 (Figure 3) constitute a third isomer of the hydroxonium ion (H₁₁O₅)+ and between (H₁₁O₅)+ and di-metallic ion (H₁₁O₅)° (Figure 2e) that can be considered as a supramolecular ionic aggregate as discussed by Bernal and Watkins. The characteristics of the hydrogen bonds in the hydroxonium ion (H₁₁O₅)+ and between (H₁₁O₅)+ and di-metallic ion [Zr₂(C₂O₄)₅(H₂O)₄]° are reported in Table S2. Zirconium Ammonium or Alkali Metal Double Oxalates Na₂[Zr(C₂O₄)₃]·2H₂O (Na₂ZrOx3), M(H₇O₃)[Zr(C₂O₄)₃]·H₂O (M = K, KHZrOx3; M = NH₄, NH₄HZrOx3), M(H₂ZrOx3)₀.₅[H₂O]₀.₅[Zr(C₂O₄)₃] (M = Rb, RbHZrOx3: M = Cs, CsHZrOx3). The structure of (Na₂ZrOx3) was determined in the space group P1; (KHzrOx3) and (NH₄HZrOx3) are isorstructural and the structures determined in the space group P2₁/c, (RbHzrOx3) and (CsHZrOx3) are isorstructural and the structures determined in the space group P1. Crystal data and structure refinement parameters are reported in Table 2. In the five compounds, the zirconium atom is coordinated by eight oxygen atoms forming a bicapped 4-4 trigonal prism and belonging to four bidentate oxalate ions that create a [Zr₂(C₂O₄)₅]° entity (Figure 3) with an overall geometry between square and tetrahedron. Its description as a pseudosquare rather than a distorted tetrahedron is more appropriate (the sides of the pseudosquare are between 4.249(1) and 4.620(8) Å, the diagonals between 5.518(4) and 5.587(1) Å, four M–Zr–M angles are between 92.52(1) and 104.1(1)°, and two others between 139.54(1) and 143.98(1)° (Table S3). The use of a

Figure 3. [Zr(C₂O₄)₃]° structural building unit, the overall polyhedron around Zr, the bicapped 4-4′ trigonal environment of Zr, and the zirconium-oxalate ribbons in (a) (Na₂ZrOx3), (b) (KHZrOx3) and (NH₄HZrOx3), and (c) (RbHzrOx3) and (CsHZrOx3). (× green) = inversion center. M, is the middle of the C–C bond of Ox₂ (i = 1–4).
Table 2. Crystal Data and Structure Refinement Parameters for Na2[Zr(C2O4)3]·2H2O (Na2ZrOx3), K(H7O3)[Zr(C2O4)3]·H2O (KHZrOx3), (NH4)·H2O)[Zr(C2O4)3]·H2O ((NH4)HZrOx3), Rb(H5O2)0.5(H9O4)0.5[Zr(C2O4)3] (RbHZrOx3), and Cs(H5O2)0.5(H9O4)0.5[Zr(C2O4)3] (CsHZrOx3)

