Available online at www.sciencedirect.com
SCIENCE DIRECT®

ELSEVIER

Polyhedron 25 (2006) 2401–2406

POLYHEDRON
www.elsevier.com/locate/poly

Interaction of barium oxide and hydroxide with methanol: X-ray single crystal study of $Ba(OH)_2$ methanol solvates

Zoya A. Starikova [a], Vadim G. Kessler [b,*], Nataliya Ya. Turova [c], Ilya A. Dantsker [c], Alexandr P. Bobyljov [c], Alexander S. Mitiaev [c]

[a] *A.N. Nesmeyanov Institut of Organoelement Compounds, Russian Academy of Sciences, 117813 Moscow, Russia*
[b] *Department of Chemistry, SLU, Box 7015, S-75007 Uppsala, Sweden*
[c] *Department of Chemistry, M.V. Lomonosov Moscow State University, 119899 Moscow, Russia*

Received 20 October 2005; accepted 9 February 2006
Available online 20 March 2006

Abstract

Dissolution of BaO in 90–95% MeOH provides $[Ba(OH)_2(H_2O)_2](MeOH)_2$ (**1**) as rectangular platelet crystals. Interaction of BaO or $Ba(OH)_2$ with 98–100% methanol results in the formation of needle shaped crystals of $[Ba(OH)_2(MeOH)_2](MeOH)$ (**2**). The structure of **1** is composed of planar layers of tetragonally distorted $[Ba(OH)_{4/2}(H_2O)_{4/2}]$ cubes altered by the layers of alcohol molecules oriented in the direction perpendicular to the metal hydroxide layers. The structure of **2** is formed by layers of distorted antiprisms of $Ba(\mu_3\text{-ROH})(\mu\text{-OH})_4(\mu\text{-ROH})_2(ROH)]$ and $[Ba(\mu_3\text{-ROH})_2(\mu\text{-ROH})_2(\mu\text{-OH})_4]$ composition. IR spectra of **1** and **2** are in good agreement with the observed structures. The structures of compounds **1** and **2** are compared with those of $Ba(OH)_2 \cdot nH_2O$ ($n = 1, 3$).

Keywords: Precursors of ceramic materials; Hydroxide; Methanol solvates; Barium alkoxide hydrolysis; Layered structures; X-ray

1. Introduction

There is still considerable interest in the development and characterization of accessible Ba-containing precursors for the sol–gel synthesis of related complex oxide materials. Thus in approach to $BaTiO_3$ and derived solid solutions, in particular BST (barium–strontium titanate), via an alkoxide-based sol–gel route, there has been the reported application of not only alkoxides, but also carboxylates and the large-scale use of barium oxide and hydroxide [1,2]. The term alkoxide-based is commonly applied for all these types of barium precursors as the other reactant is in this approach always a titanium alkoxide. The reactions of alcoholysis of oxides and hydroxides of alkaline earth metals have been claimed to provide easy access to the corresponding alkoxides under industrial conditions [1]. The barium oxide–methanol system, BaO–MeOH, has been proposed as a starting material for the synthesis of a number of coordination compounds of barium such as, for example, β-ketoesters [3].

The nature of the interaction products of $Ba(OH)_2$ or BaO with alcohols remained, however, unexplored until recently. Already in the XIX century Dumas and Berthelot, and later de Forcrand described several compounds crystallizing in the $Ba(OH)_2$–MeOH system and formed through methanolysis of barium oxide or hydroxide or on hydrolysis of $Ba(OMe)_2$. The authors described them as barium oxide solvates, $BaO \cdot n\text{MeOH} \cdot m\text{H}_2\text{O}$ [4]. Scholder and Kreutz [5] isolated crystalline complexes, which they described as $Ba(OH)_2 \cdot 2\text{MeOH} \cdot n\text{H}_2\text{O}$ ($n = 1, 2$) and $Ba(OH)(OMe) \cdot \text{MeOH}$, on the basis of the microanalysis data and the nature of their desolvation products at 100–300 °C. The exact chemical composition and structure of these compounds remained unknown, while in the numerous recent articles devoted to sol–gel technology, complexes of this kind are usually denoted as M(OR)(OH) (for example, [6]).

---

[*] Corresponding author. Tel.: +46 18671541; fax: +46 18673392.
E-mail address: Vadim.Kessler@kemi.slu.se (V.G. Kessler).

0277-5387/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2006.02.014

The present study reports the improved conditions of the synthesis and also the structural characterization of the crystalline phases formed in the $Ba(OH)_2$–MeOH system.

2. Experimental

Anhydrous $Ba(OH)_2$ was prepared by dehydration of $Ba(OH)_2 \cdot 8H_2O$, and BaO by decomposition of BaO_2, at 400 and 800 °C, respectively. Methanol was dehydrated by refluxing over $Mg(OMe)_2$, and was subsequently applied in preparation of solutions with exact concentrations of water. All operations were carried out in dry argon or nitrogen atmosphere. The barium concentration was determined by acidimetric titration with Methyl Orange as indicator (using distilled water, purified from carbon dioxide by prolonged refluxing under an inert atmosphere). FTIR spectra have been recorded with the dry powders of the samples between KBr pellets on a Perkin–Elmer FTIR 1600 Instrument.

