

# Single-Crystal Investigation of a New Ruthenium Chloride Oxide, $\text{Ba}_7\text{Ru}_4\text{O}_{15}\text{Cl}_2$

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The previously unknown compound  $\text{Ba}_7\text{Ru}_4\text{O}_{15}\text{Cl}_2$  has been prepared using the flux technique, yielding well-developed single crystals. Characterization has been made by X-ray diffraction methods.  $\text{Ba}_7\text{Ru}_4\text{O}_{15}\text{Cl}_2$  builds up a new structure type with rhombohedral symmetry (space group  $R\bar{3}m$ ;  $a = 5.7785$ ,  $c = 51.673$  Å). It can be described as a 21-layer structure of a Ba/O and Ba/Cl framework which incorporates corner-connected  $\text{Ru}_2\text{O}_6$  double octahedra. Relationships to other structures are discussed.

Dedicated to Professor Sten Andersson on the occasion of his 60th birthday.

Within recent decades several studies on the crystal chemistry of alkaline-earth oxoruthenates have been published. For example, the following compounds were investigated by X-ray methods:  $\text{BaRuO}_3$ ,<sup>1,2</sup>  $\text{Ba}_3\text{MRu}_2\text{O}_9$  ( $M = \text{Mg, Ti, Sr, Sm, In, Rh}$ ),<sup>3–7</sup>  $\text{Ba}_2\text{MRuO}_6$  ( $M = \text{La, In, Rh}$ ),<sup>7–10</sup>  $\text{BaRu}_6\text{O}_{12}$ ,<sup>11</sup>  $\text{Ba}_3\text{RuO}_5$ ,<sup>12</sup>  $\text{Ba}_2\text{RuO}_4$ ,<sup>12,13</sup>  $\text{SrRuO}_3$ ,<sup>14</sup>  $\text{Sr}_2\text{RuO}_4$ <sup>14,15</sup> and  $\text{Sr}_3\text{Ru}_2\text{O}_7$ .<sup>13,15</sup> All these compounds contain ruthenium in octahedral coordination by oxygen. In some the  $\text{RuO}_6$  octahedra share faces to form  $\text{Ru}_2\text{O}_6$  and  $\text{Ru}_3\text{O}_{12}$  groups, respectively. Considering halogeno-oxoruthenates, only one compound, of composition  $\text{Ba}_5\text{Ru}_2\text{O}_9\text{Cl}_2$ ,<sup>16</sup> is known. An interesting feature of this structure is the concentration of  $\text{Cl}^-$  ions within relatively small domains of the crystal structure. In order to find out whether or not this is a characteristic of halogeno-oxoruthenates we synthesized and studied  $\text{Ba}_7\text{Ru}_4\text{O}_{15}\text{Cl}_2$ , and determined its crystal structure.

## Experimental

To synthesize single crystals of  $\text{Ba}_7\text{Ru}_4\text{O}_{15}\text{Cl}_2$  a flux technique was used. A 2:1:20 molar mixture of  $\text{BaCO}_3$ , ruthenium powder and  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  was thoroughly ground in an agate mortar. After heating in a corundum crucible in air for 14 d at 1323 K, the melt was slowly cooled to room temperature. From the reaction product black prismatic crystals of approximate size 0.01–0.3 mm were isolated. These were identified by Weissenberg and Buerger precession photographs as the recently investigated compound  $\text{Ba}_5\text{Ru}_2\text{O}_9\text{Cl}_2$ .<sup>16</sup> After the specimen had been heated in air at 1323 K for another 7 d and then