| Compound                  | Na2[Zr(C2O4)3]·2H2O | KHZrOx3 | (NH4)HZrOx3 | RbHZrOx3 | CsHZrOx3 |
|---------------------------|----------------------|---------|-------------|----------|----------|
| CCDC number               | 2011398              | 2011399 | 2011400     | 2011400  | 2011402  |
| Empirical formula         | Na2ZrC6O14H4         | KZrC6O16H19 | ZrC6O16NH13 | RbZrC6O16H9 | CsZrC6O15H7 |
| Form weight               | 437.29               | 467.45  | 446.39      | 495.81   | 540.73   |
| Temperature/K             | 296                  | 296     | 296         | 296      | 296      |
| Crystal system            | monoclinic           | monoclinic | monoclinic   | monoclinic | monoclinic |
| Space group               | C2/c                 | P21/c   | P21/c       | P1       | P1       |
| a/Å                       | 13.8646(9)           | 9.2166(9) | 9.3411(7)   | 8.9788(6) | 9.1847(5) |
| b/Å                       | 10.4241(6)           | 11.169(1) | 11.1701(8)  | 8.9788(6) | 9.1847(5) |
| c/Å                       | 8.9290(5)            | 14.094(2) | 14.2537(9)  | 10.6518(7) | 10.6352(5) |
| α/°                       | 90                   | 90      | 90          | 90       | 79.179(3) |
| β/°                       | 90.743(3)            | 107.718(5) | 107.699(2)  | 72.476(4) | 72.333(2) |
| γ/°                       | 1284.00(13)          | 1382.03(2) | 1416.85(17) | 678.70(8) | 696.41(6) |
| Volume/Å³                 | 1284.00(13)          | 1382.02(2) | 1416.85(17) | 678.70(8) | 696.41(6) |
| Z                          | 4                    | 4       | 4           | 2        | 2        |
| μ/mm²                     | 1.006                | 1.191   | 0.871       | 4.459    | 3.449    |
| F(000)                    | 856                  | 928     | 896         | 480      | 511      |
| Radiation                 | Mo Kα (λ = 0.71073)  |         |             |          |          |
| 2θ range for data         | 4.90—59.36           | 4.64—53.06 | 4.72—67.34  | 4.69—66.00 | 5.60—68.52 |
| Reflections collected     | 1722 [Rint = 0.0385, Rsigma = 0.0440] | 2668 [Rint = 0.0389, Rsigma = 0.0087] | 5638 [Rint = 0.0219, Rsigma = 0.0446] | 1886 [Rint = 0.0411, Rsigma = 0.0655] | 5777 [Rint = 0.0322, Rsigma = 0.0463] |
| Goodness-of-fit on        | 1.068                | 1.060   | 1.043       | 1.026    | 0.973    |
| F²                         | 2.34—3.59            |         |             |          |          |
| Final R indexes [I ≥ 2σ(I)] | R1 = 0.0286         | R1 = 0.0291 | R1 = 0.0248 | R1 = 0.0367 | R1 = 0.0377 |
| Final R indexes [all      | wR2 = 0.0534         | wR2 = 0.0593 | wR2 = 0.0583 | wR2 = 0.0900 | wR2 = 0.0900 |
| data]                     | R2 = 0.0368          | R2 = 0.0422 | R2 = 0.0340 | R2 = 0.0524 | R2 = 0.0486 |
| Largest diff. peak/hole/e Å⁻³ | 0.77/—0.38         | 0.42/—0.50 | 0.70/—0.43 | 0.90/—0.99 | 2.34/—3.59 |

In (Na₂ZrOx₃), the entities [Zr(C₂O₄)₃] are connected by two centrosymmetric Ox₁ oxalate ions acting as bidentate and directed in a cis configuration toward the extremities of the side M₁—M₁ of the pseudosquare, giving a steppied chain [Zr—Ox₁] with an Ox₁—Zr—Ox₁ = Zr—Zr—Zr angle of 98.27(1)°. The Zr—Zr distance is 5.903(1) Å. The bond valence sums are 3.78 and 3.85 Åv.

In (KHZrOx₃), the entities [Zr(C₂O₄)₃] are connected by two noncentrosymmetric Ox₁ oxalate ions related to the 21 axis and directed in a trans configuration toward a diagonal of the pseudosquare. The bis-bidentate character of the two Ox₁ oxalate ions leads to the formation a zig-zag chain [Zr—Ox₁] with Ox₁—Zr—Ox₁ = Zr—Zr—Zr angle of 141.07(1)° and 140.98(1)° for M = K and NH₄, respectively. The Zr—Zr distance is 5.923(1) and 5.926(1) Å for M = K and NH₄, respectively.

