Dibarium zirconium tetraoxalate trihydrate

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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), Ba$_2$Zr(C$_2$O$_4$)$_4$·3H$_2$O or [Ba$_2$Zr(C$_2$O$_4$)$_4$·3H$_2$O]$_n$, 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 C$_2$ 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 BaTiO(C$_2$O$_4$)$_2$·4H$_2$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 oxalate is well documented (Rhine et al., 1992). In contrast, very little work has been performed in the case of the 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 BaZrO$_3$·(C$_2$O$_4$)$_2$·1.5H$_2$O phase. In the present study, the structural refinement of single-crystal data indicates a Ba$_2$Zr(C$_2$O$_4$)$_4$·3H$_2$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 Pb$_2$Zr(C$_2$O$_4$)$_4$·nH$_2$O (Boudaren et al., 2000) and in Cd$_2$Zr(C$_2$O$_4$)$_4$·4H$_2$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 C$_2$ symmetry, the Zr and Ba atoms lying on crystallographic twofold axes. The Zr atom is eightfold coordinated by O atoms from bridging 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
metal-organic compounds

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 Kα 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

Bravo (BaZr(C₂O₄)₄·3H₂O)

Mₐ = 772.03

Monoclinic, P2₁/a

a = 9.2010 (12) Å

b = 29.032 (5) Å

c = 9.079 (17) Å

β = 115.45 (3)°

V = 2221.0 (7) Å³

Z = 4

D₀ = 2.309 Mg m⁻³

Mo Kα radiation

Cell parameters from 35 reflections

θ = 4.9–12.2°

μ = 4.05 mm⁻¹

T = 293 (2) K

Prismatic, colourless

0.03 × 0.02 × 0.02 mm

Data collection

Bruker P4 diffractometer

2θ_max scans

Absorption correction: ψ scan

(North et al., 1968)

 Tmin = 0.907, Tmax = 0.922

6582 measured reflections

1964 independent reflections

1510 reflections with I > 2σ(I)

Refinement

Refinement on F²

wR(F²) = 0.124

S = 1.05

w = 1/[σ²(F²) + (0.038P)²]

+ 45.4129P

where P = (F² + 2F*c) / 3

(Δ/σ)max < 0.001

Δρ_max = 2.05 e Å⁻³

Δρ_min = –0.80 e Å⁻³

H-atom parameters not refined

Experimental

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Δρ_min = –0.80 e Å⁻³

H-atom parameters not refined

Table 1

Selected interatomic distances (Å).

Ba₁–O₁0W 2.778 (14) Ba₂–O₁ 2.854 (8)

Ba₁–O₁0Ⅱ 2.799 (7) Zr₁–O₁ 2.172 (6)

Ba₁–O₁0Ⅲ 2.864 (7) Zr₁–O₂ 2.173 (7)

Ba₁–O₁0Ⅳ 2.986 (7) Zr₁–O₄ 2.213 (7)

Ba₁–O₁ 3.224 (6) O₉W–O₁Ⅳ 2.789 (11)

Ba₂–O₁0Ⅳ 2.764 (7) O₉W–O₁Ⅳ 2.863 (11)

Ba₂–O₁0Ⅷ 2.793 (9) O₁0W–O₁Ⅷ 3.059 (7)

Symmetry codes: (i) x+1, 1−y, z; (ii) −x, −y, −z; (iii) −x+1, −y, −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


