

Rapid communication

Two crystalline modifications of RuO₄

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Abstract

RuO₄ was prepared by oxidation of elemental ruthenium. Two different modifications were obtained and investigated by X-ray single crystal diffraction. RuO₄-I has cubic symmetry ($P4_3-3n, Z = 8, a = 8.509(1) \text{ \AA}$), 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, RuO₄-II, is monoclinic ($C2/c, Z = 4, a = 9.302(4) \text{ \AA}, b = 4.3967(10) \text{ \AA}, c = 8.454(4) \text{ \AA}, \beta = 116.82(3)^\circ$) and isotypic with OsO₄. There is one independent molecule in the unit cell, which shows distances Ru–O of 1.697 and 1.701 Å, respectively.

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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 RuO₄ has attracted considerable attention in organic chemistry because it shows remarkable difference in reactivity compared to OsO₄ [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 RuO₄ are reported up to now. There is only one paper from the late 1960s that claims isotypism of RuO₄ with OsO₄ based on powder diffraction measurements [6]. In the present communication, we present the molecular and crystal structures of two modifications of RuO₄. It is only the second example of a structurally characterized octavalent binary compound. With respect to the potential of RuO₄ 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 RuO₄ according to the literature procedure by oxidation of elemental ruthenium in a KMnO₄/KOH melt, and further treatment with KMnO₄ and diluted H₂SO₄ in aqueous solution [7]. Upon heating the reaction mixture, RuO₄ 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 RuO₄ and all manipulations must be done under special safety precautions. RuO₄ is very toxic and highly volatile. It is necessary to work in a well ventilated hood and to wear appropriate eye protection.

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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 RuO₄-I and a needle-shaped single crystal of RuO₄-II were measured with an IP diffractometer (IPDS II, Stoe & Cie) at 170 K. The structure solutions were successful assuming the space group $P4_3-3n$ for RuO₄-I and $C2/c$ for RuO₄-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 RuO₄ is dimorphic and has a cubic and monoclinic crystal structure. In the unit cell of the cubic modification, hereafter named RuO₄-I, two crystallographically independent RuO₄ molecules are present. One RuO₄ 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 $2a$ of space group $P4_3-3n$. Accordingly, the molecule shows six ideal tetrahedral angles (Table 2). The other molecule exhibits four symmetry (S_4) with ruthenium on the $6c$ position, and only minor distortions from ideal

Table 1
Crystallographic data of the two modifications of RuO₄

	RuO ₄ -I	RuO ₄ -II
Formula weight (g/mol)	165.03	165.03
Unit cell parameters	$a = 8.509(1) \text{ \AA}$	$a = 9.302(4) \text{ \AA}$ $b = 4.3967(10) \text{ \AA}$ $c = 8.454(4) \text{ \AA}$ $\beta = 116.82(3)^\circ$
Cell volume	$616.1(1) \text{ \AA}^3$	$308.6(2) \text{ \AA}^3$
Z	8	4
Exp. density	3.559 g/cm^{-3}	3.553 g/cm^{-3}
Crystal shape	Block	Needle
Crystal size	$0.1 \times 0.1 \times 0.15 \text{ mm}^3$	$0.1 \times 0.1 \times 0.3 \text{ mm}^3$
Crystal system	Cubic	Monoclinic
Space group	$P4_3-3n$	$C2/c$
Measuring device		Stoe IPDS II
Radiation		Mo-K α (graphite monochromator; $\lambda = 71.07 \text{ pm}$)
Temperature		170 K
θ_{max}	28°	28°
Index range	$-11 \leq h \leq 11$ $-11 \leq k \leq 11$ $-11 \leq l \leq 11$	$-12 \leq h \leq 12$ $-5 \leq k \leq 5$ $-11 \leq l \leq 10$
ω -range; ω -increment	$0^\circ < \omega < 180^\circ$; 2° (2 runs at $\varphi = 0^\circ, 90^\circ$)	$0^\circ < \omega < 180^\circ$; 2° (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}
$T_{\text{min}}/T_{\text{max}}$	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 ($I > 2\sigma(I)$)	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	
Depository no.	CSD415303	CSD415306

Table 2
Atomic coordinates, Wyckoff notation and selected distances and angles for RuO₄-I and RuO₄-II