In (RbHZrOx₃), M = Rb and Cs; the entities [Zr(C₂O₄)₃] are connected by two centrosymmetric crystallographic independent oxalate ions Ox₂ and Ox₃ directed in a trans configuration toward the diagonal of the pseudosquare. The oxalate ions Ox₂ and Ox₃ are both bidentate. Overall, it gives a zig-zag chain [Zr—Ox₁—Zr—Ox₁—Zr—Ox₁] with Ox₁—Zr—Ox₁ = Zr—Zr—Zr angle of 140.83(2)° and 140.34(1)° for M = Rb and Cs, respectively. The Zr—Zr distances are 5.885(15) and 5.905(15) Å for Zr connected by Ox₂ and Ox₃, respectively, for M = Rb and 5.888(8) and 5.900(8) Å for M = Cs.

The ribbons are very similar for the four (MHZrOx₃) compounds, the main difference being the symmetry of the chains with the presence of a 2₁ axis along the chain for M = K.
and NH₄ and inversion centers at the middle of the C−C bonds of connecting oxalates for M = Rb and Cs (Figure 3).

Several actinide oxalates with formulae M₄[An(C₂O₄)₄]·nH₂O (An = Th, U, Np, Pu) are built of metal-oxalate chains 1∞[An−Ox] very similar to that in (MHZrOx₃), M = Rb and Cs. However, because of the largest ionic radius for AnIV compared to ZrIV, AnIV ions tend to adopt a 9 or 10 coordination. In M₄[An(C₂O₄)₄]·nH₂O, the actinides atoms are coordinated by five bidentate oxalates and the ribbons are formulated 1∞[An−(C₂O₄)₄]⁴⁻. According to the geometry of the overall environment of the metal atom (square pyramid or trigonal bipyramid), the chains are corrugated with An−An−An angles close to 160° or quasilinear with a An−An−An angle of 178.215(2)° in (NH₄)₄Th(C₂O₄)₄·4H₂O.⁵⁸

**Interchain Cohesion.** Na₂[Zr(C₂O₄)₃]·2H₂O (Na₂ZrOx₃). The 1∞[ZrOx₃(H₂O)₂] ribbons are arranged in layers parallel to the plane (1 0 0) (Figure 4a). The ribbons are held together by the charge-balancing Na⁺ ions (Figure 4b), which are surrounded by eight oxygen atoms at distances between 2.413 and 2.709 Å, six belonging to three oxalate ligands (one Ox1 and two Ox2) and two belonging to water molecules (Figure 4c). Two NaO₈ polyhedra are connected by a H₂O−H₂O bridge to form a dimer. These dimers are connected by apex to give a layer parallel to the plane (1 0 0) (Figure 4d). The structure can therefore be described as a succession of Zr layers and Na layers in the direction [1 0 0] (Figure 4e).

