

Acta Crystallographica Section C

**Crystal Structure
Communications**

ISSN 0108-2701

Editor: **George Ferguson**

Dibarium zirconium tetraoxalate trihydrate

Bénédicte Vertruyen, Bénédicte Robertz, Bernard Guillaume, André Rulmont and Marie-Rose Spirlet

Copyright © International Union of Crystallography

Author(s) of this paper may load this reprint on their own web site provided that this cover page is retained. Republication of this article or its storage in electronic databases or the like is not permitted without prior permission in writing from the IUCr.

Dibarium zirconium tetraoxalate
trihydrateBénédicte Vertruyen,^a Bénédicte Robertz,^a Bernard
Guillaume,^a André Rulmont^a and Marie-Rose Spirlet^{b*}^aLCIS/SUPRATECS, Institut de Chimie B6, Université de Liège, Sart Tilman, B-4000
Liège, Belgium, and ^bDépartement de Physique B5, Université de Liège, Sart Tilman,
B-4000 Liège, Belgium

Correspondence e-mail: mrspirlet@ulg.ac.be

Received 2 February 2004

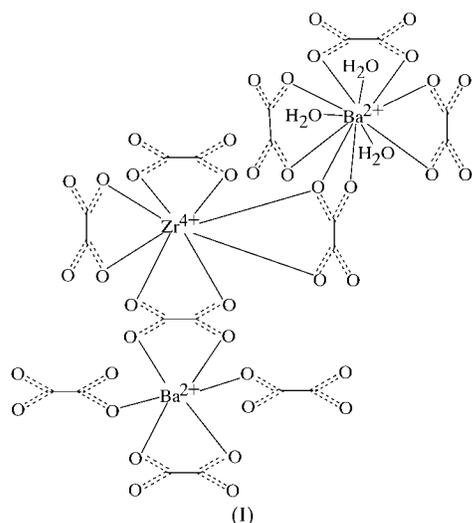
Accepted 23 March 2004

Online 11 May 2004

A new mixed barium zirconium oxalate, triaquatetra- μ -oxalato-dibarium(II)zirconium(IV), $\text{Ba}_2\text{Zr}(\text{C}_2\text{O}_4)_4 \cdot 3\text{H}_2\text{O}$ or $[\text{Ba}_2\text{Zr}(\text{C}_2\text{O}_4)_4(\text{H}_2\text{O})_3]_n$, has been synthesized. The complex is built from eightfold-coordinated Zr atoms and eleven- and sixfold-coordinated Ba atoms, linked by oxalate groups. The Zr atom, the two Ba atoms and one water O atom lie on crystallographic twofold axes, so that each coordination polyhedron has imposed C2 symmetry. Packing in the crystal is also assumed through hydrogen bonds.

Comment

Oxalate complexes can be used as precursors in the formation of ternary oxides. For example, the barium titanate perovskite BaTiO_3 can be synthesized by thermal decomposition of the mixed oxalate $\text{BaTiO}(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$ (Wada *et al.*, 2003). Due



to the great interest in the dielectric and ferroelectric properties of BaTiO_3 , the crystallographic structure of barium titanate is well documented (Rhine *et al.*, 1992). In contrast, very little work has been performed in the case of the

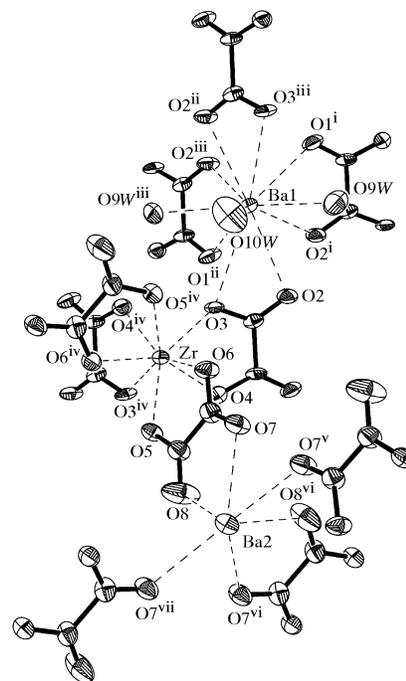


Figure 1

The oxygen coordination spheres around the Zr and Ba atoms in (I). [Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$; (iii) $\frac{1}{2}+x, \frac{1}{2}+y, \frac{3}{2}+z$; (iv) $\frac{1}{2}+x, \frac{1}{2}+y, \frac{5}{2}+z$; (v) $x-\frac{1}{2}, -y, 1+z$; (vi) $x-\frac{1}{2}, \frac{1}{2}+y, \frac{3}{2}+z$; (vii) $x, \frac{1}{2}-y, \frac{1}{2}+z$.]

barium zirconium oxalate, even though it might be a precursor for the formation of barium zirconate. BaZrO_3 is of potential interest as a refractory material, due to its ability to resist the corrosive fluxes encountered during the synthesis of copper-based superconducting phases (Erb *et al.*, 1995). The manufacture of BaZrO_3 crucibles requires very good densification behaviour, influenced by the morphology and size distribution of the particles (Robertz *et al.*, 2001). Therefore, the determination of the crystallographic structure of the title compound, (I), a potential precursor, is of some interest.

