Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Solid State Chemistry 178 (2005) 3206–3209
JOURNAL OF SOLID STATE CHEMISTRY
www.elsevier.com/locate/jssc

Rapid communication

Two crystalline modifications of RuO_4

Martin Pley, Mathias S. Wickleder*

Institut für Reine und Angewandte Chemie, Universität Oldenburg, P.O. Box 2503, 26111 Oldenburg, Germany

Received 24 May 2005; received in revised form 21 July 2005; accepted 23 July 2005
Available online 26 August 2005

Abstract

RuO_4 was prepared by oxidation of elemental ruthenium. Two different modifications were obtained and investigated by X-ray single crystal diffraction. RuO_4-I has cubic symmetry ($P4;^{-}3n, Z = 8, a = 8.509(1)$ Å), and two independent tetrahedral molecules are present in the unit cell. Within the standard uncertainties in both molecules the distances Ru–O are 1.695 Å. The second modification, RuO_4-II, is monoclinic ($C2/c, Z = 4, a = 9.302(4)$ Å, $b = 4.3967(10)$ Å, $c = 8.454(4)$ Å, $\beta = 116.82(3)^\circ$) and isotypic with OsO_4. There is one independent molecule in the unit cell, which shows distances Ru–O of 1.697 and 1.701 Å, respectively.

Keywords: Solid state structures; Molecular structures; Ruthenium; Oxides

1. Introduction

In course of our investigations of compounds with complex oxo-anions [1] we use the tetraoxides of osmium and ruthenium as starting materials for the synthesis of ruthenates and osmates [2]. The tetraoxides are known to be low melting volatile molecular solids. Despite of their toxicity both compounds are used as oxidants for various purposes [3]. In particular RuO_4 has attracted considerable attention in organic chemistry because it shows remarkable difference in reactivity compared to OsO_4 [4]. Furthermore, it is frequently used as a staining agent for polymers [5]. With respect to these important applications, it is astounding that no structural data of RuO_4 are reported up to now. There is only one paper from the late 1960s that claims isotypism of RuO_4 with OsO_4 based on powder diffraction measurements [6]. In the present communication, we present the molecular and crystal structures of two modifications of RuO_4. It is only the second example of a structurally characterized octavalent binary compound. With respect to the potential of RuO_4 and its various applications, we consider the structure of this compound as a basic information of utmost importance.

2. Experimental

2.1. Synthesis

We prepared RuO_4 according to the literature procedure by oxidation of elemental ruthenium in a $KMnO_4$/KOH melt, and further treatment with $KMnO_4$ and diluted H_2SO_4 in aqueous solution [7]. Upon heating the reaction mixture, RuO_4 was driven off and condensed in a cooling trap as yellow-orange crystals. Interestingly, two different crystal forms could be distinguished: needles and cubes. Inspection of the crystals under a polarizing microscope revealed that their symmetry must be different. Thus, a specimen of each form was investigated by X-ray single crystal diffraction.

Caution: The preparation of RuO_4 and all manipulations must be done under special safety precautions. RuO_4 is very toxic and highly volatile. It is necessary to work in a well ventilated hood and to wear appropriate eye protection.

*Corresponding author. Fax: +49 441 798 3352.
E-mail address: mathias.wickleder@uni-oldenburg.de (M.S. Wickleder).

0022-4596/$ - see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2005.07.021

2.2. X-ray crystallography

The reflection intensities of a block-shaped single crystal (approx. $0.1 \times 0.1 \times 0.15$ mm) of RuO_4-I and a needle-shaped single crystal of RuO_4-II were measured with an IP diffractometer (IPDS II, Stoe & Cie) at 170 K. The structure solutions were successful assuming the space group $P4;^{-}3n$ for RuO_4-I and $C2/c$ for RuO_4-II using direct methods provided by the program SHELXS-86 [8]. Least-squares refinements were carried out with SHELXL-97 [8], and for all atoms anisotropic thermal displacement parameters were introduced. Finally, numerical absorption corrections were carried out using the programs X-SHAPE and X-RED [9]. Details of the data acquisition and the crystallographic data are summarized in the Tables 1 and 2. Additionally, the data have been deposited with the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (crysdata@FIZ-Karlsruhe.de) and are available on quoting the deposition numbers given in Table 1.

3. Results and discussion

The X-ray single crystal investigations revealed that RuO_4 is dimorphic and has a cubic and monoclinic crystal structure. In the unit cell of the cubic modification, hereafter named RuO_4-I, two crystallographically independent RuO_4 molecules are present. One RuO_4 molecule has the symmetry 23 (T with respect to the nomenclature of Schoenflies) according to the location of the respective ruthenium atom on the Wyckoff position 2*a* of space group $P4;^{-}3n$. Accordingly, the molecule shows six ideal tetrahedral angles (Table 2). The other molecule exhibits four symmetry (S_4) with ruthenium on the 6*c* position, and only minor distortions from ideal

Table 1
Crystallographic data of the two modifications of RuO_4

	RuO_4-I	RuO_4-II
Formula weight (g/mol)	165.03	165.03
Unit cell parameters	$a = 8.509(1)$ Å	$a = 9.302(4)$ Å
		$b = 4.3967(10)$ Å
		$c = 8.454(4)$ Å
		$\beta = 116.82(3)^\circ$
Cell volume	616.1(1) Å^3	308.6(2) Å^3
Z	8	4
Exp. density	3.559 g/cm^{-3}	3.553 g/cm^{-3}
Crystal shape	Block	Needle
Crystal size	$0.1 \times 0.1 \times 0.15$ mm^3	$0.1 \times 0.1 \times 0.3$ mm^3
Crystal system	Cubic	Monoclinic
Space group	$P4;^{-}3n$	$C2/c$
Measuring device		Stoe IPDS II
Radiation		Mo-$K\alpha$ (graphite monochromator; $\lambda = 71.07$ pm)
Temperature		170 K
Θ_{max}	28°	28°
Index range	$-11 \leqslant h \geqslant 11$	$-12 \leqslant h \geqslant 12$
	$-11 \leqslant k \geqslant 11$	$-5 \leqslant k \geqslant 5$
	$-11 \leqslant l \geqslant 11$	$-11 \leqslant l \geqslant 10$
ω-range; ω-increment	$0^\circ < \omega < 180^\circ$; 2°	$0^\circ < \omega < 180^\circ$; 2°
	(2 runs at $\varphi = 0^\circ, 90^\circ$)	(2 runs at $\varphi = 0^\circ, 90^\circ$)
Number of exposures	180	180
Irradiation/exposure	4 min	5
Detector distance	100 mm	100 mm
Absorption correction		Numerical, after crystal shape optimisation [12]
Absorption coefficient	4.895 mm^{-1}	4.887 mm^{-1}
T_{min}/T_{max}	0.2970, 0.5638	0.2990, 0.5839
Measured reflections	9480	1522
Unique reflections	257	371
Observed with $I > 2\sigma(I)$	189	347
R_{int}/R_σ	0.0674/0.0141	0.0871/0.0540
Structure determination		SHELXS-86, SHELXL-97 [11]
Scattering factors		Intern. Tables. Vol. C
Goodness of fit	1.11	1.18
R_1; wR_2 (I > 2σ(I))	0.0245; 0.0540	0.0431; 0.1162
R_1; wR_2 (all data)	0.0254; 0.0600	0.0442; 0.1170
Flack-x	0.26	
Depositiory no.	CSD415303	CSD415306