\[ M(H₄O₉)[Zr(C₂O₄)₃]·2H₂O \ (M = K, (KHZrOx₃); \ M = NH₄, (NH₄HZrOx₃) \] The negative charge of the zirconium-oxalate ribbon 1∞[ZrOx₃]²⁻ is balanced by the hydroxonium ion.
(H$_7$O$_3$)$^+$ and the M$^+$ ion (M$^+$ = K$^+$ and NH$_4^+$). The (H$_7$O$_3$)$^+$ ion presents the geometry of the isomer 2, (H$_5$O$_2$)$^+(H_2$O) (Figure 5a), described by Bernal and Watkins.$^{56}$ As in the hydroxonium ion (H$_{11}$O$_5$)$^+$ present in ($H_2$Zr$_2$O$_{x5}$), the O−O distance in the (H$_5$O$_2$)$^+$ ion is short (2.454(9) for M = K and 2.458(4) Å for M = NH$_4$) and the H atom approximately at the midway between O and O joining. The ion (H$_7$O$_3$)$^+$ is hydrogen-bonded to oxygen atoms of oxalate ligands of four ribbons (Figure 5b). The M atom is coordinated by eight oxygen atoms forming a distorted square antiprism MO$_8$, four oxygen atoms are oxalates, two water oxygens, and two pertain to two different (H$_7$O$_3$)$^+$ ions. Two MO$_8$ polyhedra share a square base to form a dimer M$_2$O$_{12}$ (Figure 5c). K$^+$ and NH$_4^+$ occupy the same position and have similar environments; the increase of the M−O distances with average values 2.884 and 2.975 Å for M = K$^+$ and NH$_4^+$, respectively (Table S5), are in agreement with the increase of the ionic radius ($r_{K^+} = 1.5152$ and $r_{NH4^+} = 1.66$ Å$^{59}$ for C.N. = 8). The bond valence sum calculated with the value of the bond valence parameters is given by Brese and O’Keeffe$^{55}$ for K$^+$ ($r_0 = 2.13$) and by Garcia-Rodriguez et al.$^{60}$ for NH$_4^+$ ($r_0 = 2.219$) and the universal value of $B = 0.37$ is 1.06 vu for the two cations. These results are in accordance with an ammonium cation behaving like an alkaline cation; however, N−H···O bondings are present (Figure S2), the three shorter N−O bonds are established with nonoxalate oxygens (two water oxygens an one oxygen of a (H$_7$O$_3$)$^+$ ion) and are hydrogen bonds involving H10, H13, and H11. The fourth hydrogen atom H12 of the ammonium group is on the line joining the N atom and the midpoint between the two acceptor atoms O4 and O12 and established a bifurcated hydrogen bond as commonly observed for a five-coordinated ammonium ion.$^{59}$ The water molecules that belong to the MO$_8$ entities also participate in the cohesion of the 3D arrangement of (H$_7$O$_3$)$^+$ ribbons and M$_2$O$_{12}$ dimers (Figure 5d) owing to the establishment of hydrogen bonds with oxygen oxalates. The characteristics of the hydrogen bonds in the hydroxonium ions (H$_7$O$_3$)$^+$, between (H$_7$O$_3$)$^+$ or H$_2$O and $^{1}_{\infty}$[ZrO$_x$]$_2$$^{2-}$ ribbons, are reported in Table S6.

$^{1}_{\infty}$M(H$_5$O$_2$)O$_{0.5}$(H$_9$O$_4$)O$_{0.5}$[Zr(C$_2$O$_4$)$_3$] (M = Rb, (RbHZrO$_{x3}$); M = Cs, (Cs$_4$HZrO$_{x3}$)). The charge neutrality is provided by M$^+$ cations and hydroxonium ions (H$_5$O$_2$)$^+$ and (H$_9$O$_4$)$^+$. Two O13 atoms linked by an inversion center are distant from 2.445(5) Å and the common hydrogen located on the Fourier synthesis at the inversion center constitutes a symmetrical Zundel ion (H$_5$O$_2$)$^+$ (Figure 6a). Two O15 atoms linked by an inversion center are distant from 2.445(5) Å and are hydrogen-bonded to water oxygen, creating a symmetric hydroxonium ion (H$_9$O$_4$)$^+$ (Figure 6b). The hydroxonium ions (H$_5$O$_2$)$^+$ and (H$_9$O$_4$)$^+$ connect the ribbons $^{1}_{\infty}$[ZrO$_x$]$_2$$^{2-}$ via hydrogen bonds involving O13 oxygens for (H$_5$O$_2$)$^+$ (Figure 6c) and oxalates O13 and O4 for (H$_9$O$_4$)$^+$ (Figure 6d). The M atom is coordinated by eight oxygen atoms, six oxygen atoms belonging to six different oxalate ions, one from the Zundel ion (H$_5$O$_2$)$^+$, and one from the (H$_9$O$_4$)$^+$ part of the (H$_9$O$_4$)$^+$ ion (Figure 6e). Two MO$_8$ polyhedra share an edge O11−O11 to form a dimer M$_2$O$_{14}$ Dimers participate in the cohesion of the structure (Figure 6f).