slowly cooled, the original prismatic crystals disappeared and black hexagonal plates of approximate size 0.01–0.2 mm were observed and separated. Adhering  $\text{BaCl}_2$  was dissolved with warm water. Well-developed single crystals were analysed by energy-dispersive X-ray spectrometry (electron microscope SR 50 Leitz, EDX system Link AN 10000) and were shown to contain barium and ruthenium. The presence of chlorine in this compound was proved by comparison of these spectra with EDX spectra of Cl-free and Cl-containing  $\text{BaRuO}_3$  and  $\text{Ba}_5\text{Ru}_2\text{O}_9\text{Cl}_2$  single crystals, respectively. In Cl-containing ruthenates the ruthenium *L*- and chlorine *K*-peak coincide almost exactly, leading to a broadening of the composite peak. The semi-quantitative EDX analysis (no standard method: NOSTD program)<sup>17</sup> shows a lower Ba:Ru ratio in  $\text{Ba}_7\text{Ru}_4\text{O}_{15}\text{Cl}_2$  than in  $\text{Ba}_5\text{Ru}_2\text{O}_9\text{Cl}_2$ . These results were confirmed by a subsequent crystal structure analysis.

However, polycrystalline powder of  $\text{Ba}_7\text{Ru}_4\text{O}_{15}\text{Cl}_2$  can be prepared by heating a well-ground mixture of  $\text{BaO}_2$ , Ru powder and  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  in the molar ratio 6:4:1 under the following temperature conditions: 100 K h<sup>-1</sup> up to 1148 K, annealing for three days and cooling slowly to room temperature. X-Ray powder diffraction patterns show a slight impurity of  $\text{BaRuO}_3$ .

Single-crystal X-ray data were collected at room temperature using an automatic four-circle diffractometer. Information concerning collection and reduction of the intensity data, as well as the refinement, is presented in Table 1. From Laue photographs and systematically absent reflections  $R\bar{3}2$ ,  $R\bar{3}m$  and  $R\bar{3}m$  were deduced as possible space groups. The crystal structure was solved in  $R\bar{3}m$  with the direct method program SHELXS-86,<sup>18</sup> leading to the heavy metal positions. The chlorine and oxygen positions were

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Table 1. Crystal data and structure refinement for Ba<sub>7</sub>Ru<sub>4</sub>O<sub>15</sub>Cl<sub>2</sub> (with standard deviations in parentheses).

Crystal system	Trigonal
Space group	$R\bar{3}m-D_{3d}^5$ (No. 166)
Cell dimensions	$a = 5.7785(4)$ Å $c = 51.673(6)$ Å $V = 1494.29$ Å <sup>3</sup>
Formula units per unit cell	$Z = 3$
Diffractometer	Four-circle, Siemens AED 2
Radiation	Graphite-monochromated Mo K $\alpha$ , $\lambda = 0.71069$ Å
Corrections	Background, polarisation and Lorentz factor
Empirical absorption correction	Psi-scan, program EMPIR (Stoe & Cie, Darmstadt, FRG)
2 $\theta$ -range/°	5–70
Scan mode	$\Omega/2\theta$
$\Omega$ -step scan width/°	0,025
Time/step	Variable, 1–4 s
No. of measured reflections	1480
No. of unique reflexions	885
No. of unique reflexions used for refinement	743 [ $F_o > 3\sigma(F_o)$ ]
No. of parameters refined	27
Residual value	$R = 0.053$

obtained from Fourier and difference Fourier syntheses. The program SHELX-76<sup>19</sup> was used for least-squares refinement of the atomic fractional coordinates. The final parameters and the anisotropic temperature factors are listed in Table 2. A selection of the most important interatomic distances is given in Table 3; a list of observed ( $F_o$ ) and calculated ( $F_c$ ) structure factors has been deposited.\*

\* Further details concerning the crystal structure investigation may be requested by Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH., D-7514 Eggenstein-Leopoldshafen 2, quoting the number CSD-54995, together with the author and journal citation.

Table 3. Selected interatomic distances (in Å) and bond angles (in °) (with standard deviations in parentheses).