2.1. Crystallography

The crystals were placed in glass capillaries, and sealed under nitrogen gas. The data were collected for compounds **1** and **2** using a SMART CCD 1k instrument at room temperature (295 K) using graphite monochromated Mo Kα radiation, $\lambda = 0.71073$ Å. The experimental details are summarized in Table 1. The structures were solved by direct methods. Barium atoms were located from the initial solutions, and the other non-hydrogen atoms were isolated in subsequent difference Fourier syntheses. All non-hydrogen atoms were refined by least squares techniques on F^2, first in isotropic and then in anisotropic approximations. The coordinates of hydrogen atoms were added geometrically and applied in isotropic approximations riding on the corresponding carbon atoms. Hydrogen atoms of the OH-groups and solvating water molecules within the metal–oxygen cores could not be objectively located in the Fourier syntheses and the assignment of the nature of oxygen atoms was made on the basis of bond distances in comparison with the literature data (see below). Doubtless location of hydrogen atoms in the structures of barium hydroxide solvates or halide solvates can be achieved only in low temperature neutron diffraction experiments. The residual electron density 2.364 e/Å^3 for **1** and 5.426 e/Å^3 for **2** was located in the proximity of the barium atoms.

Table 1
Crystallographic data for complexes **1** and **2**

Compound	**1**, Plates	**2**, Needles
Formula	$C_2H_{14}O_6Ba$	$C_3H_{14}O_5Ba$
Formula weight	271.48	253.46
Crystal size, mm	$0.35 \times 0.10 \times 0.10$	$0.55 \times 0.35 \times 0.10$
Crystal system	tetragonal	monoclinic
Space group	$I\bar{4}$	$P2(1)/c$
a (Å)	4.6297(6)	10.8208(14)
b (Å)	4.6297(6)	18.711(3)
c (Å)	22.404(5)	8.1899(19)
α (°)	90	90
β (°)	90	99.497(3)
γ (°)	90	90
V (Å^3)	480.20(13)	1635.4(5)
Z	2	8
Reflections collected	1457	6469
Independent reflections [R_{int}]	557 [0.2154]	2126 [0.1317]
Data/restraints/parameters	557/0/23	2126/0/153
Goodness-of-fit on F^2	1.194	0.855
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0656$, $wR_2 = 0.1628$	$R_1 = 0.0634$, $wR_2 = 0.1725$
R indices (all data)	$R_1 = 0.0659$, $wR_2 = 0.1644$	$R_1 = 0.0789$, $wR_2 = 0.1874$
Absolute structure parameter	0.1(3)	

*2.2. Synthesis and isolation of **1** and **2***

Preparation of the crystals was carried out using solutions of BaO or $Ba(OH)_2$ in anhydrous MeOH and also in MeOH containing up to 10% water (for comparison). After long-term stirring at 0 °C with the Ba-containing reactant, taken in large excess, the concentration of solutions achieved 20–23 mass% in relation to $Ba(OH)_2$. The solutions were removed from the residual solids by decantation and concentrated in vacuum or in a dessicator with P_2O_5 until crystallization commenced. The obtained crystalline samples were washed with anhydrous MeOH and dried in vacuum at room temperature. Crystallo-optical investigation of the samples revealed normally the presence of several types of crystals. In addition to the compounds **1** and **2** described below, there have been also observed "rectangular rods" (described in [5]), which could not be isolated in the form of single crystals suitable for X-ray studies. Phases of the same type could only be isolated under controlled conditions as described below.

*2.2.1. $[Ba(OH)_2(H_2O)_2](MeOH)_2$ (**1**)*

Crystallized as rectangular plates from solutions of BaO in 90–95% methanol at 20 °C (this phase was isolated from solutions of BaO in 90%-methanol according to [5]). *Anal.* Calc. for $BaC_2H_{14}O_6$: Ba, 50.6. Found: Ba, 50.3%. IR, cm^{-1}: 3575 s, 3483 s, 3360 vs br, 2914 vs, 2860 vs, 2783 s sh, 1645 w, 1473 s, 1154 s, 1060 m, 836 vs, 720 m.

*2.2.2. $[Ba(OH)_2(MeOH)_2](MeOH)$ (**2**)*

Crystallized as thin needles from 98% to 100% methanol solutions of BaO or $Ba(OH)_2$ subjected to reflux for 2–3 h with subsequent cooling to 0–20 °C. *Anal.* Calc. for $BaC_3H_{14}O_5$: Ba, 51.3. Found: Ba 51.0%. IR, cm^{-1}: 3580 vw, 3386 vs br, 2915 s, 2851 s, 2780 m, 1655 sh, 1439 sh, 1176 vw, 1141 w, 1062 vs, 824 vs, 720 w. (The needle-shaped form described in [5] as $Ba(OH)_2 \cdot 2MeOH \cdot H_2O$, crystallized from solutions not subjected to reflux at 20 °C).

The total concentration of $Ba(OH)_2$ in the mother liquors over **1** and **2** was about 20%, but the isolated crystalline products are almost insoluble in MeOH or $MeOC_2H_4OH$.