**Figure 6.** In (MHZrO$_{x3}$), M = Rb and Cs, the (H$_5$O$_2$)$^+$ (a) and (H$_9$O$_4$)$^+$ (b) ions connect the ribbons $^{1}_{\infty}$[ZrO$_x$]$_2$$^{2-}$ via hydrogen bonds involving O13 oxygens (c) and O1x and O4x oxygens (d), respectively. The MO$_8$ polyhedra share an edge to form dimers M$_2$O$_{14}$ (e) that connect the ribbons $^{1}_{\infty}$[ZrO$_x$]$_2$$^{2-}$ (f).
The exothermic peak at about 250 °C is due to the presence of carbon produced during the combustion.

For the three compounds, the black color of the powder observed during the plateau on the TG between about 350 and 540 °C is due to the presence of carbon produced during the disproportionation of carbon monoxide. The presence of carbon has already been observed during thermal decomposition in air of some zirconium oxalates.\textsuperscript{33,61} At about 560 °C, carbon dioxide is released because of the oxidation of carbon and ZrO\textsubscript{2} crystallizes. The HTXRDs of the three compounds reveal that tetragonal-ZrO\textsubscript{2} (t-ZrO\textsubscript{2}) is first obtained at low temperature, about 550, 425, and 400 °C, respectively. Monoclinic-ZrO\textsubscript{2} (m-ZrO\textsubscript{2}) appears only above 725 °C. As it is well known, zirconia is monoclinic at ambient temperature and transforms into t-ZrO\textsubscript{2} at 1205 °C and to cubic fluorite structure (c-ZrO\textsubscript{2}) at 2377 °C.\textsuperscript{62} Tetragonal and cubic forms can be stabilized at ambient temperature by creation of oxygen vacancies, essentially by substitution of Zr\textsuperscript{4+} by trivalent or divalent cations (Y\textsuperscript{3+}, Ca\textsuperscript{2+}...). Tetragonal pure zirconia has been obtained at ambient temperature by precipitation and calcination, the stabilization of the high temperature tetragonal phase being attributed to a crystallite size effect.\textsuperscript{63} During the preparation by the oxalate method in ethanol solution of a precursor of YSZ powder, Gongyi et al.\textsuperscript{5} obtained, among many amorphous phases, a crystallized compound (sample no. 2S) with X-ray pattern and TG/DTA behavior close to that of Zr(OH)\textsubscript{2}·(C\textsubscript{2}O\textsubscript{4})\textsubscript{2}. Note that a black nonstoichiometric stabilized tetragonal zirconia was obtained by heating amorphous zirconia in an oxygen-free atmosphere.\textsuperscript{64} Many mechanisms of tetragonal phase stabilization in pure ZrO\textsubscript{2} have been reported.\textsuperscript{65,66} During the decomposition under air of the three zirconium oxalates (ZrO\textsubscript{3x}), (H\textsubscript{2}Zr\textsubscript{2}O\textsubscript{2x}5), and (NH\textsubscript{4}H\textsubscript{3}ZrO\textsubscript{3}), the crystallization of the t-ZrO\textsubscript{2} occurs simultaneously with the oxidation of residual carbon and the stabilization of t-ZrO\textsubscript{2} could be due to the energy generated by this combustion.

In all the zirconium oxalates structurally characterized, the coordination number of Zr\textsuperscript{4+} is 8 and the more common environment is formed by four bidentate oxalates giving isolated ions Zr(C\textsubscript{2}O\textsubscript{4})\textsubscript{4−}. In many metal complexes, the oxalate ion acts as bis-bidentate, creating di-metallic ions or chains. A di-metallic ion [Z\textsubscript{2}r(C\textsubscript{2}O\textsubscript{4})\textsubscript{2}]\textsuperscript{4−} has been described in K\textsubscript{0}([Zr(C\textsubscript{2}O\textsubscript{4})\textsubscript{2}·(μ-C\textsubscript{2}O\textsubscript{4})\textsubscript{2}]·4H\textsubscript{2}O)\textsuperscript{0.67} in (H\textsubscript{2}Zr\textsubscript{2}O\textsubscript{5}).