The unindexed powder diffraction pattern published by Reddy & Mehrotra (1979) is attributed to a $\text{BaZrO}(\text{C}_2\text{O}_4)_2 \cdot 4.5\text{H}_2\text{O}$ phase. In the present study, the structural refinement of single-crystal data indicates a $\text{Ba}_2\text{Zr}(\text{C}_2\text{O}_4)_4 \cdot 3\text{H}_2\text{O}$ composition. The Ba:Zr ratio is confirmed by energy-dispersive spectrometry. A similar composition was found by other authors, in the case of the lead zirconium oxalate $\text{Pb}_2\text{Zr}(\text{C}_2\text{O}_4)_4 \cdot n\text{H}_2\text{O}$ (Boudaren *et al.*, 2000) and in $\text{Cd}_2\text{Zr}(\text{C}_2\text{O}_4)_4 \cdot 4\text{H}_2\text{O}$ (Jeanneau *et al.*, 2001).

The complex three-dimensional structure of (I) is built from Zr and Ba atoms linked by oxalate groups (Fig. 1). The coordination polyhedra have imposed C2 symmetry, the Zr and Ba atoms lying on crystallographic twofold axes. The Zr atom is eightfold coordinated by O atoms from bridging bidentate oxalate groups. There are two symmetrically non-equivalent Ba atoms per asymmetric unit. One Ba atom, Ba1, is surrounded by eight O atoms from four bidentate oxalate ligands (two symmetrically non-equivalent). Atom Ba1 is also linked to three water O atoms (from two symmetry-distinct water molecules), reaching a coordination number of 11. The

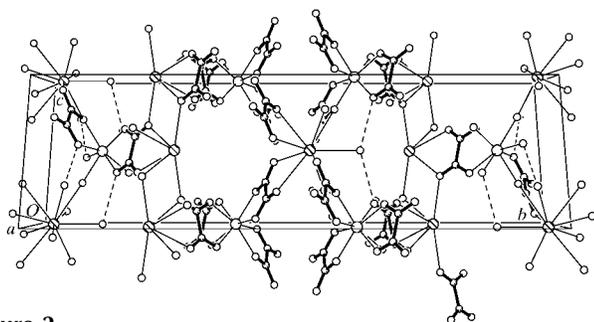


Figure 2
The crystal packing in (I), viewed along [100]. The *c* axis is horizontal from left to right. Dashed lines indicate O(water)···O(oxalate) interactions.

second Ba atom is sixfold coordinated to four O atoms, which belong to two (symmetrically equivalent) bidentate and to two (symmetrically equivalent) monodentate oxalate anions, respectively.

Intermolecular contacts (Table 1) indicate probable hydrogen bonding between water and oxalate O atoms. Fig. 2 shows how the metal atoms alternate in the crystal packing of (I).

Experimental

The Ba₂Zr(C₂O₄)₄·3H₂O phase was synthesized by precipitation at the interface between an ethyl oxalate organic phase and an aqueous solution of barium chloride (BaCl₂) and zirconyl chloride (ZrOCl₂). Since diethyl oxalate is only very slightly soluble in water, it provides a slow release of oxalic acid at the interface between the organic and aqueous phases (Ryu *et al.*, 1999). This procedure should give good control over the crystallization kinetics. The Ba:Zr ratio in the solution was varied between 1:1 and 2:1, with total cationic concentrations ranging between 0.125 and 0.19 M. The mixtures were held for 2 d at different temperatures (279, 293 and 318 K). The white precipitates which formed were filtered off and washed with water and acetone. All precipitates were characterized by powder X-ray diffraction (Siemens D-5000 diffractometer with Cu K α radiation) and displayed similar diffraction patterns. Energy-dispersive analysis coupled to a scanning electron microscope (Philips XL-30 ESEM FEG) revealed a 2:1 Ba:Zr ratio in all samples, without a detectable secondary phase. From these results, it appears that the same phase is formed independently of the initial Ba:Zr ratio and of the crystallization temperature. In contrast, scanning electron microscopy shows that the morphology of the crystals depends on the crystallization temperature. At room temperature or below, elongated crystallites form 'bundles' of crystals. At 318 K, larger tabular crystals were obtained, but intergrowth and twinning was frequently observed. The single crystal of (I) used for the present structure determination was taken from the batch prepared at 318 K with a 1:1 Ba:Zr ratio.