Ba(1)–O(1)	2.8893(2)	(6×)	Ba(4)–Cl	3.112(8)
Ba(1)–O(3)	2.963(8)	(6×)	Ba(4)–Cl	3.387(2)
Ba(2)–O(2)	2.836(9)	(3×)	Ru(1)–O(3)	1.966(8)
Ba(2)–O(3)	2.897(4)	(6×)	Ru(1)–O(1)	1.9779(8)
Ba(2)–O(1)	2.9700(9)	(3×)	Ru(2)–O(2)	1.877(8)
Ba(3)–O(3)	2.737(7)	(3×)	Ru(2)–O(3)	2.096(8)
Ba(3)–O(2)	2.912(5)	(6×)	Ru(1)–Ru(2)	2.725(2)
Ba(3)–Cl	2.988(8)		Cl–Ba(4)–Cl	80.02(14)
Ba(4)–O(2)	2.661(9)	(3×)	Cl–Ba(4)–Cl	117.06(8)

## Discussion

It has been mentioned above that Ba<sub>7</sub>Ru<sub>4</sub>O<sub>15</sub>Cl<sub>2</sub> represents a new structure type. The structure may be described as a 21-layer structure consisting of a Ba–O and Ba–Cl framework. As Fig. 1(a) shows, Ba(1) and Ba(2) are coordinated by 12 oxygen atoms. Ba(3) is coordinated by 9 oxygen atoms and one chlorine atom [Fig. 1(b)]. The coordination polyhedron can be derived from a close-packed BaO<sub>12</sub> polyhedron by replacing three oxygen atoms with one chlorine atom. In this way, Ba(1), Ba(2), Ba(3) and all oxygen atoms form perovskite-like blocks, five oxygen layers thick. The ruthenium atoms are located in octahedral holes of the oxygen framework. Calculations using the MAPLE concept<sup>20,21</sup> show that the Ru(1) position is occupied by Ru<sup>4+</sup> and the Ru(2) position by Ru<sup>5+</sup> ions. Two Ru(1)O<sub>6</sub> and Ru(2)O<sub>6</sub> octahedra form face-sharing Ru<sub>2</sub>O<sub>9</sub> double octahedra with a relatively short Ru(1)–Ru(2) distance (2.725 Å). However, a comparison of this distance with that of the ideal centres of the Ru(1)O<sub>6</sub> and Ru(2)O<sub>6</sub> octahedra (2.362 Å) shows an increase in the former. Each Ru<sub>2</sub>O<sub>9</sub> group is corner-linked to three others via the O<sup>2-</sup> ions of one face of the Ru(1) octahedra [Fig. 2(b)]. As a result the crystal structure shows a corrugated two-dimensional network of Ru<sub>2</sub>O<sub>9</sub> groups parallel to (001) [Figs. 1(b) and 2(b)]. The five oxygen layers forming the blocks of the RuO<sub>6</sub> octahedra are connected by double layers of Ba<sub>2</sub>Cl<sub>2</sub>

Table 2. Atomic fractional coordinates (x, y, z) and temperature factors (in Å<sup>2</sup>) (with standard deviations in parentheses).

Atom	Wyckoff notation	x	y	z	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub> /U <sub>23</sub> <sup>a</sup>
Ba(1)	3a	0.0	0.0	0.0	0.0069(5)	0.0069(5)	0.0123(7)	0.0034(2)	0.0
Ba(2)	6c	0.0	0.0	0.71422(2)	0.0072(3)	0.0072(3)	0.0070(5)	0.0036(2)	0.0
Ba(3)	6c	0.0	0.0	0.08441(3)	0.0089(4)	0.0089(4)	0.0190(6)	0.0044(2)	0.0
Ba(4)	6c	0.0	0.0	0.79754(3)	0.0237(5)	0.0237(5)	0.0101(6)	0.0119(3)	0.0
Ru(1)	6c	0.0	0.0	0.35390(3)	0.0010(4)	0.0010(4)	0.0025(5)	0.0005(2)	0.0
Ru(2)	6c	0.0	0.0	0.40665(3)	0.0038(4)	0.0038(4)	0.0063(6)	0.0019(2)	0.0
Cl	6c	0.0	0.0	0.1422(2)	0.0616(45)	0.0616(45)	0.0137(29)	0.0308(22)	0.0
O(1)	9e	0.5	0.0	0.0	0.0094(22) <sup>b</sup>				
O(2)	18h	0.504(1)	0.496(1)	0.9086(2)	0.0126(17) <sup>b</sup>				
O(3)	18h	0.183(1)	0.817(1)	0.0451(2)	0.0067(14) <sup>b</sup>				