### EXPERIMENTAL SECTION

**Synthesis.** Zirconium oxinate (ZrO(ONO\textsubscript{2})\textsubscript{2}) was purchased from Aldrich, Alfa Aesar, and Acros Organics. The X-ray diffraction patterns of the three products (Figure S6) correspond in fact to hydrated basic zirconium nitrates Zr(ON\textsubscript{2})\textsubscript{2}·3xH\textsubscript{2}O whose structures differ according to x=3,4,5.\textsuperscript{41} The product from Acros Organics, with the formula Zr(ON\textsubscript{2})\textsubscript{2}·3H\textsubscript{2}O, was chosen for synthesis.

**Zr(OH)\textsubscript{2}(C\textsubscript{2}O\textsubscript{4})(ZrOx).** Dihydroxide zirconium oxolate was obtained by slow evaporation of a basic zirconium nitrate and oxalic acid solution. Zr(ON\textsubscript{2})\textsubscript{2}(ONO\textsubscript{2})·4.7H\textsubscript{2}O (1 g, 3 mmol) was dissolved under stirring in 200 mL of nitric acid 0.05 M at 50 °C. An oxalic acid solution 0.5 M was added (12.5 mL), giving a pH of about 1.3. The evaporation of half the solution at 50 °C produced a microcrystalline powder (Figure 7) of the basic oxalate.

(H\textsubscript{2}O)\textsubscript{2}Zr\textsubscript{2}(C\textsubscript{2}O\textsubscript{4})\textsubscript{3}(H\textsubscript{2}O\textsubscript{2})\textsubscript{2}(H\textsubscript{2}Zr\textsubscript{2}O\textsubscript{5}). A solution obtained by dissolution of 0.25 mmol (0.0821 g) of Zr(ON\textsubscript{2})\textsubscript{2}(ONO\textsubscript{2})·4.7H\textsubscript{2}O in 4 mL of water was added with 9 mL of ethanol and further with 1.25 mL (0.625 mmol) of a solution of oxalic acid.
The atomic positions for all atoms and the anisotropic displacement parameters for non-H atoms were included in the last cycles of refinement. The isotropic displacement parameters of the H atoms retrieved from difference Fourier maps were taken with coefficients being 1.2 times larger than the respective equivalent isotropic displacement parameters of parent O or N atoms.

**Thermal Analysis.** Thermogravimetric (TG) analysis and differential thermal analysis (DTA) were carried out with a SETARAM 92 thermal-1600 instrument at a heating at 1 °C·min⁻¹ using platinum crucibles, up to 800 °C, under air with heating at 1 °C·min⁻¹. This instrument was coupled with an evolved gas analyzer Pfeiffer Omnistar Mass Spectrometer.

HTXRD experiments were performed under dynamic air (5 L·h⁻¹) with an Anton Paar HTK1200N of a D8 Bruker diffractometer (θ–θ mode, Cu Kα radiation) equipped with an Anton Paar HTK 1200 high-temperature chamber and a Vantec1 linear position sensitive detector. Several diagrams were recorded every 25 °C between ambient temperature and 800 °C, in the range of 10–80° (2θ), with a step of 0.02° and heating at 0.08 °C·min⁻¹.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03224.

Hydrogen bonds in Na2ZrOx3; environment of NH⁺ in (NH4)2H2ZrOx3; TG/DTA/MSA analyses and HTXRD patterns of ZrOx, H2Zr2Ox5, and NH4H2ZrOx3; X-ray powder patterns of zirconium nitrates; hydrogen bonds in H2Zr2Ox5; characteristics of the overall environment of Zr in Na2Zr2O7 and MH2ZrOx3; Zr–O distances and valence bond sum; M–O distances and bond valences in MH2ZrOx3 (M = K, NH4); and hydrogen bonds in KHZrOx3 and NH4H2ZrOx3 (PDF)

Crystallographic data of ZrOx (CIF)

**Accession Codes**

CCDC 2011396–2011402 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes
The authors declare no competing financial interest.

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