Crystal data

[Ba ₂ Zr(C ₂ O ₄) ₄ (H ₂ O) ₃]	<i>D_x</i> = 2.309 Mg m ⁻³
<i>M_r</i> = 772.03	Mo K α radiation
Monoclinic, <i>I</i> 2/ <i>a</i>	Cell parameters from 35 reflections
<i>a</i> = 9.2010 (12) Å	θ = 4.9–12.2°
<i>b</i> = 29.032 (5) Å	μ = 4.05 mm ⁻¹
<i>c</i> = 9.2079 (17) Å	<i>T</i> = 293 (2) K
β = 115.45 (3)°	Prismatic, colourless
<i>V</i> = 2221.0 (7) Å ³	0.03 × 0.02 × 0.02 mm
<i>Z</i> = 4	

Data collection

Bruker P4 diffractometer	<i>R</i> _{int} = 0.060
2 θ / ω scans	θ _{max} = 25.0°
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	<i>h</i> = -10 → 9
<i>T</i> _{min} = 0.907, <i>T</i> _{max} = 0.922	<i>k</i> = -34 → 34
6582 measured reflections	<i>l</i> = -9 → 10
1964 independent reflections	3 standard reflections
1510 reflections with <i>I</i> > 2 σ (<i>I</i>)	every 97 reflections
	intensity decay: none

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.038P)^2 + 45.4129P]$
<i>R</i> (<i>F</i>) = 0.047	where $P = (F_o^2 + 2F_c^2)/3$
<i>wR</i> (<i>F</i> ²) = 0.124	(Δ/σ) _{max} < 0.001
<i>S</i> = 1.05	$\Delta\rho$ _{max} = 2.05 e Å ⁻³
1964 reflections	$\Delta\rho$ _{min} = -0.80 e Å ⁻³
139 parameters	
H-atom parameters not refined	

Table 1

Selected interatomic distances (Å).

Ba1—O10W	2.778 (14)	Ba2—O7	2.854 (8)
Ba1—O9W	2.785 (8)	Zr1—O3	2.172 (6)
Ba1—O2 ⁱ	2.799 (7)	Zr1—O6	2.173 (7)
Ba1—O2	2.864 (7)	Zr1—O5	2.209 (6)
Ba1—O1 ⁱ	2.968 (7)	Zr1—O4	2.213 (7)
Ba1—O3	3.224 (6)	O9W···O1 ⁱⁱⁱ	2.789 (11)
Ba2—O7 ⁱⁱ	2.764 (7)	O9W···O4 ^{iv}	2.863 (11)
Ba2—O8	2.793 (9)	O10W···O5 ^{iv}	3.059 (7)

Symmetry codes: (i) $\frac{1}{2} + x, 1 - y, z$; (ii) $-\frac{1}{2} - x, \frac{1}{2} - y, \frac{3}{2} - z$; (iii) $-\frac{1}{2} - x, y, 1 - z$; (iv) $x, y, z - 1$.

Data collection: XSCANS (Siemens, 1996); cell refinement: XSCANS; data reduction: SHELXTL (Siemens, 1991); program(s) used to solve structure: SHELXTL; program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

The authors are grateful to the Inter-University Institute for Nuclear Sciences and to the National Fund for Scientific Research (Brussels) for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1040). Services for accessing these data are described at the back of the journal.

References

- Boudaren, C., Auffredic, J. P., Louër, M. & Louër, D. (2000). *Chem. Mater.* **12**, 2324–2333.
- Erb, A., Walker, E. & Fluekiger, R. (1995). *Physica C*, **245**, 245–251.
- Jeanneau, E., Audebrand, N., Auffredic, J.-P. & Louer, D. (2001). *J. Mater. Chem.* **11**, 2545–2552.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Reddy, V. B. & Mehrotra, P. N. (1997). *Thermochim. Acta*, **31**, 31–37.
- Rhine, W. E., Hallock, R. B., Davis, W. M. & Wong-Ng, W. (1992). *Chem. Mater.* **4**, 1208–16.
- Robertz, B., Boschini, F., Cloots, R. & Rulmont, A. (2001). *Int. J. Inorg. Mater.* **3**, 1185–1187.
- Ryu, K., Huh, W. & Lee, C. (1999). *Anal. Sci. Tech.* **12**, 230–234.
- Siemens (1991). SHELXTL. Release 4.1. Siemens Analytical X-ray Instruments Inc., Karlsruhe, Germany.
- Siemens (1996). XSCANS. Version 2.2. Siemens Analytical X-ray Instruments Inc., Karlsruhe, Germany.
- Wada, S., Narahara, M., Hoshina, T., Kakemoto, H. & Tsurumi, T. (2003). *J. Mater. Sci.* **38**, 2655–2660.