<sup>a</sup>  $T = \exp [-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ . <sup>b</sup> Isotropic temperature factor refinement for oxygen atoms:  $T = \exp (-8\pi^2U \sin^2\theta/\lambda^2)$ .

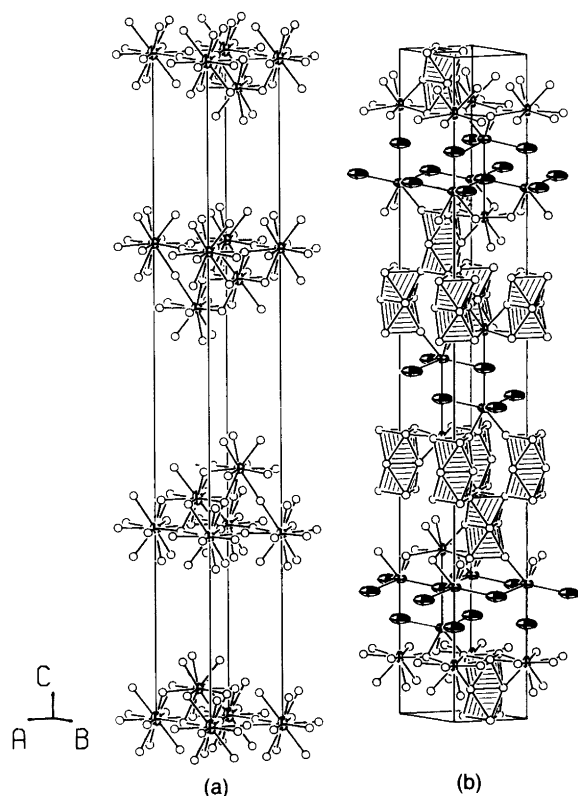


Fig. 1. (a) Representation of the Ba(1) and Ba(2) (small ellipsoids elongated parallel to [001]) coordination by oxygen (open spheres). (b) Illustration of the Ba(3) (small ellipsoids elongated parallel to [001]) and Ba(4) (small ellipsoids elongated perpendicular to [001]) coordination by chlorine (large ellipsoids with octant shading) and oxygen (open spheres); ruthenium/oxygen polyhedra are hatched.

[with Ba(4)] as illustrated in Fig. 1(b). The coordination polyhedron  $\text{BaO}_3\text{Cl}_4$  around Ba(4) is shown in Fig. 2(a). The three oxygen atoms are part of the perovskite-like blocks. The 3+1 chlorine atoms lie on the opposite side of the Ba(4) coordination polyhedron, leading to a relatively loose chlorine packing in planes parallel to (001). This correlates with the anomalously high anisotropic displacement parameters of Ba(4) and Cl [Table 2, Fig. 1(b)]. An

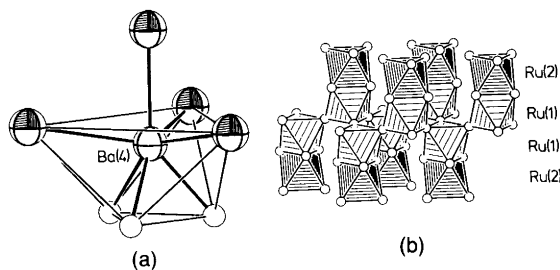


Fig. 2. (a) Schematic drawing of the distorted capped coordination polyhedron around Ba(4) by chlorine (sphere with octant shading) and oxygen (open spheres). (b) Illustration of the corner-linked  $\text{Ru}_2\text{O}_9$  double-octahedra.

alternative description of the Ba(4) environment is a distorted monocapped octahedron formed by three close O atoms, three more distant Cl atoms and a fourth Cl atom which caps one of the octahedral faces [Fig. 2(a)].