Atom	Wyckoff	<i>x/a</i>	<i>y/a</i>	<i>z/a</i>
<i>RuO₄-I</i>				
Ru1	2 <i>a</i>	0	0	0
Ru2	6 <i>c</i>	3/4	1/2	0
O1	8 <i>e</i>	0.8850(9)	<i>x</i>	<i>x</i>
O2	24 <i>i</i>	0.8647(6)	0.3887(6)	0.8809(4)
<i>RuO₄-II</i>				
Ru1	4 <i>e</i>	0	0.2408(1)	3/4
O1	8 <i>f</i>	0.1186(4)	0.4658(9)	0.6938(4)
O2	8 <i>f</i>	0.1180(4)	0.0165(9)	0.9238(4)
<i>Distances(Å) and angles(°)</i>				
<i>RuO₄-I</i>				
Ru1–O1	1.695(13) (4 <i>x</i>)			
Ru2–O2	1.696(5) (4 <i>x</i>)			
O1–Ru1–O1	109.47 (6 <i>x</i>)			
O2–Ru2–O2	109.3(1) (4 <i>x</i>)			
	109.8(3) (2 <i>x</i>)			
<i>RuO₄-II</i>				
Ru1–O1	1.697(3) (2 <i>x</i>)			
Ru1–O2	1.701(4) (2 <i>x</i>)			
O1–Ru1–O1	108.9(3)			
O2–Ru1–O2	108.9(2)			
O1–Ru1–O2	109.4(2) (2 <i>x</i>)			
O1–Ru1–O2	110.1(2) (2 <i>x</i>)			

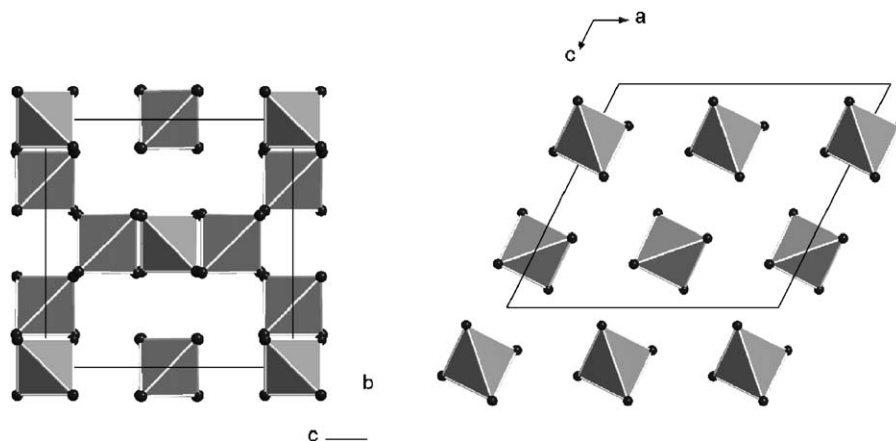


Fig. 1. Crystal structures of RuO₄-I (left) and RuO₄-II (right). Both crystals consist of tetrahedral RuO₄ molecules, which are drawn in a polyhedral style. The arrangement of the molecules is different in the two modifications leading to cubic (RuO₄-I) and monoclinic (RuO₄-II) symmetry, respectively.

tetrahedral symmetry are found with respect to the observed angles. In both molecules the Ru–O distances are equal within the standard uncertainties, and found to be 1.695 Å (Table 2). The monoclinic modification of ruthenium tetroxide, RuO₄-II, is isotypic with OsO₄ [10]. Crystallographically, there is only one RuO₄ molecule in the unit cell, which has the symmetry 2 (C₂ according to Schoenflies) with respect to the location of the Ru atom on the 4*e* site of space group C2/*c*. However, judged from the nearly identical distances Ru–O of 1.697(3) and 1.701(4) Å (Table 2) and the almost tetrahedral angles O–Ru–O (108.9(2)–110.1(2)°) the molecule is essentially a perfect tetrahedron. Within the standard deviations the distances Ru–O are almost

the same as found for RuO₄-I. Moreover, the distances of both modifications are only slightly different from those reported for OsO₄ (1.684 and 1.710 Å, respectively) [10]. However, the deviation from ideal tetrahedral symmetry is more prominent in OsO₄ as can be seen from the respective angles O–Os–O which range from 106.6° to 110.7°.

The difference between the crystal structures of the two modifications of RuO₄ is the arrangement of the RuO₄ molecules with respect to each other (Fig. 1). This can be seen best by comparing the distances between the tetrahedra-centers in both compounds. In the crystal structure of RuO₄-II one RuO₄ molecule is surrounded by 12 other molecules, leading to distances Ru–Ru

between 4.397 and 5.144 Å. Contrastingly, in the structure of RuO₄-I one of the two crystallographically different molecules has 12 neighbor tetrahedra with the distances Ru–Ru being uniformly 4.757 Å, and the second RuO₄ molecule has even 14 neighbors with the respective distances ranging from 4.255 to 5.211 Å. Although the packing of the tetrahedral molecules is different in both modifications, the molar volumes are identical (46.4 cm³/mol).

Another description of the two crystal structures can be given, when the arrangement of the oxygen atoms in both structures is regarded as a ccp of spheres. Then, 1/8 of the tetrahedral voids must be filled by the metal atoms. It is easy to imagine that there will be different possibilities to distribute the metal atoms over the tetrahedral holes, and that the structures of RuO₄-I and RuO₄-II are only two of the possible filling patterns. As another example the crystal structure of SnI₄ (space group *Pa*3) can be given, which follows the same motif [11]. Finally it should be mentioned that a similar dimorphism as reported here for RuO₄ has been found for OsF₂O₂ some 30 years ago [12]. However, up to now we were not able to detect a phase transition between the two modifications of RuO₄ by means of temperature dependent XRD.

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