There are few similar hexagonal oxocompounds with two short and one very long lattice constants. One example is  $\text{Ba}_3\text{Fe}_{26}\text{O}_{41}$ ,<sup>22</sup> which is quite different from  $\text{Ba}_7\text{Ru}_4\text{O}_{15}\text{Cl}_2$ . The recently reported compound  $\text{Ba}_7\text{Nb}_4\text{Ti}_2\text{O}_{21}$ <sup>23</sup> represents the first 21-layer perovskite with a similar Ba-O environment; however, in this case the characteristic  $\text{BaO}_3\text{Cl}_4$  coordination of  $\text{Ba}_7\text{Ru}_4\text{O}_{15}\text{Cl}_2$  is missing. In addition, the network of face- and corner-sharing octahedra is different.

Extending the comparison to the hexagonal oxide halides already known, some resemblances can be established.  $\text{Ba}_5\text{Re}_3\text{O}_{15}\text{X}$  (X = F, Cl, Br, I)<sup>24-26</sup> and  $\text{Ba}_{5-y}\text{M}_y\text{O}_{15}\text{Cl}$  (M = Ca, Sr)<sup>27</sup> are described to apatite-like phases with fivefold coordinated  $\text{ReO}_5$  polyhedra. In  $\text{Ba}_5\text{Mn}_3\text{O}_{12}\text{Cl}$ ,<sup>28</sup>  $\text{Ba}_{8.5}\text{Cr}_5\text{AlO}_{24}\text{Cl}_2$ <sup>29</sup> and  $\text{Sr}_5\text{Cr}_3\text{O}_{12}\text{Cl}$ <sup>30</sup> the small cations are tetrahedrally coordinated by oxygen atoms.  $\text{Ba}_5\text{Ru}_2\text{O}_9\text{Cl}_2$ <sup>16</sup> and  $\text{Ba}_7\text{Ru}_4\text{O}_{15}\text{Cl}_2$  are even more similar; both compounds have  $\text{Ru}_2\text{O}_9$  double octahedra, but in the former these are not corner-linked. The coordination of barium is quite different, particularly with respect to the chlorine domains in  $\text{Ba}_5\text{Ru}_2\text{O}_9\text{Cl}_2$ . As already mentioned,  $\text{Ba}_7\text{Ru}_4\text{O}_{15}\text{Cl}_2$  contains Ba-Cl layers. A similar layer structure has been observed in  $\text{Ba}_{10}\text{Fe}_8\text{Pt}_2\text{Cl}_2\text{O}_{25}$ .<sup>31</sup> In this compound some of the barium atoms are coordinated by 12 oxygen atoms, while others have a 9+1 coordination of O and Cl that is similar to that found in  $\text{Ba}_7\text{Ru}_4\text{O}_{15}\text{Cl}_2$ . One of the main differences between both compounds arises from the 9+3 coordination of one barium position in  $\text{Ba}_{10}\text{Fe}_8\text{Pt}_2\text{Cl}_2\text{O}_{25}$ . This particular  $\text{BaO}_3\text{Cl}_3$  coordination can be described as a 3,6,3-polyhedron formed by 3 O, 3 O + 3 Cl and 3 O.

All calculations were made on a CRVAX 8550 machine (Digital Equipment Inc.) at the computer centre of the University of Kiel. The structure was plotted with a modified ORTEP program.<sup>32,33</sup>

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